Brook 転位を基盤とする [3 + 2]アニュレーション の反応機構に関する研究

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（１）学会誌等

1. K. Takeda, K. Sakurama, E. Yoshii, Low-temperature Oxyanion-Accelerated Vinylcyclopro-pane-Cyclopentene Rearrangement. Reaction of 2-(2-(Trimethylsilyl)ethenyl)cyclopropyl Acetates with Methyl Lithium *Tetrahedron Lett*. **38** (18), 3257-3260 (1997).
2. 武田　敬, ケイ素の特性を利用する炭素環形成反応の開発, *有機合成化学協会誌* **55**, 774-784 (1997).
3. 武田　敬, ケイ素の特性を利用する [3 + 2] アニュレーション法の開発とその天然物合成への応用. *薬学雑誌* **117**, 368-377 (1997).

（２）口頭発表

1. 武田　敬，櫻間啓基，佐野綾子，吉井英一，β位ヘテロ原子置換アクリロイルシランを用いる [3 + 2] アニュレーションの反応機構, 日本薬学会第１１６年会，1996，4，金沢.
2. K. Takeda, K. Kitagawa, and E. Yoshii, Synthesis of clavulones via [3 + 2] annulation using (β-(phenylthio)acryloyl)silane. 21th International Congress of Natural Product Chemistry, 1996, 9, Chicago.
3. 武田　敬，櫻間啓基，畠山規明，佐野綾子，姥山はるか，吉井英一，小泉　徹：βヘテロ原子置換アクリロイルシランを用いる [3 + 2] アニュレーションの反応機構．反応と合成の進歩シンポジウム，1996，11，岡山.
4. 武田　敬，櫻間啓基，畠山規明，吉井英一，小泉　徹, Brook 転位を利用する [3 + 2] アニュレーションの反応機構（２），日本薬学会第１１７年，1997，3，東京.

ケイ素の特性を利用する炭素環形成反応の開発

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Development of Silicon-Mediated Ring-Forming Reactions for Carbocycles

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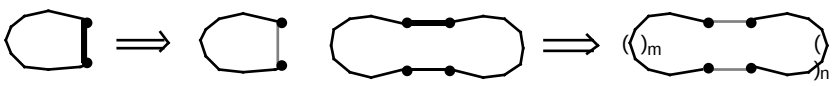
The development of methodologies for the construction of the odd-membered carbocycles such as five- and seven-membered ring systems has become a subject of great interest for synthetic chemists since the ring systems are found in a wide variety of natural products and theoretically interesting molecules. This review describes Brook rearrangement-mediated [3 + 2] and [3 + 4] annulation methodologies which permit highly efficient construction of five- and seven-membered carbocycles, respectively.

1．はじめに

炭素環形成反応の重要性は，炭素環構造が多くの生物活性天然物や医薬品そして理論的に興味がもたれる化合物に含まれていることから近年ますます高まっており，種々の新しい方法論が開発されてきている．[1] 代表的な環形成法としては，一つの炭素-炭素結合形成反応により環を構築する分子内環化法 (cyclization) 法と，複数の結合の形成により環形成を行うアニュレーション法 (annulation) があるが，立体選択的な置換基の導入や基質の合成の容易さを考えた場合，一般的にはアニュレーション法が優れていると考えられる．アニュレーション法では，用いるフラグメントおよびそれらを構成する原子の数に基づき [m + n + - - -] アニュレーションと呼称されており，炭素環の員数に応じて様々な組み合わせが報告されている．



分子内環化法 (cyclization)　　アニュレーション法 (annulation)
[m + n] annulation

Fig. 1

五員環や七員環のような奇数の原子からなる炭素環の環形成反応は，Diels-Alder 反応に代表される六員環形成反応と比較すると，基質の入手の容易さや立体制御の点でまだ同じレベルに達しているとは言い難い．[2] その最も大きな理由は，1,3 位 や1,5 位といった奇数位に双極子あるいはラジカルを発生させるのが困難なためで，

反応性の高い三炭素単位や五炭素単位をいかに発生させるかが奇数環の合成を行う場合の重要な鍵となる.

[3 + 2] アニュレーション　　[3 + 4] アニュレーション

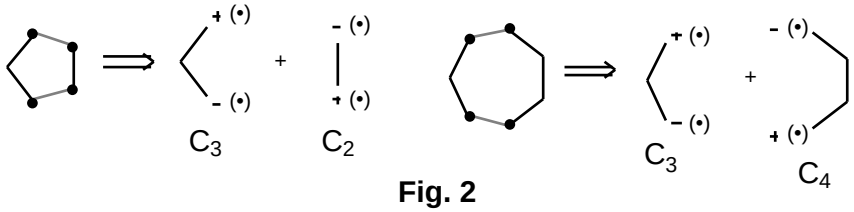


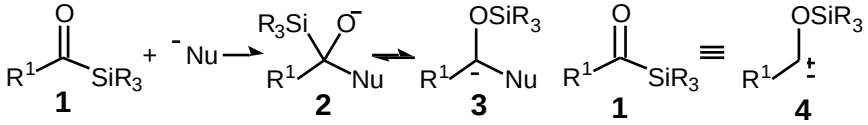
Fig. 2

本総合論文では，従来の手法とは概念的に全く異なる，Brook 転位を利用した[3 + 2] および[3 + 4] アニュレーション法の開発について詳述する.

2. Brook 転位を利用する[3 + 2] アニュレーションの開発

2.1 Brook 転位[3)]

Brook 転位とはα-シリルアルコキシド **2** におけるケイ素の炭素原子から酸素原子への1,2-アニオニック転位のことで(**2** →**3**)，今から４０年程前にBrook によって発見されたものである．α-シリルアルコキシド**2** の発生法としては数種の方法があるが，最も一般的なのはアシルシラン**1** と求核剤との反応を用いるもので，アシルシランのカルボニル基が形式的な求電子・求核剤**4** として機能するという極めてユニークな性質を示す．[4)] Brook 転位はその発見以来，主に反応機構的な観点から研究が展開されてきており，合成反応としての有用性はかなり限定されたものであった．その最も大きな原因はこの転位が平衡反応であるという点にある．すなわち，**2** と転位により生成するα-シロキシカルバニオン**3** との間の平衡は一般に**2** の側に偏っており，**3** の側に平衡を移動させるためには生成するカルバニオンを安定化し得るような置換基を導入する必要がある.

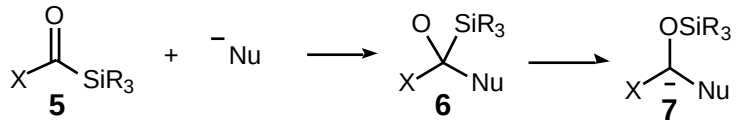


Scheme 1

われわれが１９９０年にこのプロジェクトを開始した時点では，Brook,[3b)] Reich ら[5)] によるα-位に脱離基をもつアシルシランあるいは求核剤を用いる位置選択的なエノールシリルエーテルの合成などが，合成化学への応用としては代表的なものであった.

2.2 β-カルボニル基による**Brook** 転位の加速

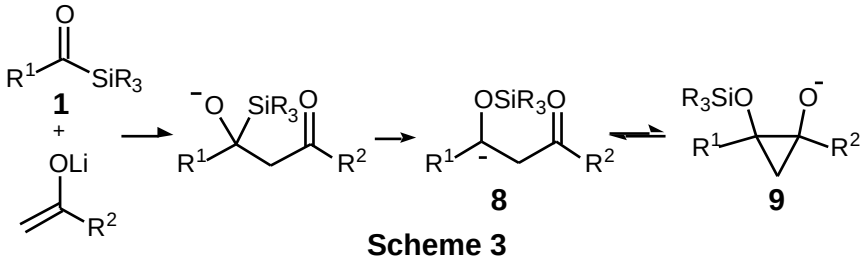
上述したように，Brook 転位を合成反応に取り込むためには何らかの方法により生成するカルバニオンを安定化させなければならない．合成反応としての柔軟性を考慮に入れ最初に着目したのは，アシルシランのカルボニル基にα-カルバニオンを安定化するヘテロ原子 X が直接結合した**5** のような化合物であった．**5** と求核剤との反応で Brook 転位が起こればα-位にヘテロ原子をもつカルバニオン**7** が生成し，種々の官能基変換が可能と考えられた．しかしながら，それらの合成を種々の方法で検討したが，文献既知の化合物**5** (X = $SiMe_3$, R = Me)[6)] は極めて不安定であり，また他の化合物の合成も不成功に終わった.



X = $SiMe_3$, SPh, S(O)Ph, SO_2Ph, P(O)$(OMe)_2$

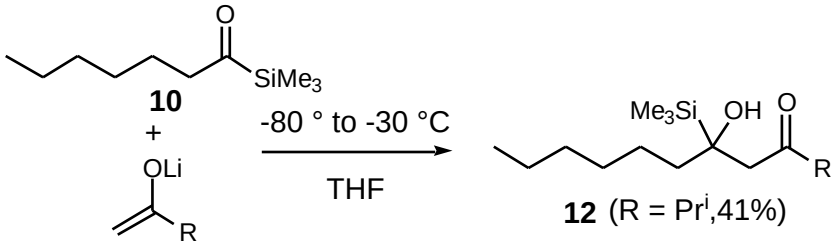
Scheme 2

そこで次に，求核剤としてケトンエノラートを用いれば転位により生成するカルバニオン**8** が，β-カルボニル基によってシクロプロパノラート**9** として捕捉され，Brook 転位が加速されるのではないかと考えた．アシルシランとケトンエノラートとの反応はほとんど報告がなく，桑島らによるβ位に脱離基を持つアシルシランとの反応[7] と，Soderquist らによる通常のアルドール反応[8] のみであった．



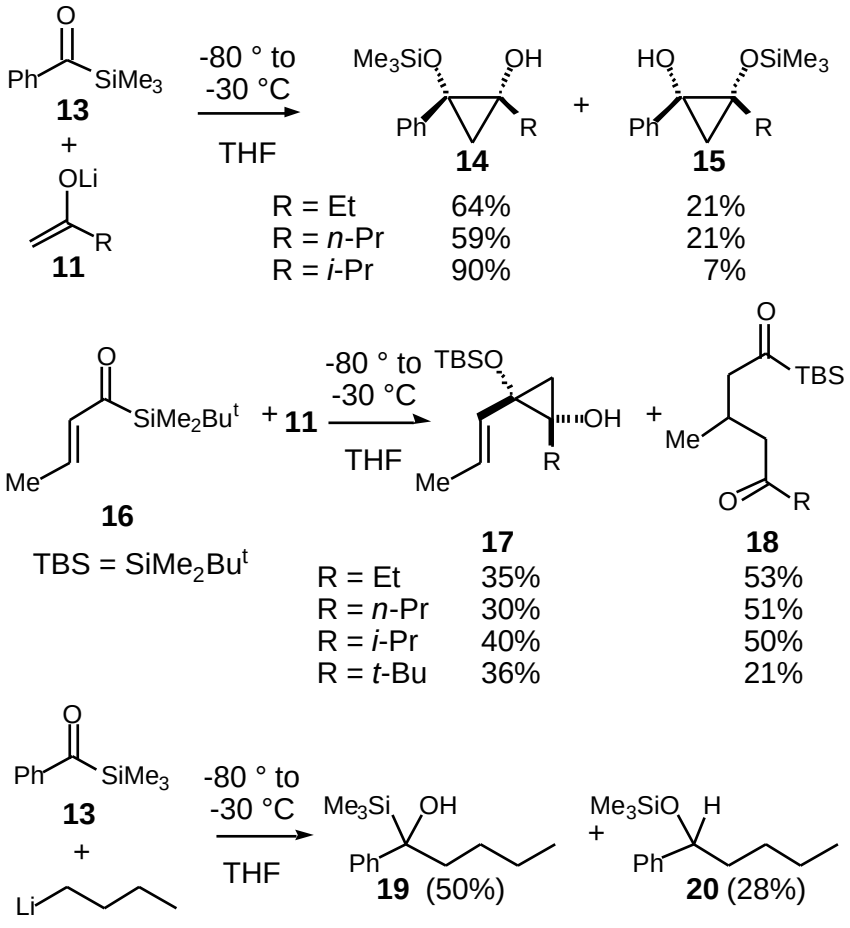
Scheme 3

まず，ヘプタノイルシラン**10** とケトンエノラート**11** との反応を行ったが，付加体**12** のみが生成し，Brook 転位体は得られなかった．



Scheme 4

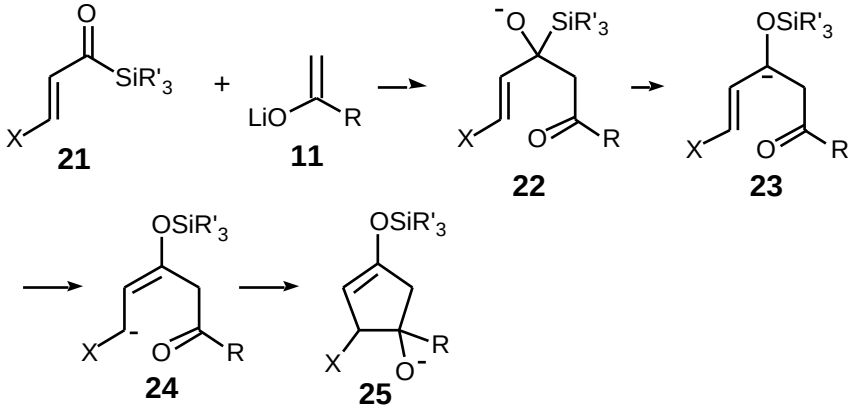
しかし，ベンゾイルシラン**13** との反応では， Brook 転位で生成したカルバニオンがβ-カルボニル基を攻撃して生じたシクロプロパンジオール誘導体**14** とそのシリル転位体 **15** が得られた．同様の反応は，クロトノイルシラン**16** でも進行し1,4-付加体**18** が副生するもののプロペニルシクロプロパノール**17** が得られた．一方，カルボニル基の求電子性がケトンより低いエステルエノラート**19** との反応では，Brook 転位体**21** およびそのトリメチルシラノール脱離成績体**22** に加えて，1,2-付加体**20** が生成した．さらに，カルボニル基を持たない *n*-ブチルリチウムとの反応では，1,2-付加体**23** と転位体**24** の両方が生成するが，付加体**23** が主成績体であった．これらの結果は，Brook 転位を効率よく進行させるためには，β-カルボニル基単独では不十分であり隣接する不飽和基の存在が不可欠だが，β-カルボニル基による加速効果はかなりあるということを示している．[9]



Scheme 5

2.3 Brook 転位を利用する [3 + 2] アニュレーション[10)]

アニオン安定化能をもつヘテロ原子がアシルシランのカルボニル基に直接結合した化合物5 の合成が不成功に終わったので，次にそのビニロガス誘導体である25 と，Brook **転位を加速することが明らかになったケトンエノラート11 との反応に着目した．エノラートの**1,2**-付加体26 においてBrook 転位が起こればアリルカルバニオン27 が生成し，27 がアリル転位をおこして28 のようなヘテロ原子により安定化されたアリルアニオンとなった後，分子内でカルボニル基を攻撃すれば五員環29 が生成するはずである．**



Scheme 6

25 のβ-ヘテロ原子としては，ケイ素およびイオウを用いることとし，31 および32 は Reich **らの方法**[11)] **に従い**allenoylsilane **30 を経て合成した．**

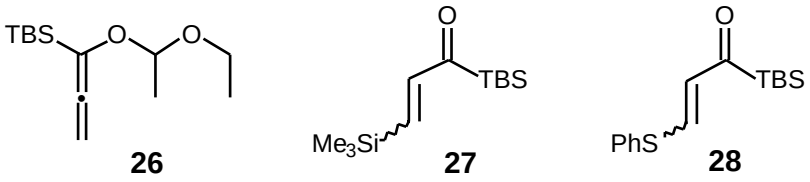
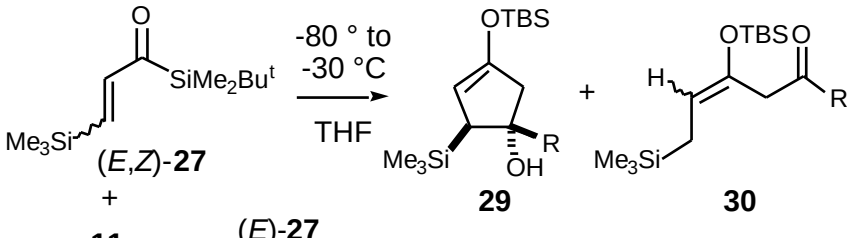


Fig. 3

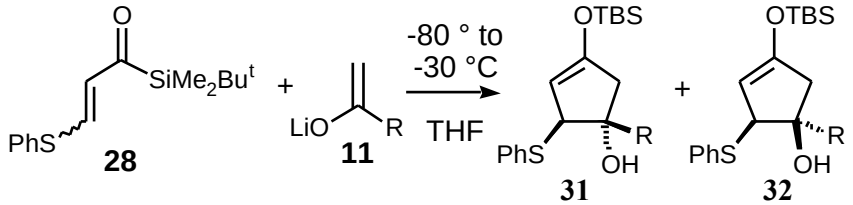
最初に，β-トリメチルシリル体**31** を用いて反応を行った．LDA により調製したエノラート**11** を-80 °C で**31** のTHF 溶液に加えた後-30 °C まで昇温したところ，1 種類の環化体**33** と非環化体**34**（*E*/*Z* 混合物）が生成した．興味深いことには，*E* 体と*Z* 体でこれらの生成比が逆転し，*E* 体からは**34** が，*Z* 体からは**33** が主成績体として得られた．期待通りに反応が進行し五員環が生成することが明らかとなったが，合成反応として用いるためには収率の点で満足のゆくものではなかった．



(*E*)-**27**	R = Et	17%	43%
	R = *n*-Pr	11%	57%
	R = *i*-Pr	14%	63%
(*Z*)-**27**	R = Et	48%	16%
	R = *n*-Pr	55%	22%
	R = *i*-Pr	51%	21%

Scheme 7

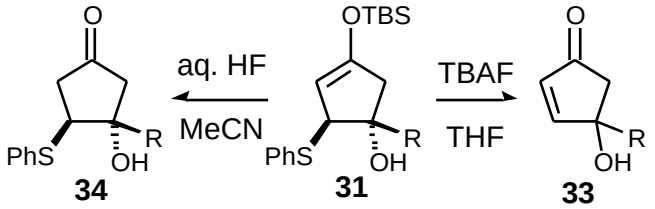
一方，β-フェニルチオ体**32** を用いて同様に反応を行ったところ，二種類の五員環**35**，**36** が高収率で生成し，これらの生成比は純粋な(*E*)-**32**, (*Z*)-**32** を用いてもほとんど変化がなかった．アクリロイルシランのβ-置換基やジオメトリーに依存して生成物分布や生成物が異なる結果を説明する反応機構については，次節で述べる．



R = Et	70%	5%
R = *n*-Pr	74%	7%
R = *i*-Pr	55%	19%
R = *n*-octyl	71%	8%

Scheme 8

本アニュレーションで得られるシクロペンテノール**35** は，高度に官能基化されているため種々の官能基変換が考えられるが，フッ化テトラブチルアンモニウム(TBAF) で処理すると容易にシクロペンテノン**37** を与え，また，アセトニトリル中フッ化水素酸と反応させるとフェニルチオ基を保持したシクロペンタノン**38** が得られた．[10)]



R = Et 83%
R = *n*-Pr 87%
R = *i*-Pr 79%

R = Et 70%
R = *n*-Pr 77%
R = *i*-Pr 77%

Scheme 9

この環化反応の合成反応としての有用性は，4-ヒドロキシ-2-シクロペンテノン骨格を含む数種の天然物の合成を行うことにより実証した．詳細については原報を参照されたい．[10),12),13)]

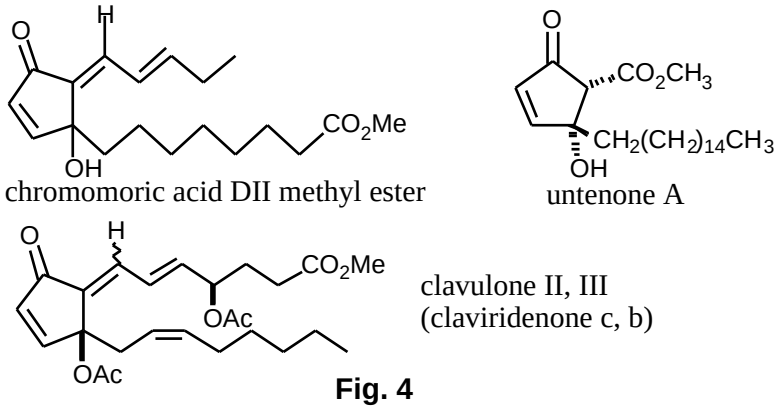
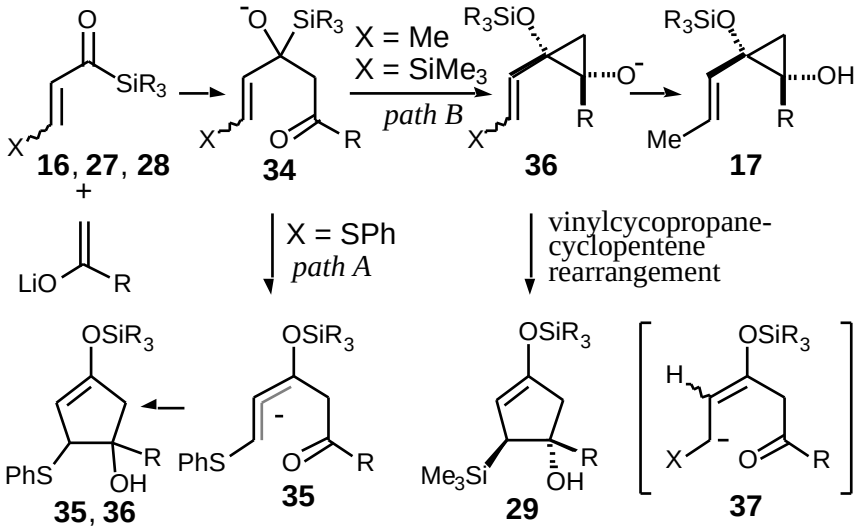


Fig. 4

2.4 Brook 転位を利用する[3 + 2]アニュレーションの反応機構

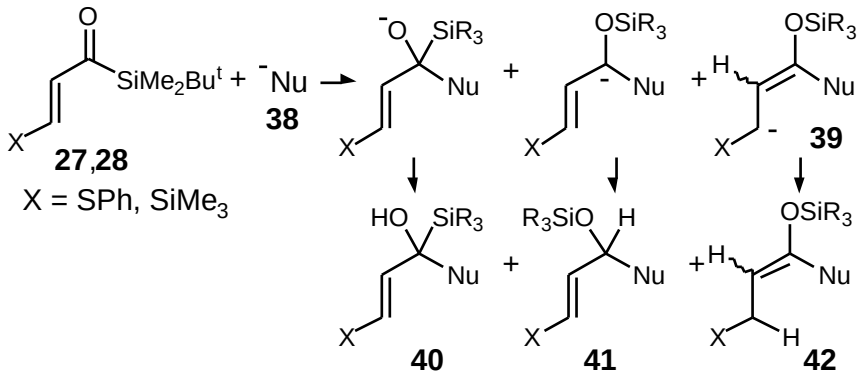
前節で述べたように，β-フェニルチオ体**32**ではその*E*/*Z* 比に無関係に２種の五員環が生成するのに対し，β-トリメチルシリル体**31**の場合は*E*体，*Z*体いずれからも１種類の五員環と非環化体が得られるが，その生成比は*E*体と*Z*体で逆転している．また，β-置換基がメチル基の場合は五員環は生成せずシクロプロパノール**17** が得られる(Scheme 5)．以上の結果を統一的に説明する機構として，アクリロイルシランのβ-置換基のα-カルバニオン安定化能の違いに基づく次のような仮説をたてた．すなわち，1,2-付加体**38** におけるBrook 転位/カルバニオンのアリル転位により生成するアリルアニオン**41** が置換基X により安定化される場合(X = SPh)，速やかに非局在化して**39** となる(path A)．二重結合のジオメトリーの違いは**39** で消失するので生成物には反映されず，*E*体,*Z*体いずれからも同じ比率で生成物を与える．一方，メチル基のようにα-カルバニオンを不安定化する基の場合，カルバニオンの生成とβ-カルボニル基への攻撃が協奏的に起こって，ビニルシクロプロパノラート**40** が生成するというものである(path B)．問題となるのはトリメチルシリル基の場合だが，仮にそのα-カルバニオン安定化能がフェニルチオ基に較べてかなり劣ると考えれば説明が可能である．すなわち，メチル基の場合と同様にシクロプロパノラート**40** となった後，ビニルシクロプロパン-シクロペンテン転位(**40** →**33**) により五員環を生成するというもので，この場合アクリロイルシランのジオメトリーは**40** でも保持されているので，**40** →**33** においてビニル基の*E*/*Z* でその反応性に差があれば異なる生成物分布**33**/**34** も理解できる．



Scheme 10

この仮説を検証するためには，(1) フェニルチオ基とトリメチルシリル基のα-カルバニオン安定化能の比較，(2) -30 °C 以下の低温で **40** (X = $SiMe_3$) のオキシアニオン加速ビニルシクロプロパン-シクロペンテン転位が進行するかどうか，また進行するのならば*E* 体と*Z* 体でその反応性に差があるのかどうか，を明らかにする必要がある．

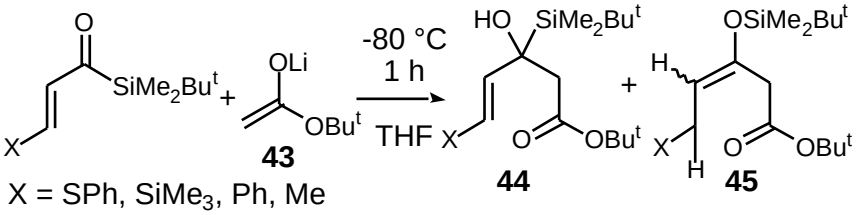
2.4.1 フェニルチオ基とトリメチルシリル基のα-カルバニオン安定化能の比較[14] イオウやケイ素等のヘテロ原子は超共役や d-軌道の関与によりα-カルバニオンを安定化することは良く知られており，この性質は種々の合成反応に有効に利用されている．しかし，それらの溶液中での安定化能の比較についてはあまり研究がなされていない．われわれは，Brook 転位を利用してヘテロ原子のα-カルバニオン安定化能を比較しようと考えた．すなわち，β-置換アクリロイルシラン**31**, **32** と求核剤 **42** との反応において，1,2-付加体**44** とBrook 転位体**45**,**46** の両方が生成するような求核剤および反応条件を設定し，それらの生成比に基づいてβ-置換基のα-アニオン安定化能を比較しようとするものである．付加体のBrook 転位/カルバニオンのアリル転位により生成する **43** においてX のアニオン安定化能が大きければ大きいほど，Brook 転位体**45** および**46** の生成比が1,2-付加体**44** に比較して大きくなるはずである．



Scheme 11

求核剤としては，ケトンカルボニルと比べてカルボニル基の求電子性が低く付加体とBrook 転位体の両方を与えることがわかっている，エステルエノラート**19** (Scheme 5) を用いることにした．反応は，アシルシラン

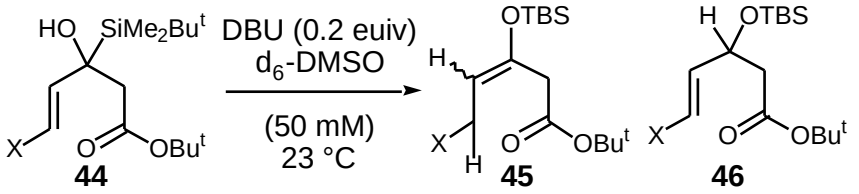
のTHF 溶液に**19** を加え-80 ℃ で 1 時間撹拌した後，1 当量の酢酸で処理するという方法で行った．比較のために行ったメチル基とフェニル基の結果から明らかなように，この反応はβ-置換基のアニオン安定化能を評価するのに適した系であると考えられる．フェニルチオ基とトリメチルシリル基の結果は，フェニルチオ基のほうがα-カルバニオンをより安定化するということを示しているが，微妙な反応条件の違いに影響を受けるためか，収率に幅があり再現性は必ずしも良くはなかった．



X	**44** (%)	**45** (%)
SPh	0-33	34-68
$SiMe_3$	51-64	8-12
Ph	45-51	24-38
Me	90	0

Scheme 12

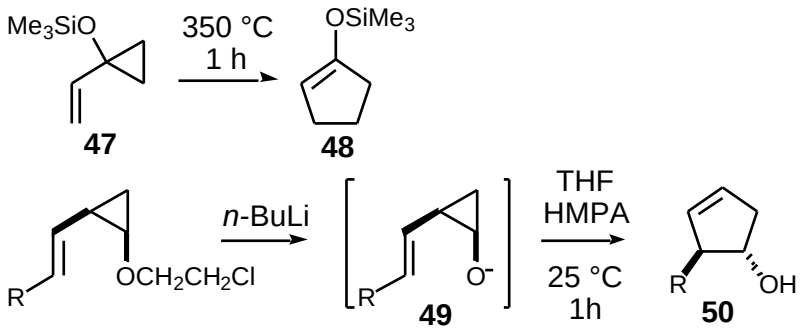
そこで次に，**47** を単離しその塩基触媒による**48** への転位の速度を比較することにより，α-カルバニオン安定化能を比較することにした．反応は，d_6-DMSO 中塩基としてDBU (0.2 当量) を用いて行い，室温下^{1}H NMR で追跡した．その結果をScheme 13 に示す．予想したように，トリメチルシリル基のα-カルバニオン安定化能はフェニルチオ基よりかなり小さいことが明らかになった．



X	product	$t_{1/2}$ (min)
SPh	**45**	3.2
$SiMe_3$	**45**, **46** (*ca.* 2 : 1)	27.5
Ph	**45**	5.5

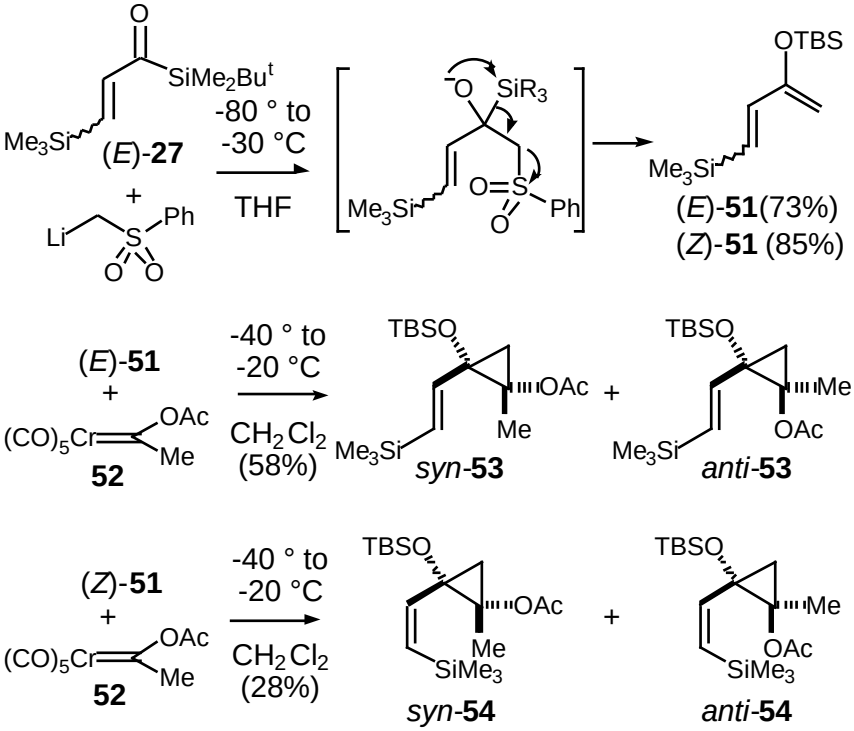
Scheme 13

2.4.2 低温オキシアニオン加速ビニルシクロプロパン転位[15] フェニルチオ基とトリメチルシリル基のα-アニオン安定化能の違いがはっきりしたので，次にビニルシクロプロパン-シクロペンテン転位が低温で起こるかどうかの検討に移った．熱的ビニルシクロプロパン転位は有用な五員環形成反応の一つで天然物の合成などにも用いられているが，一般に250 ℃ から600 ℃ の高温を要するため(**50** →**51**)，[16] 共存できる官能基に制限があった．[17] １９８０年に Danheiser はシクロプロパン環上にオキシアニオンを導入する事により劇的に反応が加速されるということを発見した(**52** →**53**)．[18),19)] しかし，その場合でも室温以下では進行せず，またHMPA のような極性溶媒の使用が必須であった．



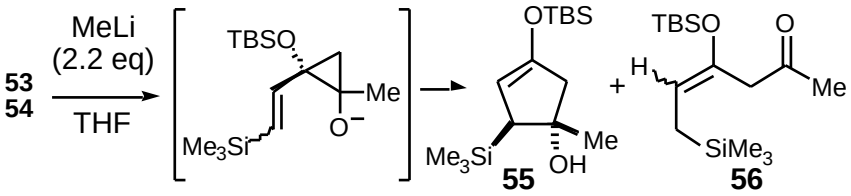
Scheme 14

したがって，40 →33 (Scheme 10) **が**-30 °C **以下の低温で進行するかどうかは疑問であり，この点を明らかにするためには40 を別ルートで合成する必要があった．低温で転位が進行するかどうかを調べるのが目的なので，40 のアルコキシドは，**-80 °C **以下の低温でしかも瞬時に発生させる必要がある．種々のルートを検討した結果，次のような方法により合成できることがわかった．すなわち，**Reich **らの**Brook **転位を利用する方法**[5)] **により合成したジエノールシリルエーテル**(*E,Z*)-**54 **に対し，アセトキシ**Fischer **カルベン錯体55**[20)] **を低温で反応させたところ，それぞれ二種類のシクロプロピルアセテート56,57 を得ることができた．**



Scheme 15

56,57 とメチルリチウム(2.2 **当量**)**との反応は，**THF **中**(0.02 M) **三種の条件；**1) -80 °C 30 **分**(entry 1, 4, 7, 10), 2) -80 °~-50 °C, 30 **分**(entry 2, 5, 8, 11), 3) -80 ° ~ -30 °C, 30 **分**(entry 3, 6, 9, 12) **を用いて行った（表1）．**



entry	**53**	conditions[a]	yield (%) **55**	**56**	entry	**54**	conditions[a]	yield (%) **55**	**56**
1	*syn*	A	0	81	7	*syn*	A	52	20
2	*syn*	B	45	40	8	*syn*	B	61	5
3	*syn*	C	54	31	9	*syn*	C	76	16
4	*anti*	A	0	89	10	*anti*	A	59	10
5	*anti*	B	45	39	11	*anti*	B	72	6
6	*anti*	C	63	34	12	*anti*	C	76	14

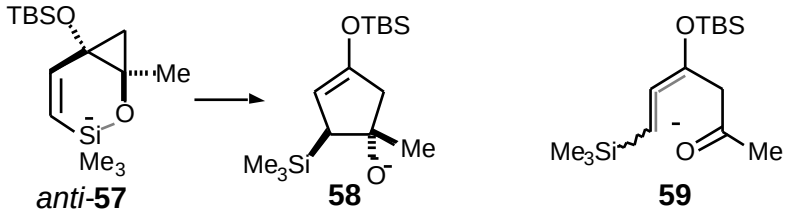
a conditons A: -80 °C, 30 min; B: -80 ° to -50 °C; C: -80 ° to -30 °C

Table 1

entry 1, 4 (-80 °C, 30 分) 以外は，[3 + 2] アニュレーションで得られたものと同じ立体配置をもつシクロペンテノール**58** および開環体**59** が生成した．表 1 の結果は次のようにまとめることができる．(1) 従来，室温以下では進行しないとされていたオキシアニオン加速ビニルシクロプロパン転位が -30 °C 以下の低温でも進行する．特に*Z* 体**57** の場合-80 °C でもかなり反応が進んでいる(entry 7, 10)．(2) 低温では開環体が，昇温すると環化体が優先して生成し，この傾向は特に*E* 体で大きい．(3) *Z* 体の方が*E* 体に較べて環化体の割合が高い．(4) アセトキシ基とビニル基の間の立体化学は生成物分布にほとんど影響を及ぼさない(例えば entry 9, 12).

以上のように，ビニルシクロプロパンが**40** のような置換様式をもつ場合著しく反応が加速され-30 °C 以下の低温でも短時間でシクロペンテンへ転位することが明らかになった．しかし，ビニルシクロプロパノラートの *E*/*Z* およびアセトキシ基とビニル基の立体化学(*syn*/*anti*)には依存せず同一の五員環を与えるという転位の立体過程は，単純な協奏的1,3-シグマトロピー転位を経る経路では説明ができない．また，環化体**58** が*Z* 体からより多く生成するという事実は，シクロプロパノラートの開環により生成する自由回転可能な非局在化アリルアニオン**64** の分子内アルドール反応を経由する機構とは矛盾する．これらの結果を説明する反応機構として，以下に示す作業仮説をたてた．すなわち，**56**, **57** から生成する 4 種のシクロプロパノラート**60**, **61** の間には低温で **63** を経由する平衡が存在し，シクロペンテノラート**62** は*anti*-**61** の協奏的1,3-シグマトロピー転位によってのみ生成するというものである．*anti*-**61** からの転位が速いのは，ケイ素とアルコキシドの分子内キレーションによりビニル側鎖が転位に適したコンホメーションに固定される結果と考えられる．開環体**59** は，一見すると**64** のプロトン化により生成したように見えるが，温度上昇とともに**59** が減少し，それに伴い環化体**58** が増加すること，そして上述したように**64** を中間体とする機構では反応の立体化学が説明できないことから，未反応の **60**, **61** から後処理の段階で生成したものと考えられる．**59** が*E* 体(*syn,anti*-**60**) から優先して生成する結果は，*E* /*Z* の異性化が*syn*/*anti* の異性化より遅い，すなわち*syn,anti*-**60** から*anti*-**61** への異性化が*syn*-**61** から

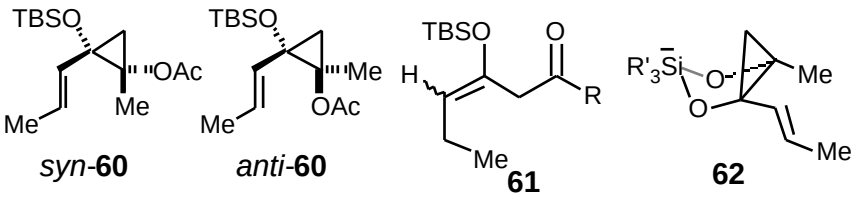
anti-**61** への異性化に比べて遅いと考えれば説明が可能である．



anti-**57** **58** **59**

Scheme 16

この仮説を検証するためにはさらに検討が必要と考えられるが，β-トリメチルシリル基が重要な役割を果たしていることは，β-メチル体*syn*-**65** とメチルリチウムとの反応では五員環は生成せず対応するシクロプロパノールが単離されることから明らかである．一方，*anti*-**65** とメチルリチウムとの反応ではシクロプロパノールではなく開環体**66**を与えた．この結果は，*syn*-**65**では**67** のような五配位型ケイ素を含む分子内キレーションにより，シクロプロパノラートが安定化されているためと考えられる．したがって*anti*-**61** におけるキレーション構造の妥当性も示唆される．



syn-**60** *anti*-**60** **61** **62**

Fig. 5

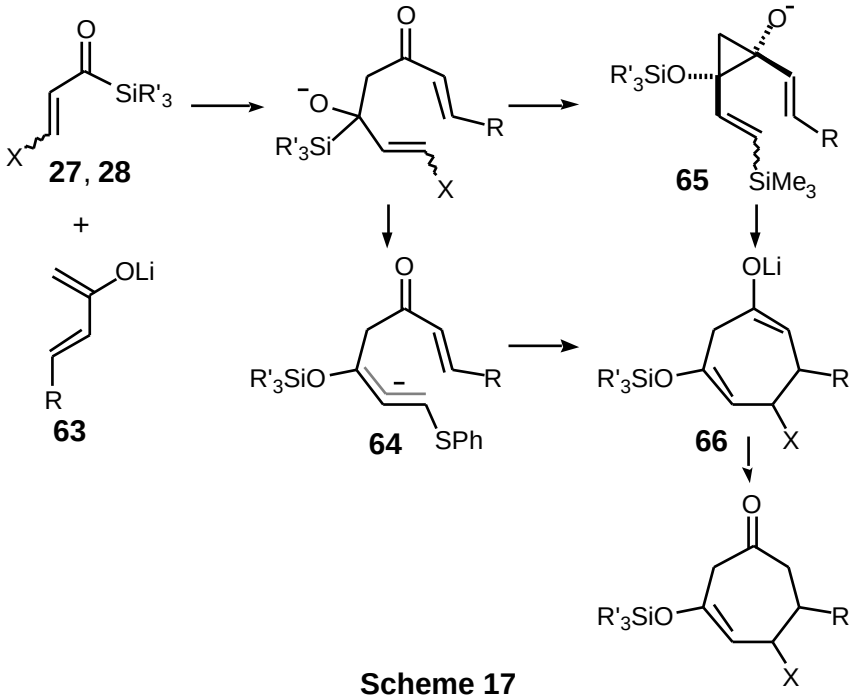
2.4.3 [3 + 2] アニュレーションの反応機構　前二節の結果は，[3 + 2] アニュレーションの機構としてわれわれが提出した経路を強く支持するものと考えられる．特に，*E* 体**56**，*Z* 体**57** のいずれからも同一の環化体**58** が生成し，*Z* 体から**58** が優先的に生成するという事実は，[3 + 2] アニュレーションの結果と良く一致する．したがって，アクリロイルシランのβ-置換基のアニオン安定化能の違いに依存して，非局在化アリルアニオン中間体あるいはビニルシクロプロパノラート中間体を経由するという推定反応機構は，大筋では正しいと思われる．しかし，生成物の立体化学，特にβ-フェニルチオ体の場合，立体的に不利と考えられるジアステレオマー**35** が優先していることなど，不明な点もあり今後の検討課題と考えている．

3. Brook 転位を利用する **[3 + 4]** アニュレーションの開発

3.1 β-トリメチルシリルアクリロイルシランを用いる **[3 + 4]** アニュレーション[21)]

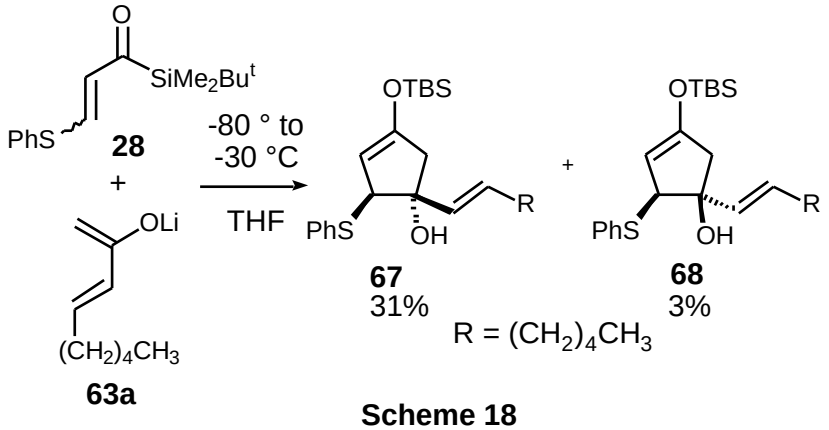
β-ヘテロ原子置換アクリロイルシランが[3 + 2] アニュレーションにおける三炭素単位として機能することがわかったので，次に四炭素単位との組み合わせを用いる[3 + 4] アニュレーションの可能性を探ることにした．Scheme 10 に示した反応機構において，メチルケトンのリチウムエノラートのかわりに，アルケニルメチルケトンのエノラート**68** を用れば，β-フェニルチオ体**32** では 1,2-付加体のBrook 転位／アリル転位により生成する非局在化アリルアニオン**69** の分子内Michael 反応により，またβ-トリメチルシリル体**31** の場合，Brook 転位により生成したカルバニオンがカルボニル基を攻撃してできる*cis*-1,2-ジビニルシクロプロパノラート**70** におい

て アニオニックoxy-Cope 転位がおきてシクロヘプテノン**71** が生成し，新しい[3 + 4] 型の環化反応[22] の開発につながるのではないかと考えた.



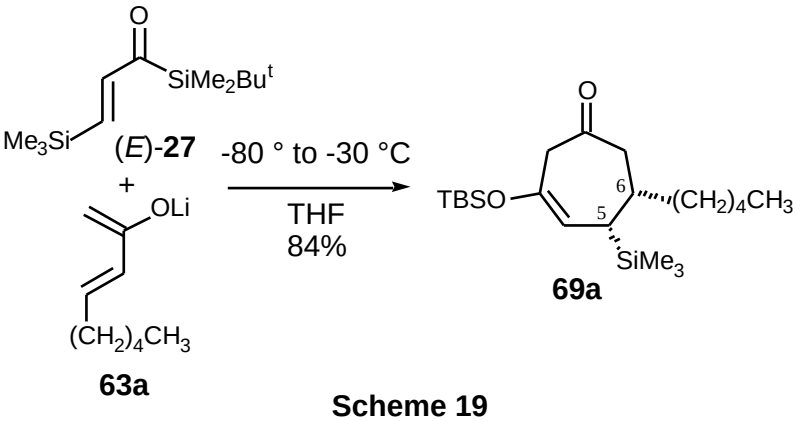
Scheme 17

最初に，β-フェニルチオ体**32** と 3-ノネン-2-オン**68a** との反応を[3 + 2]アニュレーションの場合と同条件で行ったところ，七員環は生成せず[3 + 2]型の反応が進行した**72**，**73**が得られた.



Scheme 18

一方，(*E*)-β-トリメチルシリル体**31** との反応では同条件下，84% の高収率でシクロヘプテノン**74a** が得られた．ここで注目すべき点は，得られたのは5,6-シス体のみでトランス体の生成は認められないという結果である.



Scheme 19

同形式の反応は，他のアルケニルメチルケトンあるいはシクロアルケニルメチルケトンでも好収率で進行した（表2）.

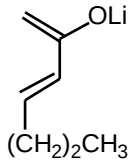
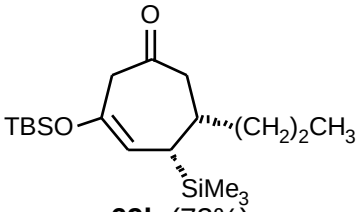
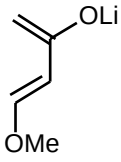
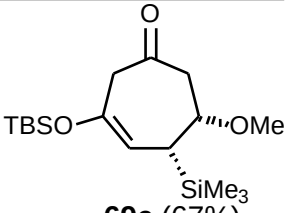
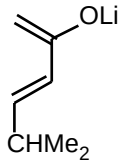
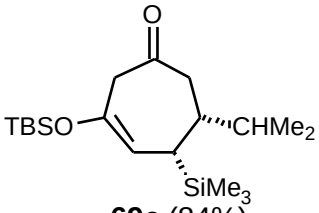
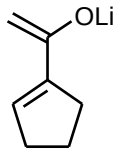
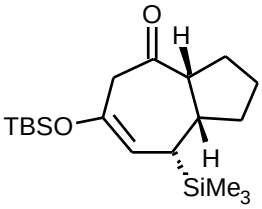
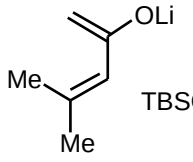
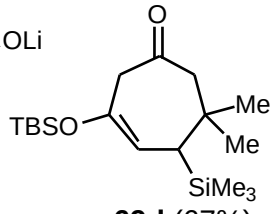
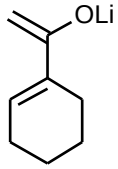
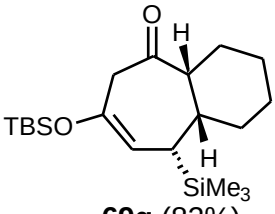
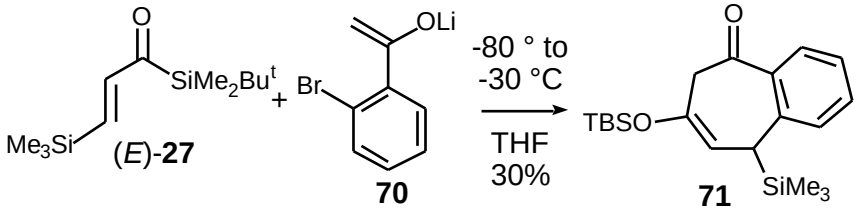
ketone enolate	product (yield)	ketone enolate	product (yield)
 **63b**	 **69b** (73%)	 **63e**	 **69e** (67%)
 **63c**	 **69c** (84%)	 **63f**	 **69f** (73%)
 **63d**	 **69d** (67%)	 **63g**	 **69g** (82%)

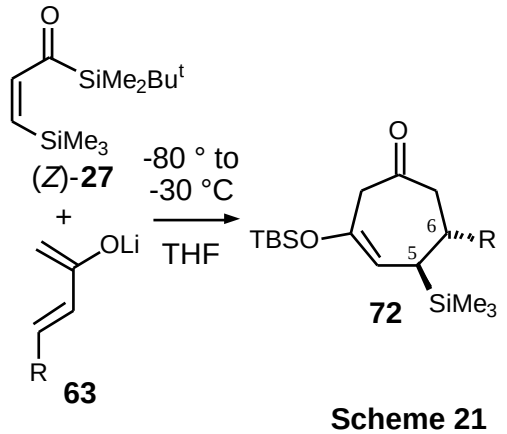
Table 2

また非常に興味深いことには，(*E*)-**31** はアセトフェノンのエノラートとは反応しなかったが，脱離基を導入した 2'-ブロモアセトフェノンのエノラート**75** とは反応し低収率ながらベンゾ縮合体**76** を与えた.



Scheme 20

一方，(*Z*)-**31** との反応は *E* 体に比べてかなり遅く多量の原料を回収するものの，得られた環化体は 5,6-トランス体のみであった．この立体特異性を含めた反応機構については後で述べる.

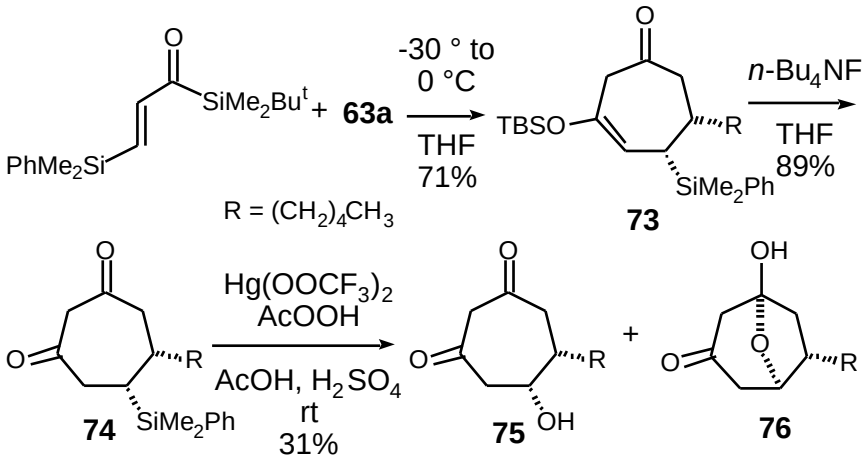


ketone enolate	yield (%) **72** (recovery of **27**)
63a	11 (59)
63b	31 (56)
63c	29 (56)
63d	18 (31)
63e	5 (24)
70	0 (77)

Scheme 21

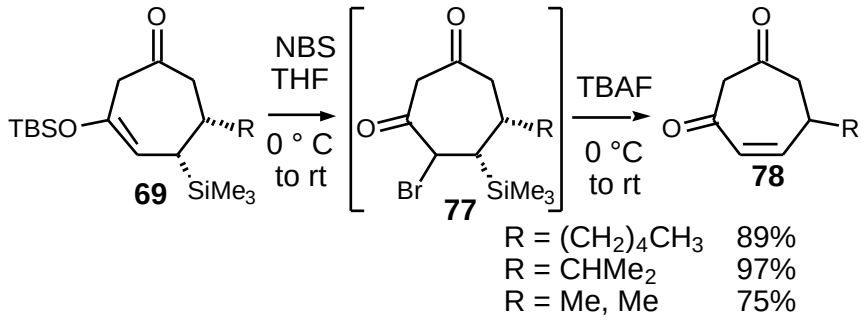
3.2 [3 + 4] アニュレーションの合成反応としての展開[23]

[3 + 4] アニュレーションで得られる**74** を合成中間体として活用するためには，シリル基を除去しなければならない．まず，炭素-ケイ素結合の最も一般的な官能基変換である酸化的脱シリル化[24] を検討することとした．**74** に準じて合成した5-ジメチルフェニルシリル体**78** をジケトン体**79** に変換した後，Fleming の条件[25] で処理したところ31%と低収率ではあるが，アルコール体**80** とその環化体**81** の平衡混合物が得られた．



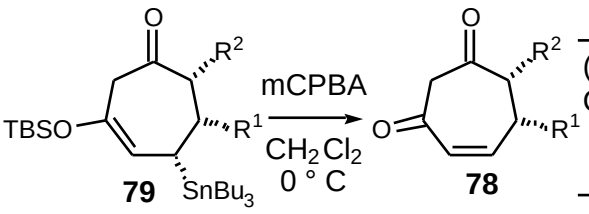
Scheme 22

次に，**74** のアリルシラン部の二重結合がエノールシリルエーテルの二重結合を構成しているという点に着目し，NBS によりα-ブロモケトン体**82** とした後 TBAF 処理を行ったところ収率良くエノン体**83** が生成した．



Scheme 23

なお，**83** は**74** と同様の方法で合成したβ-トリブチルスタンニル体**84** [26] を塩化メチレン中*m*-クロロ過安息香酸 (mCPBA) で処理するだけで得ることができた．



R^1	R^2	yield
$(CH_2)_4CH_3$	H	89%
$CHMe_2$	H	84%
Me, Me	H	76%
$-(CH_2)_3-$		89%

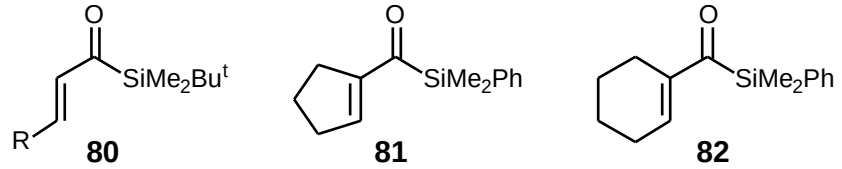
Scheme 24

ごく最近の研究では，アクリロイルシランのβ-置換基はケイ素やスズなどのヘテロ原子である必要はなく，アルキル基のもの**85** あるいは**86**, **87** のようなシクロアルケニルカルボニルシランでもアニュレーションが進行し，七員環を含む多環性化合物の合成にも適用可能であることが明らかになっている．

Fig. 6

3.3 [3 + 4] アニュレーションの反応機構

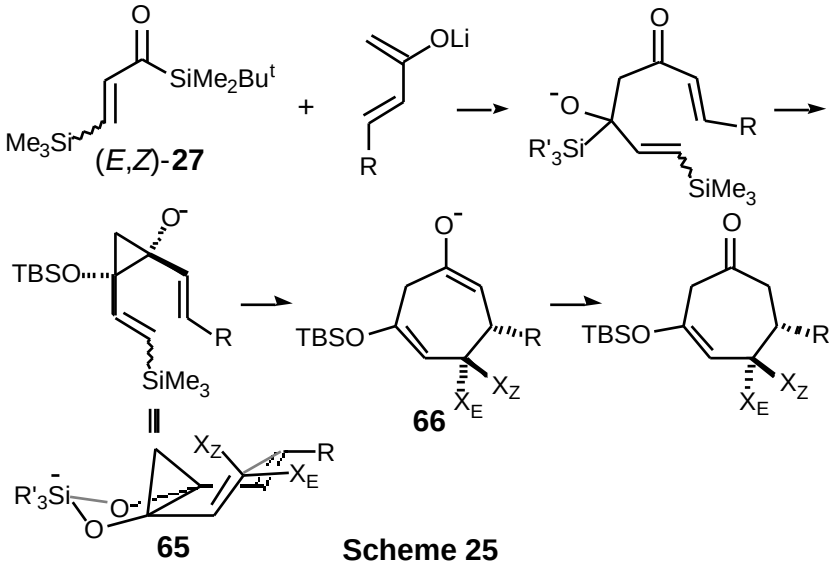
β-フェニルチオアクリロイルシラン**32** からは七員環が生成しないのに対し，β-トリメチルシリル体**31** では-30 °C 以下の低温で速やかに反応が進行し立体特異的に七員環が得られるという結果は，このアニュレーションが非局在化アリルアニオン中間体の分子内Michael 付加(**69** →**71**) ではなく，*cis*-1,2-ジビニルシクロプロパノラート**70** の アニオニックoxy-Cope 転位(**70**→**71**) を経て進行していることを示唆している(Scheme 17). 本[3 + 4] アニュレーションの大きな特徴である立体特異性と極めて高い反応性は，この反応機構によって合理的に説明することができる．すなわち，立体特異性はボート型遷移状態**70** を経るCope 転位の協奏的過程により，また高い反応性は五配位型ケイ素の分子内キレーションにより*cis*-1,2-ジビニル体**70** が選択的に生成し，その転位がオキシアニオンによって著しく加速される結果と考えられる．[27)]



R = *n*-Pr, *i*-Pr, *t*-Bu, *c*-C_6H_{11}

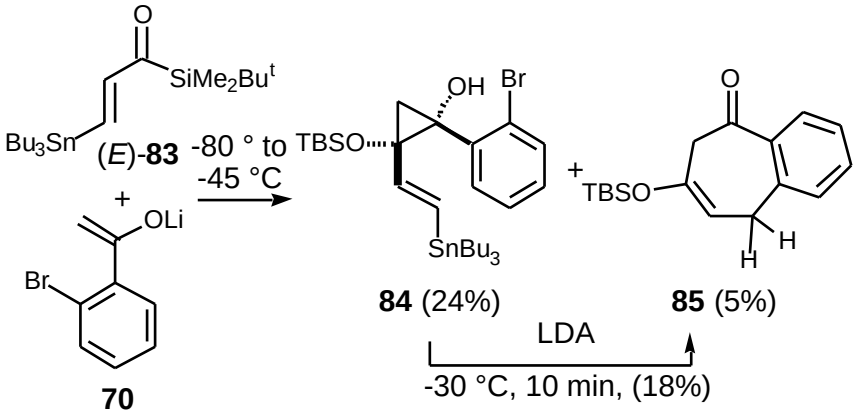
Fig. 6

この反応機構を検証するために，1,2-ジビニルシクロプロパノラート中間体**70** の捕捉そして別ルートによる合成を検討した．[23)] アクリロイルシランとしては，*E* 体の中では最も反応が遅いと予想された (*E*)-**88** と**75** との反応を，-45 °C で処理したところ24% の収率でシクロプロパノール**89** を単離することができた．これを-30 °C でLDA と反応させるとシクロヘプテノン**90** が生成した．



Scheme 25

また，[3 + 2] **アニュレーションの場合と同様に**Fischer **カルベン錯体を用いて合成した***trans*-1,2-**ジビニルシクロプロピルアセテート91**, **93 を**2.2 **当量のメチルリチウムと反応させたところ，低温・短時間でトランス→シスの異性化そして**Cope **転位がおきて立体特異的にシクロヘプテノン92**, **94 を与えた．この結果は，従来知られていなかったジビニルシクロプロパンのアニオニック**oxy-Cope **転位が，極めて速い反応であり，また熱的反応の場合と同様に立体特異的な反応であることを示しており，われわれの提出した反応機構を支持するものである．なお，対応する***cis*-1,2-**ジビニルシクロプロピルアセテートは熱的**Cope **転位が起きてシクロヘプタンジオンを生成してしまうため単離することができなかった.**



Scheme 26

E **体と***Z* **体の反応性の違いの原因を明らかにするために，(***E,Z***)-31 と68a とのの反応を低温で処理したところ，***E* **体の場合**1,2-**付加体(***E***)-95 が**43% **の収率で単離されたが，***Z* **体では**1,2-**付加体は**4% **しか得られず原料のアクリロイルシランが**77% **の収率で回収された．また，**1,2-**付加体(***E,Z***)-99 をそれぞれ**LDA **で処理したところ，***E* **体の場合七員環が主成績体であったのに対し，***Z* **体では**75% **の収率で(***Z***)-31 が得られた．したがって，エノラートの付加の段階は平衡反応であり，***Z* **体の反応が遅いのはこの平衡が原料の側に傾いているためと思われる．詳細な反応機構については今後の検討に待たなければならないが，(***E***)-88 の場合を除いて，**Brook **転位の後プロトン化された96 やシクロプロパノール体97 が検出されないことから，本アニュレーションの律速段階は，**Brook **転位/シクロプロパン化の段階で，おそらく この二段階の反応は協奏的に起こっているものと推定さ**

れる．*Z* 体の場合，Brook 転位/シクロプロパン化の遷移状態**98** が，トリメチルシリル基の立体反発によって *E* 体に比べて不利となり，さらに，1,2-付加体も *E* 体に比べて立体的に込み入っているために原料のアシルシランに戻り，反応の進行が遅く原料が回収されるものと考えられる．

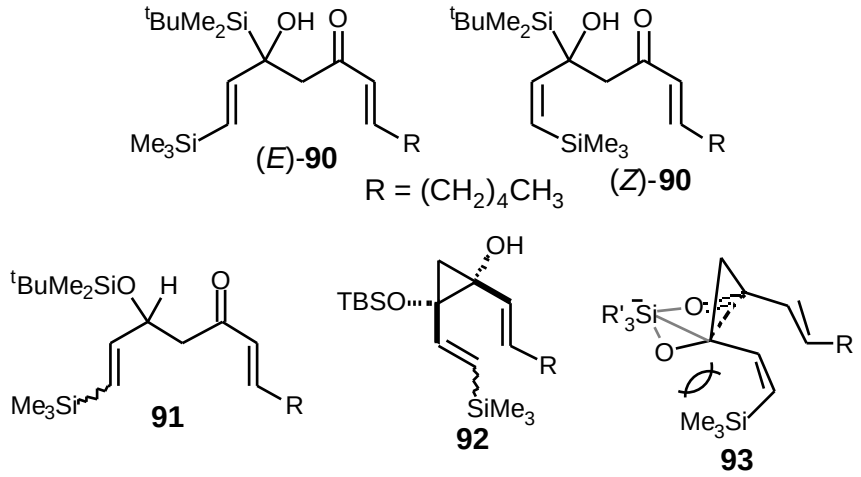


Fig. 7

4 .おわりに

以上，Brook 転位を利用した五および七員炭素環形成反応の開発について述べてきた．Brook 転位はその極めて特異な性質から，多くの新反応を生み出す可能性を秘めているように思える．この小文がそのきっかけとなることを期待したい．

本研究は富山医科薬科大学薬学部薬化学研究室において行われたものであり，日夜惜しみなく努力を払われた多くの研究協力者，佐孝幸一，中村　仁，牧野智子，藤澤正人，中島明美，中谷純子，中山伊知朗，竹田美香，櫻間啓基，北川貫次，佐野綾子，畠山規明，姥山はるか，岡本康志の諸氏に深く感謝の意を表します．また，ご指導，ご鞭撻を賜った吉井英一教授（現名誉教授）並びに小泉　徹教授に厚く御礼申し上げます．なお，本研究の一部は文部省科学研究費 (06672091, 08672416) および薬学研究奨励財団（平成５年度）の援助を受けたものであり，ここに記して感謝いたします．

1)T.-L. Ho, "*Carbocycle Construction in Terpene Synthesis*", VCH, New York, 1988.

2)(a) R.D. Little, "*Comprehensive Organic Synthesis*" Vol.5, eds. by B.M. Trost, I. Fleming, Pergamon, Oxford, 1991, p.239;　(b) J. Mulzer, H-J. Altenbach, M. Braun, K. Krohn, H.-U. Reissig, "*Organic Synthesis Highlight*", VCH, Weinheim, 1991, p.96; (c) D.L. Boger, C. E. Brotherton-Pleiss, "*Advances in Cycloaddition*"　Vol.2, ed. by　D.P. Curran, JAI Press, Greenwich, 1990, p.147; (d) T. Hudlicky, F. Rulin, T.C. Lovelace, J.W. Reed, "*Studies in Natural Products Chemistry*", ed. by T. Attaur-Rahman, Elsevier Science, Essex, U.K. 1989, p.3; (e) P. Binger, H.M. B歡h, *Top. Curr. Chem.*, **135**, 77 (1987); (f) B.M. Trost, *Angew. Chem. Int. Ed. Engl.*, **25**, 1 (1986); (g) J. Mann, *Tetrahedron*, **42**, 4611 (1986);

(h) H.M.R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **23**, 1 (1984); (i) M. Ramaiah, *Synthesis*, **1984**, 529; (j) R. Noyori, Y. Hayakawa, "*Organic Reactions*", Vol.29, eds. by R. Bittman, G.A. Boswell, Jr., S. Danishefsky, W.G. Dauben, H.W. Gschwend, R.F. Heck, R.F. Hirschmann, L.A. Paquette, G.H. Posner, H.J. Reich, B. Weinstein, John Wiley and Sons, Inc., New York, 1983, p.163

3) (a) A.G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957); (b) A.G. Brook, A.R. Bassindale, "*Rearrangements in Ground and Excited States*", ed. by P. de Mayo, Academic Press, New York, 1980, p.149; (c) Brook, A. G. *Acc. Chem. Res.*, **7**, 77 (1974)

4)(a) H. Qi, D.P. Curran, "*Comprehensive Organic Functional Group Transformations*", eds. by A.R. Katritzky, O. Meth-Cohn, C.W. Rees, C.J. Moody, Pergamon, Oxford, 1995, p. 409; (b) P.F. Cirillo, J.S. Panek, *Org. Prep. Proc. Int.*, **24**, 553 (1992); (c) P.C. Bulman Page, S.S. Klair, S. Rosenthal, *Chem. Soc. Rev.*, **19**, 147 (1990); (d) A. Ricci, A. Degl'Innocenti, *Synthesis*, **1989**, 647

5)H.J. Reich, R.C. Holtan, C. Bolm, *J. Am. Chem. Soc.*, **112**, 5609 (1990) **および引用文献**

6)A. Ricci, A. Degl'Innocenti, M. Ancillotti, G. Seconi, P. Dembech, *Tetrahedron Lett.*, **27**, 5985 (1986)

7)I. Kuwajima, K. Matsumoto, *Tetrahedron Lett.*, **42**, 4095 (1979)

8)J.A. Soderquist, E.I. Miranda, *J. Am. Chem. Soc.*, **114**, 10078 (1992)

9)K. Takeda, J. Nakatani, H. Nakamura, K. Sako, E. Yoshii, K. Yamaguchi, *Synlett*, **1993**, 841

10)K. Takeda, M. Fujisawa, T. Makino, E. Yoshii, K. Yamaguchi, *J. Am. Chem. Soc.*, **115**, 9351 (1993)

11)H.J. Reich, M.J. Kelly, R.E. Olson, R.C. Holtan, *Tetrahedron*, **39**, 949 (1983)

12)K. Takeda, I. Nakayama, E. Yoshii, *Synlett*, **1994**, 178

13)K. Takeda, K. Kitagawa, I. Nakayama, E. Yoshii, *Synlett*, **1997**, 255

14)**武田 敬，姥山はるか，小泉 徹，日本薬学会第１１７年会，１９９７年，３月，東京**

15)K. Takeda, K. Sakurama, E. Yoshii, *Tetrahedron Lett.*, **38**, 3257 (1997)

16)C. Girard, P. Amice, J. P. Barnier, J. M. Conia, *Tetrahedron Lett.*, **1974**, 3329

17)(a) T. Hudlicky, J.W. Reed, "*Comprehensive Organic Synthesis*", Vol.5, eds. by B.M. Trost, I. Fleming, Pergamon, Oxford, 1991, p. 899; (b) T. Hudlicky, T.M. Kutchan, S.M. Naqvi, *Organic Reactions*, Vol.33, eds. by R. Bittman, E. Ciganek, S. Danishefsky, H.W. Gschwend, R.F. Heck, R.F. Hirschmann, A.S. Kende, L.A. Paquette, G.H. Posner, J.B. Press, H.J. Reich, John Wiley and Sons, Inc., New York, 1985, p. 247; (c) H.N.C. Wong, M-Y. Hon, C-W. Tse, Y-C. Yip, J. Tanko, T. Hudlicky, *Chem. Rev.*, **89**, 165 (1989)

18)(a) R.L. Danheiser, C. Martinez-Davila, J.M. Morin, Jr., *J. Org. Chem.*, **45**, 1340 (1980); (b) R.L. Danheiser, C. Martinez-Davila, R.J. Auchus, J.T. Kadonaga, *J. Am. Chem. Soc.*, **103**, 2443 (1981)

19)(a) J.J. Bronson, R.L.Danheiser, "*Comprehensive Organic Synthesis*"; Vol.5, eds. by B.M. Trost, I. Fleming, Pergamon, Oxford, 1991, p.999; (b) S.R. Wilson, *Organic Reactions*, Vol.43, eds. by P. Beak, E. Ciganek, D. Curran, L. Hegedus, R.M. Joyce, R.C. Kelly, L.E. Overman, L.A. Paquette, J.B. Press, W. Roush, C. Sih, A.B. Smith, III, M. Uskokovic, J.D. White, John Wiley and Sons, Inc., New York, 1993, p.93

20)C.K. Murray, D.C. Yang, W.D. Wulff, *J. Am. Chem. Soc.*, **112**, 5660 (1990)

21)K. Takeda, M. Takeda, A. Nakajima, E. Yoshii, *J. Am. Chem. Soc.*, **117**, 6400 (1995)

22) A. Hosomi, Y. Tominaga,"*Comprehensive Organic Synthesis*", Vol.5, eds. by B.M. Trost, I. Fleming, Pergamon, Oxford, 1991, p.593

23)武田　敬，中島明美，吉井英一，未発表データ

24)玉尾皓平，有合化，**46**, 861 (1988)

25)I. Fleming, R. Henning, D.C. Parker, H.E. Plaut, P.E.J. Sanderson, *J. Chem. Soc. Perkin Trans 1*, **1995**, 317

26)K. Takeda, A. Nakajima, E. Yoshii, *Synlett*, **1996**, 753

27)(a) T. Hudlicky, R. Fan, J.W. Reed, K.G. Gadamasetti, *Organic Reactions*, Vol.41, eds. by P. Beak, R. Bittman, E. Ciganek, D. Curran, L. Hegedus, R.M. Joyce, R.C. Kelly, L.E. Overman, L.A. Paquette, J.B. Press, W. Roush, C. Sih, A.B. Smith, III, M. Uskokovic, J.D. White, John Wiley and Sons, Inc., New York, 1992, p.1; (b) E. Piers, "*Comprehensive Organic Synthesis*", Vol.5, eds. by B.M.Trost, I. Fleming, Pergamon, Oxford, 1991, p.971; (c) R.K. Hill, *ibid* Vol.5, p.785

Low-Temperature Oxyanion-Accelerated Vinylcyclopropane-Cy.clopentene Rearrangement. Reaction of 2-(2-(Trimethylsilyl)-ethenyl)cyclopropyl Acetates with Methyl Lithium

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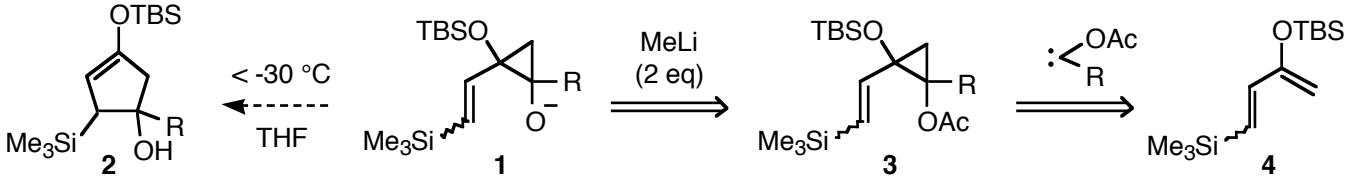
Abstract: Reactions of four diastereomeric 2-(2-(trimethylsilyl)ethenyl)cyclopropyl acetates **7**, derived from enol silyl ether **4** and Fischer carbene complex **6**, with 2.2 equiv of MeLi at -80 ° to -30 °C afforded cyclopentenol **8** as a single diastereomer and acyclic enol silyl ethers **9** via the corresponding cyclopropanolates in ratios depending on the vinylsilane geometry. Predominant formation of **8** over **9** from (*Z*)-**7** irrespective of the stereochemistry at C-1 was observed. This is the first example of oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement which proceeds at unprecedentedly low temperatures.

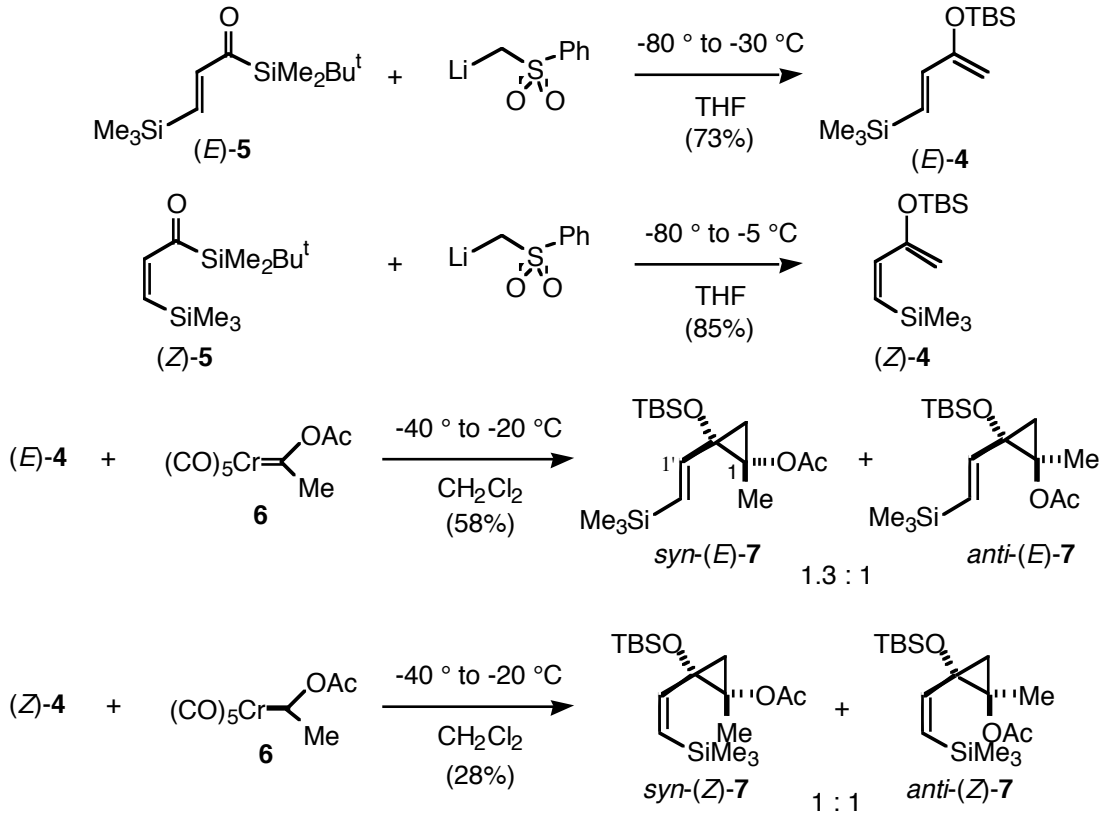
Although vinylcyclopropane-cyclopentene rearrangements have proven to be of considerable synthetic utility, the reaction suffers from a serious limitation in that the rearrangement only proceeds at high temperature, normally higher than 250 °C.[1] Danheiser found that an oxyanion substituent on the cyclopropane ring dramatically accelerated the rearrangement.[2] Even in these cases, however, the reaction requires temperatures in excess of 25 °C and the use of a highly dissociative medium such as HMPA. We now report the first example of an oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement[3] that proceeds at temperatures below -30 °C.

In connection with our investigation of the mechanism of the [3 + 2] annulation between β-heteroatom-substituted acryloylsilane and the lithium enolate of alkyl methyl ketone,[4] we became interested in whether the rearrangement of 2-(2-(trimethylsilyl)ethenyl)cyclopropanolate (**1**) to cyclopentenol (**2**) could proceed at low temperatures below -30 °C. To examine this possibility, we sought a synthetic route that would allow the rapid generation of the cyclopropanolate **1**, even at -80 °C. After considerable experimentation, we found that the reaction of 2 equiv of MeLi with the corresponding cyclopropyl acetate (**3**), prepared by the reaction of a dienol silyl ether (**4**) with an acetoxy carbene complex, was suitable for this purpose.



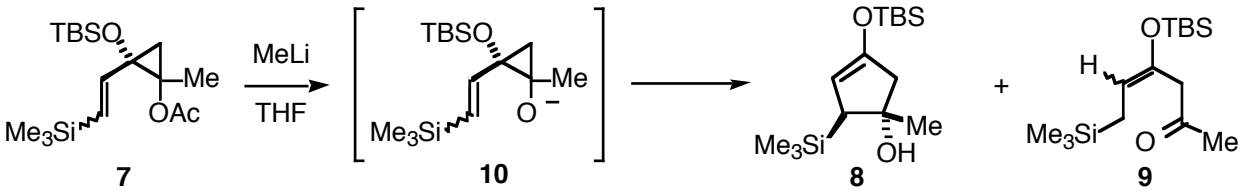
Thus, the dienol silyl ethers **4**, derived from (β-(trimethylsilyl)acryloyl)silanes (**5**)[5] and lithiomethyl phenyl sulfone according to Reich's protocol,[6] were treated with in situ generated acetoxy carbene complex (**6**)[7,8] affording separable vinylcyclopropyl acetates **7** (Scheme 1). The stereochemical assignments of **7** were based on the presence of cross peaks between 1-Me and H-1' in NOESY experiments.

Scheme 1



Reactions of the cyclopropyl acetates **7** with MeLi (2.2 equiv) were performed in THF (0.02 M) at -80 °C for 30 min and at -80 °C followed by warming to -50 °C and -30 °C over 30 min, respectively, and quenching with a solution of acetic acid (1 equiv) in THF. In most cases, a single cyclopentenol (**8**)[9] and unsaturated ketone (**9**),[10] a ring opened product, were obtained (Table 1).[11,12] The product distribution depends upon the vinylsilane geometry, but is unaffected by the *syn*/*anti* stereochemistry between the *tert*-butyldimethylsiloxy (TBSO) and acetoxy groups. Particularly noteworthy is the substantial formation of **8** from (*Z*)-**7** even at -80 °C in contrast to the reaction with (*E*)-**7**, wherein **8** is not formed under these conditions.

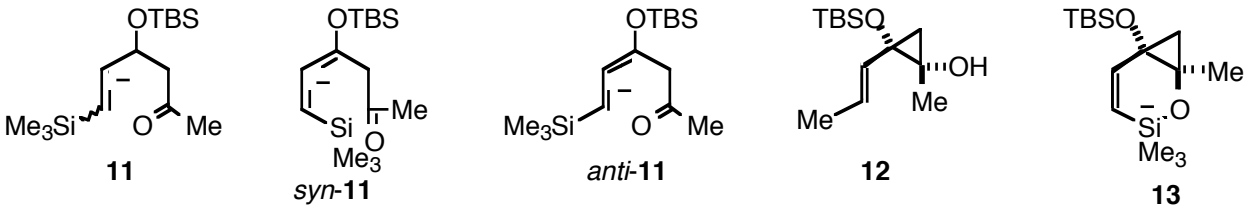
Table 1



7	conditions	yield (%)		**7**	conditions	yield (%)	
		8	**9**			**8**	**9**
syn-(*E*)	-80 °C, 30 min	0	81	*syn*-(*Z*)	-80 °C, 30 min	52	20
syn-(*E*)	-80 ° to -50 °C	45	40	*syn*-(*Z*)	-80 ° to -50 °C	61	5
syn-(*E*)	-80 ° to -30 °C	54	31	*syn*-(*Z*)	-80 ° to -30 °C	76	16
anti-(*E*)	-80 °C, 30 min	0	89	*anti*-(*Z*)	-80 °C, 30 min	59	10
anti-(*E*)	-80 ° to -50 °C	45	39	*anti*-(*Z*)	-80 ° to -50 °C	72	6
anti-(*E*)	-80 ° to -30 °C	63	34	*anti*-(*Z*)	-80 ° to -30 °C	76	14

The dependency of the product ratio upon the vinylsilane geometry seems to be inconsistent with a pathway entailing intramolecular attack of the freely-rotating delocalized allylic anion intermediate **11**, generated by ring opening followed by allylic delocalization of the resulting carbanion, on the carbonyl group. Also, a simple concerted [1,3]-sigmatropic shift is incompatible with the observation that the same cyclopentenol (**8**) is obtained irrespective of the vinylsilane geometry and of the stereochemistry at C-1 of **7**.

Although the precise mechanism to account for the results remains unclear, the trimethylsilyl group should play a crucial role in the rate acceleration because 2-propenylcyclopropanol derivative **12**[13] was recovered unchanged after exposure to methyl lithium (1 equiv) at -80 ° to -30 °C. A plausible mechanism involves kinetically controlled ring-closure of the silicon-stabilized allylic carbanion intermediates *syn*-**11** and *anti*-**11** which form from (*Z*)-**10** and (*E*)-**10**, respectively. Thus, the cyclization of *syn*-**11** to **8** can occur faster than that of *anti*-**11** and conformational interconversion between *syn*- and *anti*-**11** for some unknown reason. Another attractive but unverified mechanism is one where **8** is produced only via [1,3]-sigmatropic shift of the internally O-Si coordinated intermediate **13** which is directly derived from *anti*-(*Z*)-**7** and can be reversibly generated from three other diastereomeric cyclopropanolates **10** by ring-opening, geometric isomerization and ring-closure sequence. More facile rearrangement of **13** to **8** is presumably due to its fixed conformation suitable for the overlap of the orbitals required for the rearrangement, and the stereochemical course is in agreement with that predicted by orbital symmetry considerations, assuming the methyl group is bulkier than the solvated oxyanion.



In summary, we have demonstrated the first examples of oxyanion-accelerated vinylcyclopropane-cyclopentene rearrangement to proceed at unprecedentedly low temperatures. Further studies aimed at clarification of the reaction mechanism of the [3 + 2] annulation as well as of the vinylcyclopropane rearrangement are now underway in our laboratory and will be reported in due course.

Acknowledgment. Acknowledgment is made to the Research Foundation for Pharmaceutical Sciences and the Grant-in-Aid for Scientific Research (No. 08672416 (K. T.)) from the Ministry of Education, Science, Sports, and Culture, Japan for partial support of this research.

References and Notes

1. For reviews on vinylcyclopropane-cyclopentene rearrangement, see: Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 899-970. Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247-335. Also, see: Wong, H. N. C.; Hon, M-Y.; Tse, C-W.; Yip, Y-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165-198.

2. (a) Danheiser, R. L.; Martinez-Davila, C.; Morin, Jr.; J. M. *J. Org. Chem.* **1980**, *45*, 1340-1341. (b) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443-2446. For a carbanion-accelerated version, see: Danheiser, R. L.; Bronson, J. J.; Okano, K. *J. Am. Chem. Soc.* **1985**, *107*, 4579-4581.
3. For a review of charge accelerated rearrangement, see: (a) Bronson, J. J.; Danheiser, R. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 999-1036. (b) Wilson, S. R. *Org. React.* **1993**, *43*, 93-250.
4. Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9351-9352.
5. Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949-960.
6. Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609-5617.
7. Murray, C. K.; Yang, D. C. Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660-5662.
8. For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 1065-1113. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Libeskind, L. S., Ed.; JAI Press Inc.; Greenwich, CT, 1989; Vol. 1, pp 209-393. (c) Dötz, K. H. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587-608.
9. The relative stereochemistry was assigned on the basis of NOESY experiments and of comparison with spectroscopic data of related compounds.[4]
10. The *E*/*Z* ratios were variable although the *E* isomer always predominated, and were independent of the ratios of **8** and **9**.
11. No *E*/*Z* and *syn*/*anti* isomerization was observed in a small amount of **7** recovered from the reaction mixture.
12. Attempted trapping of **10** as an acetate with acetyl bromide and isolation of the corresponding vinylcyclopropanol by nonaqueous workup were unsuccessful.
13. Takeda, K.; Nakatani, J.; Nakamura, H.; Sako, K.; Yoshii, E.; Yamaguchi, K. *Synlett* **1993**, 841-843.

Supplementary Information (20 pages)

Low-temperature Oxyanion-Accelerated Vinylcyclopropane-Cyclopentene Rearrangement. Reaction of 2-(2-(Trimethylsilyl)ethenyl)cyclopropyl Acetates with Methyl Lithium.

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Experimental Section

General: IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer. ^{1}H NMR spectra were taken on Varian UnityPlus 500 in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26). ^{13}C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2). Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. Low- and high-resolution mass spectra (EI-MS) were obtained with a JEOL JMS-AX-505HAD spectrometer. Liquid chromatography under medium pressures (MPLC) was carried out with a JASCO PU-980 pump system by using prepacked columns (22 mm x 300 mm, 10 μ silica gel or 22 mm x 150 mm, 5 μ silica gel) (Kusano Kagakukikai Co.). For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; Merck precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Dry solvents and reagents were obtained by using standard procedures. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator.

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*E*)-4)

To a cooled (ice-water) solution of methyl phenyl sulfone (516 mg, 3.3 mmol) in THF (7 mL) was added dropwise *n*-BuLi (1.47 M hexane solution, 2.25 mL, 3.3 mmol). After stirring at the same temperature for 1 h, the mixture was added dropwise to a cooled (-80 °C) solution of (*E*)-**5** (728 mg, 3.0 mmol) in THF (7 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (15 mL). The phase was separated, and the aqueous phase was extracted with Et_2O (10 mL x 2). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 36 g; elution with hexane) to give (*E*)-**4** (562 mg, 73%). a colorless oil, R_f = 0.39 (hexane). IR (neat) 1250 cm^{-1}. ^{1}H NMR δ 0.09 (9H, s, $SiMe_3$), 0.17 (6H, s, $SiMe_2$), 0.97 (9H, s, *t*-Bu), 4.35 and 4.37 (each 1H, br s, H-1), 6.18 (1H, d, *J* = 18.6 Hz, H-3), 6.34 (1H, d, *J* = 18.6 Hz, H-4). ^{13}C NMR δ -4.5 ($SiMe_2$), -1.1 ($SiMe_3$), 18.5 (CMe_3), 26.0 (*t*-Bu), 96.7 (C-1), 130.1 (C-3), 141.4 (C-4), 155.8 (C-2). HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1657.

(*Z*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*Z*)-4)

(*Z*)-**4** was obtained from (*Z*)-**5** in 85% yield by the procedure described above for (*E*)-**4**. a colorless oil, R_f = 0.50 (hexane). IR (neat) 1250 cm^{-1}. ^1H NMR δ 0.14 (9H, s, $SiMe_3$), 0.20 (6H, s, $SiMe_2$), 0.95 (9H, s, *t*-Bu), 4.35 and 4.36 (each 1H, br s, H-1), 5.61 (1H, d, *J* = 15.2 Hz, H-3), 6.52 (1H, d, *J* = 15.2 Hz, H-4). ^{13}C NMR δ -3.6 ($SiMe_2$), 0.4 ($SiMe_3$), 19.0 (CMe_3), 26.4 (*t*-Bu), 95.8 (C-1), 132.4 (C-3), 143.9 (C-4), 157.1 (C-2). HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1643.

2-(*tert*-Butyldimethylsiloxy)-1-methyl-2-((*E*)-2-(trimethylsilyl)ethenyl)cyclopropyl acetates (*syn*-(*E*)-7 and *anti*-(*E*)-7)

To a cooled (-40 °C) suspension of tetramethylammonium (methyl(oxido)carbene)pentacarbonyl-chromium[1] (662 mg, 2.14 mmol) in CH_2Cl_2 (4 mL) was added dropwise freshly distilled acetyl bromide (180 μL, 299 mg, 2.43 mmol), and then the reaction mixture was stirred at the same temperature for 1 h. To this mixture was added dropwise a solution of (*E*)-**4** in CH_2Cl_2 (38 mL) over 1 h. The reaction mixture was allowed to warm to -20 °C over 1 h, and to stand in a freezer (-20 °C) for 12 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution (10 mL), and extracted with hexane (50 mL, 10 mL x 2). The combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 120 g; elution with 20 : 1 hexane-AcOEt) to give a 1.3:1 mixture of *syn*-(*E*)- and *anti*-(*E*)-**7** (428 mg, 58%). The diastereomeric mixture was separated by MPLC (elution with 60:1 hexane-Et_2O). *syn*-(*E*)-**7**: a colorless oil, R_f = 0.37 (20:1 hexane-Et_2O). IR (neat) 1755 cm^{-1}. ^1H NMR δ (ppm) 0.03 and 0.07 (each 3H, s, $SiMe_2$), 0.07 (9H, s, $SiMe_3$), 0.86 (9H, s, *t*-Bu), 1.03 and 1.13 (each 1H, d, *J* = 7.7 Hz, H-3), 1.37 (3H, s, 1-CH_3), 2.02 (3H, s, $COCH_3$), 5.79 (1H, d, *J* = 18.8 Hz, H-1'), 6.08 (1H, d, *J* = 18.8 Hz, H-2'). ^{13}C NMR δ -3.8 and -3.0 ($SiMe_2$), -1.1 ($SiMe_3$), 17.9 (2-Me), 18.1 (CMe_3), 21.3 ($COCH_3$), 23.9 (C-3), 25.8 (*t*-Bu), 62.1 and 63.4 (C-1 and C-2), 130.5 (C-1'), 144.9 (C-2'), 170.6 (C=O). HRMS calcd for $C_{17}H_{34}O_3Si_2$ 342.2047, Found 342.2081. *anti*-(*E*)-**7**: a colorless oil, R_f = 0.37 (20:1 hexane-Et_2O). IR (neat) 1755 cm^{-1}. ^1H NMR δ (ppm) 0.03 and 0.09 (each 3H, s, $SiMe_2$), 0.05 (9H, s, $SiMe_3$), 0.88 (9H, s, *t*-Bu), 0.99 (1H, dd, *J* = 7.5, 0.9 Hz, H-3), 1.33 (1H, d, *J* = 7.5 Hz, H-3), 1.58 (3H, s, 1-Me), 1.90 (3H, $COCH_3$), 5.72 (1H, d, *J* = 18.8 Hz, H-1'), 6.02 (1H, dd, *J* =18.8, 0.9 Hz, H-2'). ^{13}C NMR δ -3.7 and -3.0 ($SiMe_2$), -1.1 ($SiMe_3$), 16.6 (2-Me), 18.2 (CMe_3), 21.4 ($COCH_3$), 25.6 (C-3), 26.0 (*t*-Bu), 64.1 and 64.5 (C-1 and C-2), 128.3 (C-1'), 144.6 (C-2'), 170.5 (C=O). HRMS calcd for $C_{17}H_{34}O_3Si_2$ 342.2047, Found 342.2039.

2-(*tert*-Butyldimethylsiloxy)-1-methyl-2-((*Z*)-2-(trimethylsilyl)ethenyl)cyclopropyl acetates (*syn*-(*Z*)-7 and *anti*-(*Z*)-7)

A 1:1 mixture of *syn*-(*Z*)- and *anti*-(*Z*)-**7** (28%) was obtained from (*Z*)-**4** by the procedure described for the corresponding (*E*)-isomers. The diastereomeric mixture was separated by MPLC (elution with 60:1 hexane-Et_2O). *syn*-(*Z*)-**7**: a colorless oil, R_f = 0.33 (20:1 hexane-Et_2O). IR (neat) 1755 cm^{-1}. ^1H NMR δ (ppm) 0.07 and 0.13 (each 3H, s, $SiMe_2$), 0.15 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*-

1. Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445-2456.

Bu), 0.98 (1H, d, J = 7.5 Hz, H-3), 1.20 (1H, br d, J = 7.5 Hz, H-3), 1.57 (3H, s, 1-CH_3), 1.93 (3H, s, $COCH_3$), 5.76 (1H, d, J = 14.7 Hz, H-1'), 6.47 (1H, d, J = 14.7 Hz, H-2'). ^{13}C NMR δ -3.1 and -2.9 ($SiMe_2$), 0.2 ($SiMe_3$), 16.9 (2-Me), 18.2 (CMe_3), 21.6 ($COCH_3$), 25.9 (*t*-Bu), 27.1 (C-3), 63.0 (C-1 and C-2), 136.0 (C-1'), 144.2 (C-2'), 170.9 (C=O). HRMS calcd for $C_{17}H_{34}O_3Si_2$ 342.2047, Found 342.2050. *anti*-(*Z*)-**7**: a colorless oil, R_f = 0.33 (20:1 hexane-Et_2O). IR (neat) 1755 cm^{-1}. ^{1}H NMR δ (ppm) 0.08 and 0.10 (each 3H, s, $SiMe_2$), 0.15 (9H, s, $SiMe_3$), 0.85 (9H, s, *t*-Bu), 1.11 (1H, d, J = 7.5 Hz, H-3), 1.15 (1H, br d, J = 7.5 Hz, H-3), 1.36 (3H, s, 1-Me), 2.03 (3H, $COCH_3$), 5.77 (1H, d, J = 14.7 Hz, H-1'), 6.54 (1H, br d, J =14.7 Hz, H-2'). ^{13}C NMR δ -3.2 and -3.0 ($SiMe_2$), -1.1 ($SiMe_3$), 16.6 (CMe_3), 18.2 (2-Me), 21.7 ($COCH_3$), 25.9 (*t*-Bu), 26.0 (C-3), 53.6 and 60.7 (C-1 and C-2), 128.3 (C-1'), 145.1 (C-2'), 171.0 (C=O). HRMS calcd for $C_{17}H_{34}O_3Si_2$ 342.2047, Found 342.2038.

Reaction of 7 with MeLi

This procedure is representative of all reactions of **7** with MeLi. To a cooled (-80 °C) solution of *syn*-(*Z*)-**7** (54 mg, 0.158 mmol) in THF (7.9 mL) was added dropwise MeLi (0.95 M in Et_2O, 350 μL, 0.330 mmol) over 2 min. The reaction mixture was allowed to warm to -30 °C over 30 min, and then quenched by addition of AcOH (20 mg, 19 μL) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (15 mL), and then extracted with Et_2O (10 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residue was subjected to column chromatography (silica gel, 6 g; elution with 2:1 hexane-Et_2O) to give **8** (36 mg, 76%) and **9** (*E*/*Z* mixture) (4 mg, 8%). The *E*/*Z* mixture of **9** was separated by MPLC (5 μ silica gel, elution with 50:1 hexane-Et_2O). The yield (14%) of **9** was determined on the basis of the **8**/**9** ratio in ^{1}H NMR spectrum of the crude product and the isolated yield of **8**. **8**: a colorless oil, R_f = 0.35 (2:1 hexane-Et_2O). IR (neat) 3385, 1635 cm^{-1}. ^{1}H NMR δ (ppm) 0.03 (9H, s, $SiMe_3$), 0.15 and 0.16 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 1.39 (1-Me), 1.85 (1H, br m, H-2), 2.20 (1H, dd, J = 16.2, 2.6 Hz, H-5), 2.39 (1H, br s, OH), 2.43 (1H, dm, J = 16.2 Hz, H-5), 4.63 (1H, br dd , J = 2.6, 2.6 Hz, H-3). ^{13}C NMR δ -4.4 and -4.2 ($SiMe_2$), -1.6 ($SiMe_3$), 18.2 (CMe_3), 25.8 (*t*-Bu), 26.1 (1-Me), 47.0 (C-2), 50.2 (C-5), 80.2 (C-1), 103.4 (C-3), 150.6 (C-4). HRMS calcd for $C_{15}H_{32}O_2Si_2$ 300.1941, Found 300.1926. (*E*)-**9**: a colorless oil, R_f = 0.30 (12:1 hexane-Et_2O).IR (neat) 1720, 1655 cm^{-1}. ^{1}H NMR δ (ppm) 0.00 (9H, s, $SiMe_3$), 0.13 (6H, s, $SiMe_2$), 0.89 (9H, s, *t*-Bu), 1.29 (2H, d, J = 8.5 Hz, H-6), 2.17 (3H, s, H-1), 3.09 (2H, s, H-3), 4.81 (1H, t, J = 8.5 Hz, H-5). ^{13}C NMR δ -4.3 ($SiMe_2$), -1.6 ($SiMe_3$), 16.8 (C-6), 18.1 (CMe_3), 25.8 (*t*-Bu), 29.0 (C-1), 47.4 (C-3), 106.6 (C-5), 143.7 (C-4), 206.6 (C-2). HRMS calcd for $C_{15}H_{32}O_2Si_2$ 300.1941, Found 300.1934. (*Z*)-**9**: a colorless oil, R_f = 0.30 (12:1 hexane-Et_2O). IR (neat) 1720, 1660 cm^{-1}. ^{1}H NMR δ (ppm) 0.01 (9H, s, $SiMe_3$), 0.12 (6H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 1.42 (2H, d, J = 8.3 Hz, H-6), 2.19 (3H, s, H-1), 3.04 (2H, s, H-3), 4.62 (1H, t, J = 8.3 Hz, H-5). ^{13}C NMR δ -3.7 ($SiMe_2$), -1.4 ($SiMe_3$), 15.9 (C-6), 18.4 (CMe_3), 25.9 (*t*-Bu), 28.5 (C-1), 52.8 (C-3), 109.1 (C-5), 142.8 (C-4), 207.4 (C-2). HRMS calcd for $C_{15}H_{32}O_2Si_2$ 300.1941, Found 300.1935.

アクリロイルシランを用いる [3 + 4] アニュレーションの反応機構

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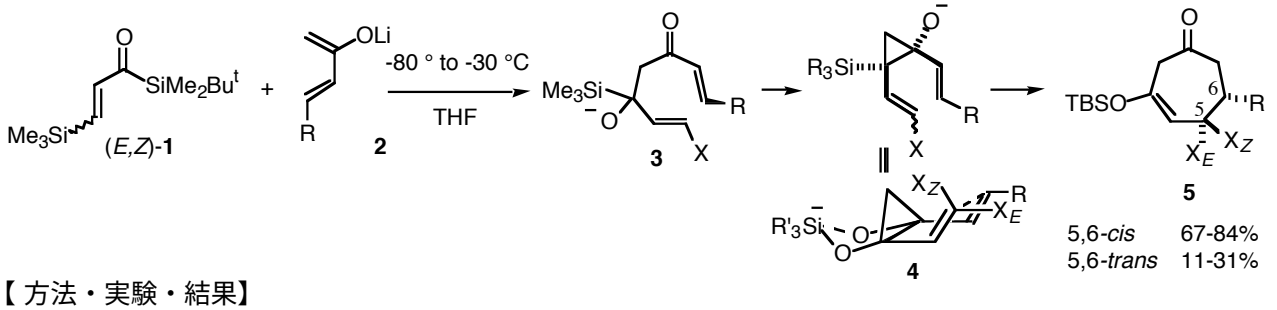
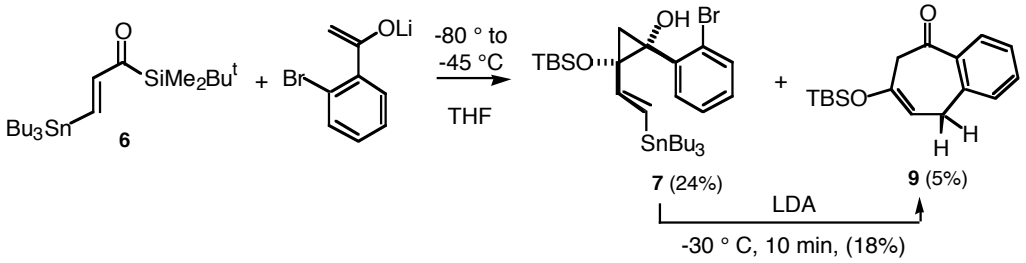
吉井英一，小泉　徹

【目的】 最近われわれは，(b-(trimethylsilyl)acrylolyl)silane **1** と alkenyl methyl ketone の lithium enolate **2** の反応を用いる新しい [3 + 4] アニュレーションを開発した(*1*)．本反応の高い立体特異性(*E*-**1** → 5,6-*cis*-**5**; *Z*-**1** → 5,6-*trans*-**5**)を説明する機構として，1,2-付加体**3** のBrook転位により生成するカルバニオンが分子内でカルボニル基を攻撃して*cis*-1,2-cyclopropanolate **4** となった後，その anionic oxy-Cope 転位を経て七員環を生成する経路を提出した．この反応機構を検証することを目的として，三員環中間体**4** の捕捉を試みる．さらに，別経路で**4** の合成を行うことにより，反応機構を明らかにするばかりでなく，これまで知られていない 1,2-divinylcyclopropane の anionic oxy-Cope 転位の反応性および立体化学についての知見を得る．



【方法・実験・結果】

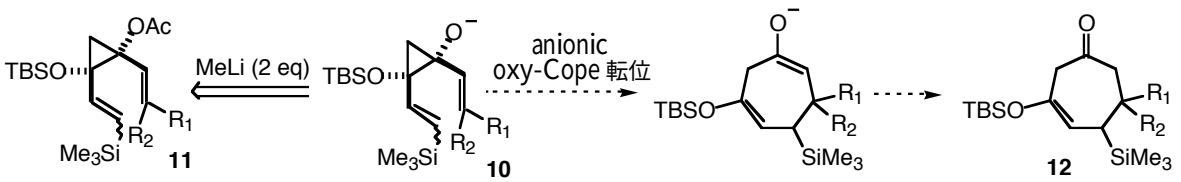
<u>三員環中間体の捕捉</u>　これまでの研究から反応が最も遅いと考えられた，b-stannyl 誘導体**6** (*2*) と 2'-bromoacetophenone の反応を用いて，cyclopropanolate 中間体**4** の捕捉を検討した．その結果，反応を -45 。C で処理したところ，24% の収率で cyclopropanol 誘導体**7** を単離することができた．**7** を -30 ℃, 10 分間 LDA と反応させたところ，環化体**9** が生成した．



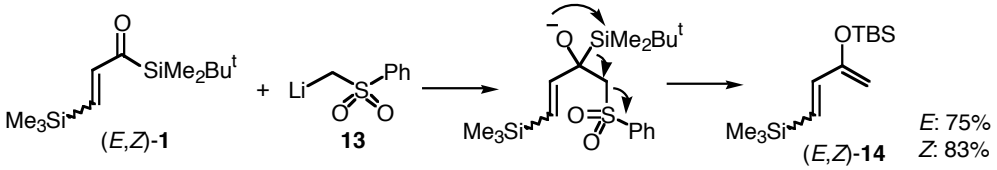
この結果は，われわれが提出した 1.2-divinylcyclopropanolate 中間体を含む反応機構を強く支持するものであるが，ここで用いた反応は芳香環の二重結合が Cope 転位に関与するもので，一般性に欠けること,そして立体化学に関する情報も得られないことから，別ルートで 1,2-divinylcyclopropanolate の合成を行うことにより，これまでに報告例の無い 1,2-divinylcyclopropane の anionic oxy-Cope 転位の反応性および立体化学を検討することにした．

<u>1,2-Divinylcyclopropyl acetate の合成</u> *cis*-1,2-divinylcyclopropanolate の anionic oxy-Cope 転位 (**10**≒**12**) は非常に速い反応であることが予想されるため，**10** の oxyanion の発生は，低温 (-80 。C) 短時間で行う必要がある．そこで，cyclopropyl acetate **11** と 2 当量の

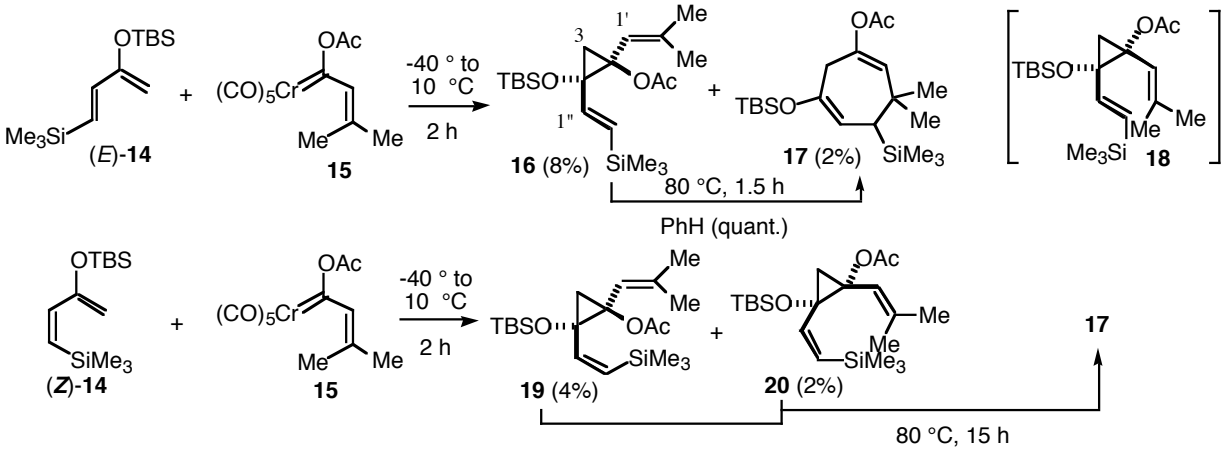
MeLi によるエステル開裂反応を利用することとし，まず，立体異性体を生成しない **11** ($R_1 = R_2 = Me$) を用いて，転位の反応性の検討から研究を開始した．



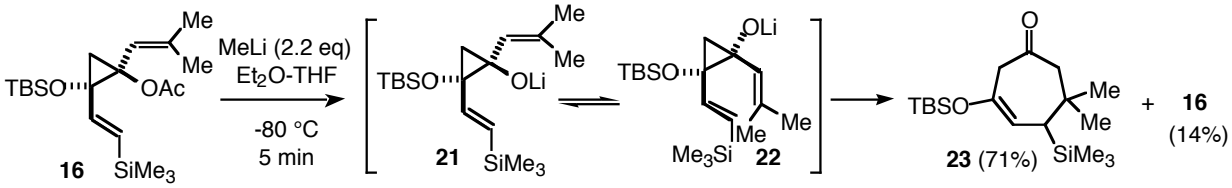
cyclopropyl acetate **11** の合成は，Reich らの方法 (*3*) を用いて acylsilane **1** と lithiomethyl phenyl sulfone **13** から Brook 転位を経て得た enol silyl ether **14** を，低温下 acetoxy carbene 錯体 **15** と反応させることにより行った．



(*E*)-体からは，低収率ながら *trans*-1,2-divinylcylopropyl acetate **16** と *cis*-体 **18** の熱 Cope 転位成績体 **17** が，(*Z*)-体からは *trans*-体 **19** および *cis*-体 **20** が得られた．**16** の **17** への変換には，benzene 中 1.5 時間の加熱を要したことから，**18** の熱 Cope 転位は室温以下で進行したものと考えられる．一方，**19**, **20** の熱 Cope 転位は benzene 中 15 時間の加熱を要した．**16**, **19**, および **20** の立体化学は，NOESY スペクトルにおける三員環上のプロトン H-3 と二つのビニル基のプロトン H-1', H-1" の間の相関の有無により決定した．

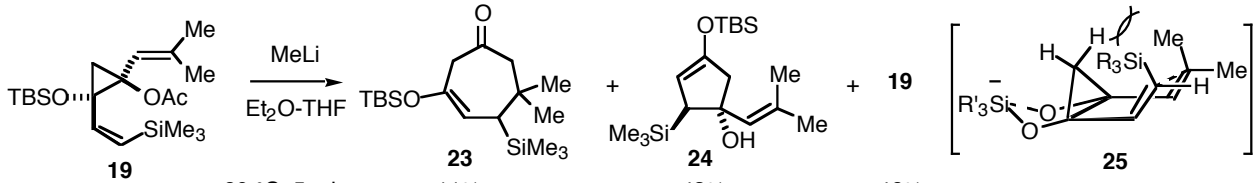


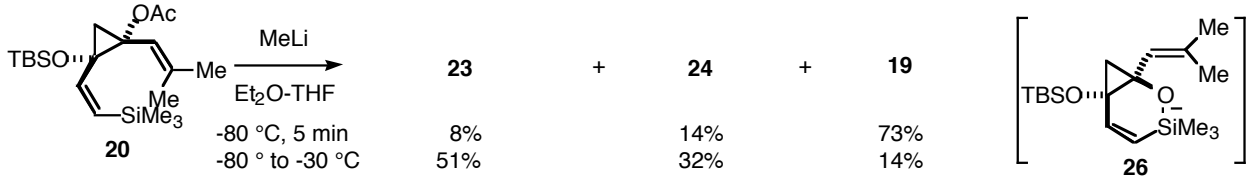
MeLi との反応は，**16**, **19**, および **20** を用いて行った．THF 中，2.2 当量の MeLi を加えたところ，**16** の場合 -80 ₀C, 5 min という条件で cycloheptenone **23** が 62% の収率で生成した．本反応は，エステル開裂，*cis/trans* 異性化，そして Cope 転位の三工程 (**16**→**21**→**22**→**23**) を含むにもかかわらず，低温 短時間で反応が進行していることから，**22** の anionic oxy-Cope 転位は極めて速い反応であることが判明した．



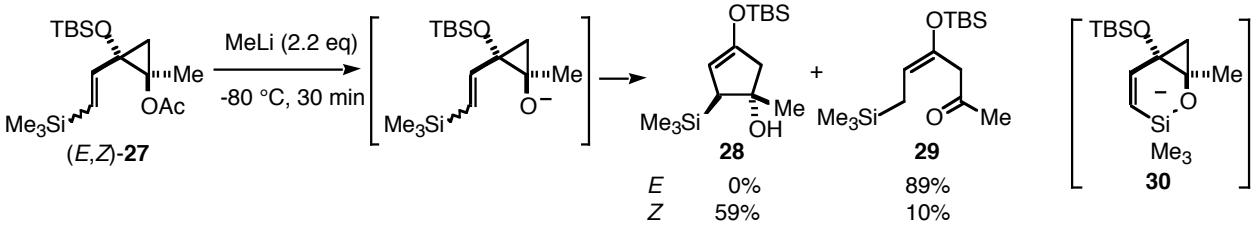
一方，(*Z*)-体 **19**, **20** の場合，同様の条件下 Cope 転位体 **23** の生成は低収率で，主成

績体は cyclopentenol **24** であった．この事実は，(*Z*)-体の反応がボート型遷移状態**25**における $SiMe_3$ 基と三員環上のプロトンとの立体反発のために (*E*)-体に比べて遅くなった結果，競合する vinylcyclopropane-cyclopentene 転位（[1,3] シグマトロピー転位）が優先するようになったためと思われる．この傾向は特に *trans*-体**19**で強いが，**19**の場合，五配位ケイ素中間体**26**を経由することによりビニル側鎖のコンフォメーションが固定され，[1.3] シグマトロピー転位が促進されたものと考えられる．



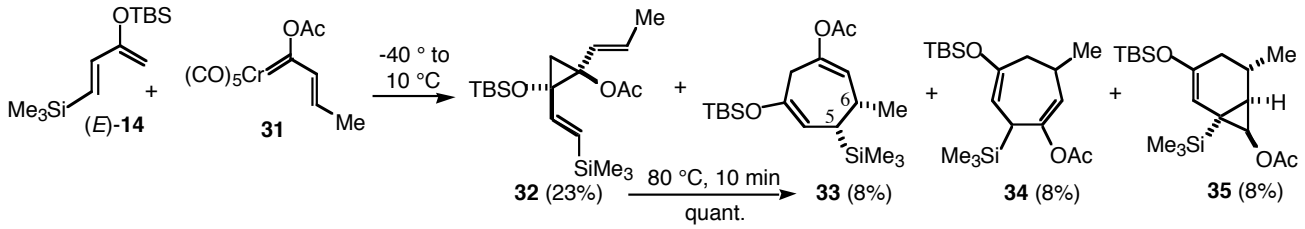


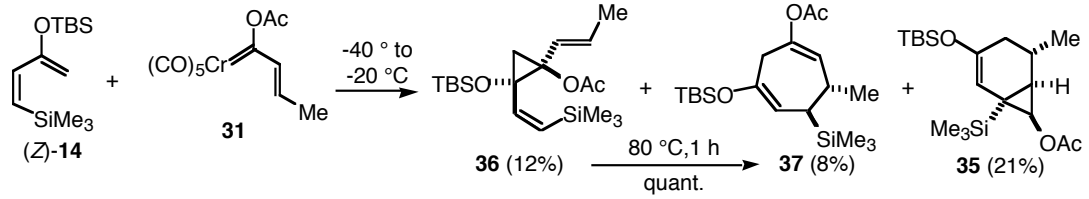
この結果は，現在われわれが同時に研究を進めている [3 + 2] アニュレーション (*4*) の反応機構に関する研究の結果ともよく一致する．すなわち，以下に示すように，2-vinylcyclopropyl acetate **27** と MeLi との反応による cyclopentenol **28** への転位反応において，*E*-体と *Z*-体とでその反応性に大きな差があり，この結果も五配位ケイ素中間体**30**の介在を仮定することにより，合理的に説明が可能である．



以上のように，1,2-divinylcyclopropane の anionic oxy-Cope 転位が極めて速い反応であるということが明らかになったので，次に propenyl 体**11** (R_1 = Me, R_2 = H) を用いて，転位の立体化学を調べることにした．

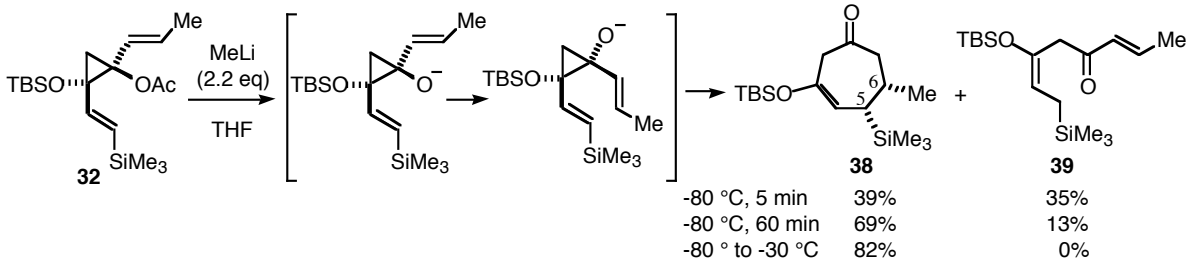
cyclopropyl acetate の合成は methylpropenyl 体**15**の場合とほぼ同様の条件で行った．予想どおりいずれの場合も *cis*-体**11** ((*E*)-$SiMe_3$; R_2 = H) は得られず，*trans*-体**32, 36** そして *cis*-体の熱 Cope 転位成績体**33, 37** が生成した．また，両異性体から Diels-Alder 反応後，分子内 C-H 挿入反応がおきた**35**が得られた．さらに，(*E*)-体では vinylsilane 部にカルベン錯体が反応した後，熱 Cope 転位がおこって生成した**34**が副生した．

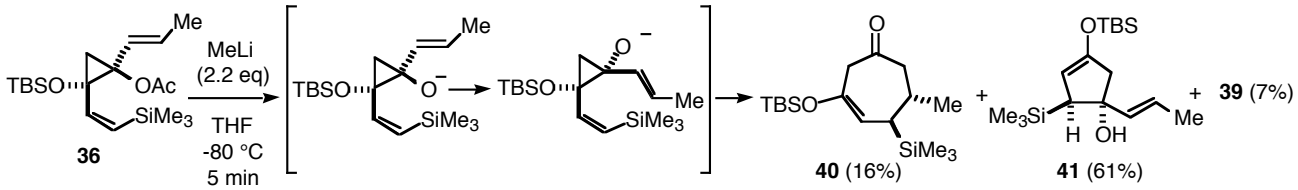




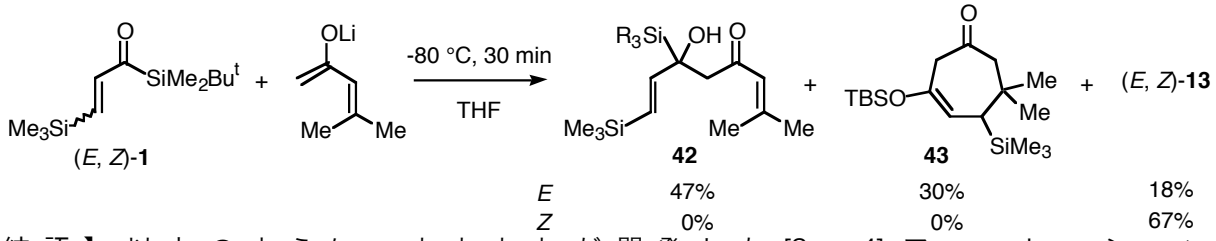
32, **36** の熱 Cope 転位は methylpropenyl 体に比べてボート型遷移状態における立体反発が少ないため，短時間で進行した．

いずれからも *cis*-1,2-cyclopropyl acetate が得られなかったので，*trans*-体 **32** および **36** を用いて MeLi との反応を行った．その結果，(*E*)-体からは 5,6-*cis* 体 **38** が，(*Z*)-体からは 5,6-*trans* 体 **40** が得られた．また，(*Z*)-体では methylpropenyl 体 **19** の場合と同様，cyclopentenol 体 **41** が主成績体であった．以上の結果から，1,2-divinylcyclopropane の anionic oxy-Cope 転位は立体特異的であることが明らかとなった．したがって，[3 + 4] アニュレーションの立体特異性も矛盾無く説明することができる．





なお，(*Z*)-体 **19**, **20**, および **36** の熱 Cope 転位が (*E*)-体に比べて遅いという実験結果は，(*Z*)-体からの [3 + 4] アニュレーションが低収率 (11-31%) である原因として Cope 転位の際の立体反発を示唆するが，以下に示す低温での反応の結果は，エノラートの付加による 1,2-付加体の生成の段階が，(*Z*)-体の場合非常に遅いということを示している．



【結語】 以上のように，われわれが開発した [3 + 4] アニュレーションが cyclopropanolate 中間体の anionic oxy-Cope 転位を経て進行しているということを，中間体の捕捉そして別経路による合成により明らかにすることができた．本アニュレーションの反応機構を確立するためには，律速段階の特定や *β* ヘテロ原子の役割など，さらに詳細な検討が必要と考えられるが，三員環中間体の anionic oxy-Cope 転位を経由していることはほぼ間違いがないと考えられる．また，1,2-divinylcyclopropane の anionic oxy-Cope 転位についての報告例はこれまでに無かったが，極めて速くそして立体特異的な過程であることが判明した．

[文献]

(1) K. Takeda, M. Takeda, A. Nakajima, and E. Yoshii *J. Am. Chem. Soc*. **1995**, *117*, 6400-6401.
(2) K. Takeda, A. Nakajima, E. Yoshii *Synlett* **1996**, 753-754.
(3) H. J. Reich, R. C. Holtan, C. Bolm, *J. Am. Chem. Soc*. **1990**, *112*, 5609-5617.
(4) K. Takeda, M. Fujisawa, T. Makino, E. Yoshii, K. Yamaguchi *J. Am. Chem. Soc*. **1993**, *115* 9351-9352.

Mechanism of the [3 + 2] Annulation Using β-Heteroatom-Substituted Acryloylsilanes.

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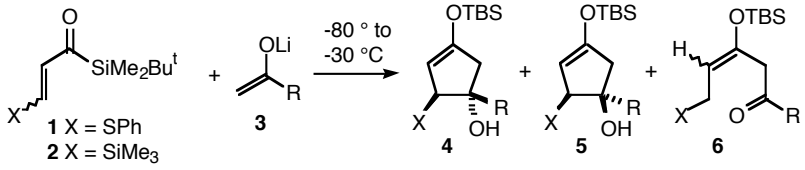
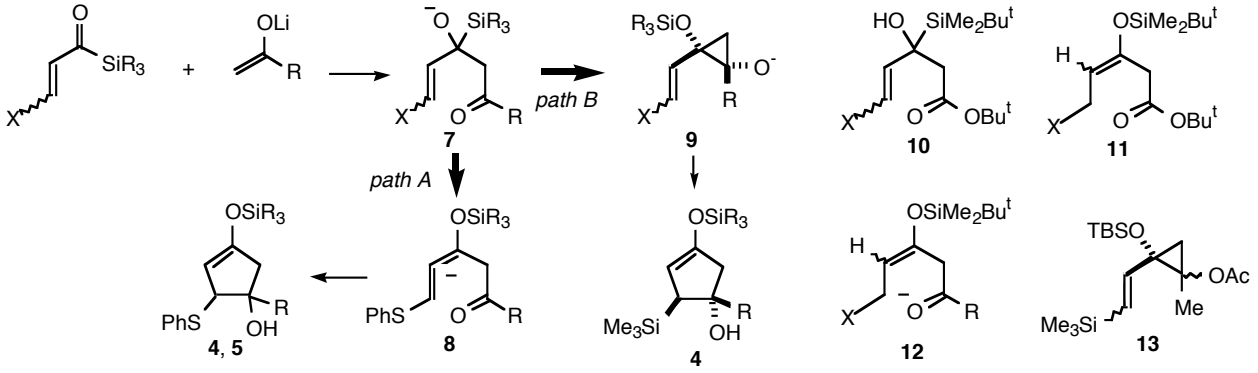
Product distributions in the reactions of β-heteroatom-substituted acryloylsilanes with ketone enolates, which was used in [3 + 2] annulation for preparation of functionalized cyclopentenols, highly depend upon the β-substituent. Thus, in contrast to the observation with (*E*)- and (*Z*)-β-phenylthio derivatives **1** in which isomeric cyclopentenols **4** and **5** (X = SPh) were obtained in almost same ratio irrespective of the acylsilane geometry, the trimethylsilyl derivative **2** afforded a single cyclopentenol **4** (X = $SiMe_3$) and uncyclized enol silyl ether **6** (X = $SiMe_3$) in the ratio depending on the vinylsilane geometry.



		yield (%)		
		4	**5**	**6**
1	(*E, Z*)	55-74	5-19	0
2	*E*	11-17	0	43-63
2	*Z*	48-55	0	16-22

In order to rationalize these results, we postulated a reaction course which involves two competing pathways depending on the α-carbanion-stabilizing ability of the β-substituents in **12**; (a) intramolecular aldol reaction of delocalized allylic anion intermediate **8**, Brook rearrangement product of 1,2-adduct **7** (*path A*), and (b) oxyanion-accelerated vinylcyclopropane rearrangement of cylcopropanolate **9** which is derived from **7** via Brook rearrangement/cyclopropanation sequence (*path B*). To get support to this proposal, we compared α-carbanion-stabilizing ability of the phenythio and the trimethylsilyl groups using the reactions of **1**, **2** with lithium enolate of *t*-butyl acetate, providing **10** and **11** in the ratio reflecting the difference of α-carbanion stabilizing ability of the group X in **12** (R = OBu^t). And we examined low-temperature oxyanion accelerated vinylcyclopropane-cyclopentene rearrangement using the reaction of four isomeric vinylcyclopropyl acetates **13** with MeLi (2.2 eq), affording **4** and **6** in the ratio depending on the vinylsilane geometry.



[3 + 4] Annulation of α,β-Unsaturated Acylsilanes with Enolates of α,β-Unsaturated Methyl Ketones: Scope and Mechanism

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Abstract

Reactions of the *E* and *Z* isomers of β-(trimethylsilyl)acryloyl(*tert*-butyl)dimethylsilanes with lithium enolate of α,β-unsaturated methyl ketones at -80 to -30 °C afford *cis*-5,6 and *trans*-5,6-disubstituted 3-cyclohepetenones, respectively. The same [3 + 4] annulation is observed in the reaction of β-(tri-*n*-butylstannyl)acryloyl)silanes. The annulation products are readily transformed into 4-cycloheptene-1,3-dione by treatment with NBS or mCPBA. The observed stereospecificity in the annulation is explained by the reaction pathway that involves an anionic oxy-Cope rearrangement of 1,2-divinylcyclopropanediol intermediate generated via Brook rearrangement of the 1,2-adduct of and a lithium enolate. Isolation of vinylcyclopropanol derivative from the reaction of β-(tri-*n*-butylstannyl)acryloyl)silanes with lithium enolate of 2'-bromoacetophenone and its transformation into cycloheptenone derivative with LDA provide strong support for the proposed mechanism. Further support is obtained from the reactions of 1,2-divinylcyclopropyl acetates with 2 equiv of MeLi affording cycloheptenones stereospecifically. Also, β-alkyl-substituted acryloylsilanes and cycloalkenylcarbonylsilanes are found to participate the [3 + 4] annulation.

[3 + 4] Annulation of α,β-Unsaturated Acylsilanes with Enolates of α,β-Unsaturated Methyl Ketones: Scope and Mechanism

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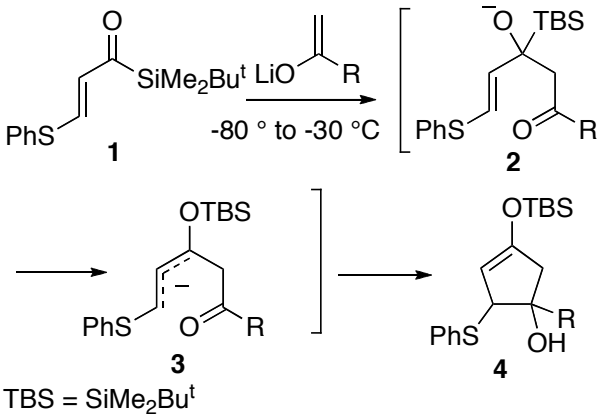
Introduction

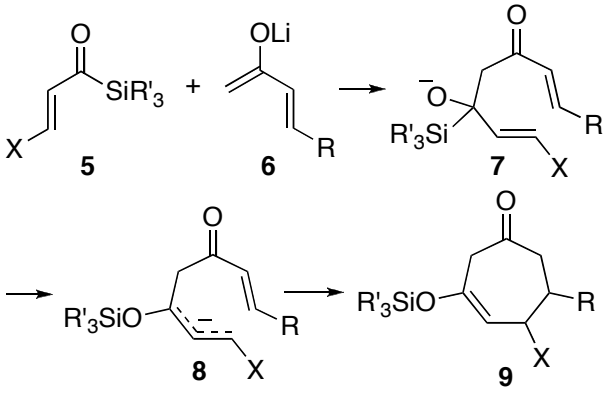
The development of methodologies that allow for efficient construction of seven-membered ring systems has become a subject of great interest and intense effort for the synthetic chemists, because the ring systems are present in a large number of natural products and theoretically interesting molecules.[1] Although considerable efforts have been invested in the synthesis of six-membered carbocycles, relatively fewer annulative methods exist for the stereoselective synthesis of seven-membered carbocycles.[2,3] One of the most efficient and general methods for the preparation of functionalized cycloheptanes would be [3 + 4] annulations,[2c] in which a three-carbon unit directly couples with a four-carbon unit forming two carbon-carbon bonds in one operation. We recently reported a new approach to highly functionalized cyclopentenol **4** using a [3 + 2] annulation involving the combination of (β-(phenylthio)acryloyl)silane **1** as the three-carbon unit and lithium enolate of alkyl methyl ketone as the two-carbon unit,[4] that relies on the formation of delocalized allylic anion **3** via the 1,2-anionic rearrangement of silicon (Brook rearrangement)[5] in the 1,2-adduct **2** followed by internal carbonyl attack by the anion (Scheme 1).

Scheme 1



We envisaged that the use of the lithium enolate diene **6** would provide a new [3 + 4] annulation via the tandem Brook/Michael sequence (Scheme 2; **7** → **8** → **9**). In this paper we describe in full detail the [3 + 4] annulation communicated earlier in a preliminary form.[6]

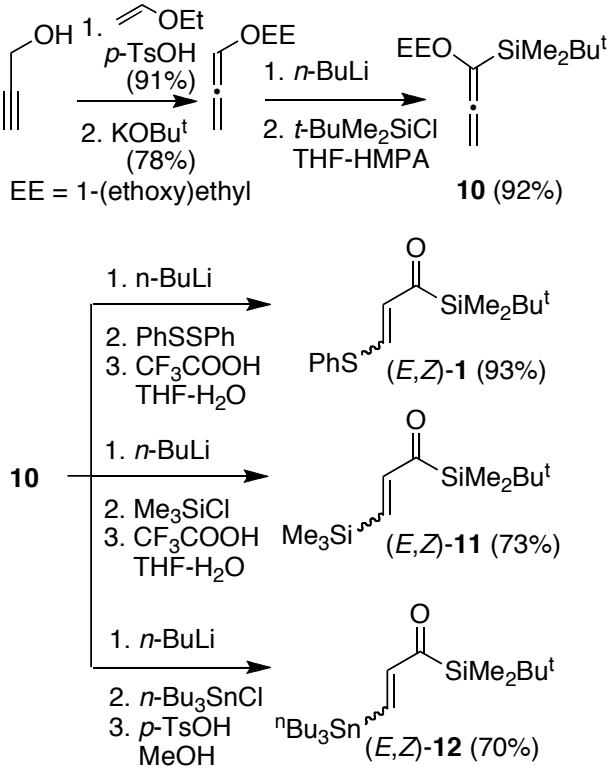
Scheme 2



Results and Discussion

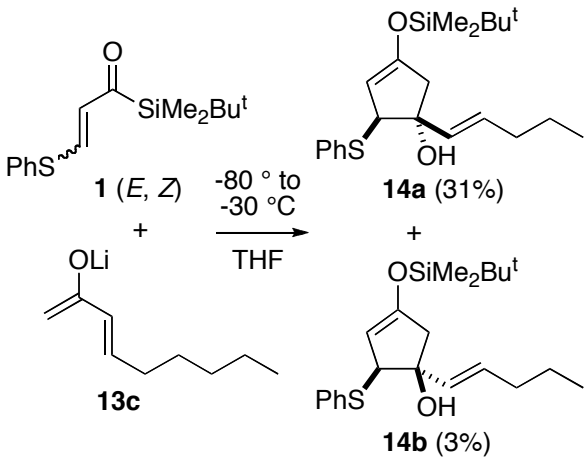
Preparation of β-Heteroatom-Substituted Acryloylsilanes. Acryloylsilanes **1**, **11** and **12** were prepared via allenylsilane **10** employing Reich's procedure,[7] except for the last hydrolysis steps in which trifluoroacetic acid for β-trimethyl derivatives and *p*-TsOH in MeOH for β-tri-*n*-butylstannyl derivatives were used in place of sulfuric acid in aqueous THF (Scheme 3). Use of trifluoroacetic acid for the hydrolysis of the β-stannyl derivative resulted in the predominant formation of (*Z*)-**12** and extensive protodestannylation. All *E* and *Z* derivatives could be separated by silica gel column chromatography.

Scheme 3



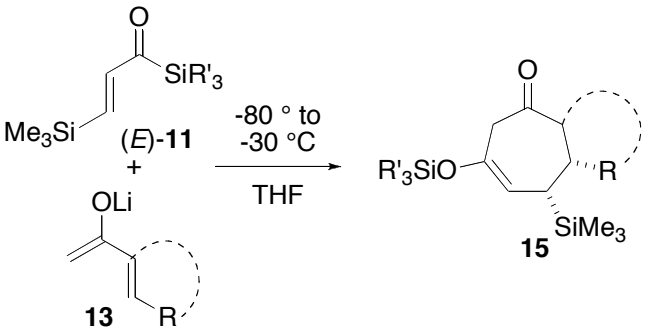
The [3 + 4] Annulation Using (β-(Trimethylsilyl)- and (β-(Tri-*n*-butylstannyl)acryloyl)-silane 11 and 12. We first attempted the reaction of (β-(phenylthio)acryloyl)silane **1** with lithium enolate **13c** under the same conditions as employed for the [3 + 2] annulation,[4] but it did not afford the desired [3 + 4] annulation products, but rather the [3 + 2] annulation products **14a** and **14b** in 31% and 3% yield, respectively (Scheme 4).

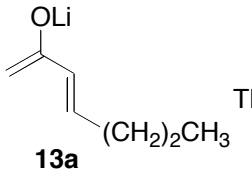
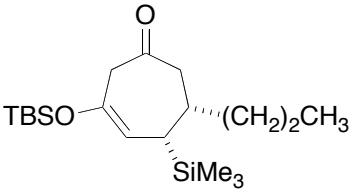
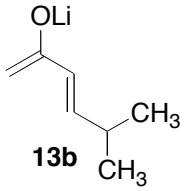
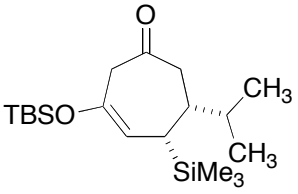
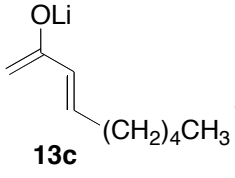
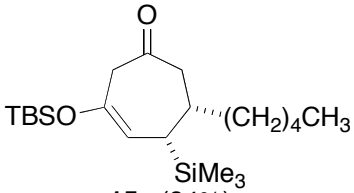
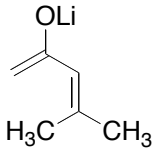
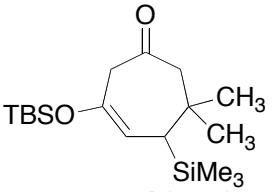
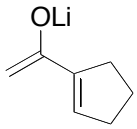
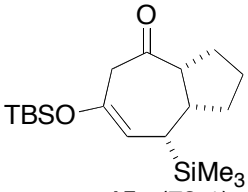
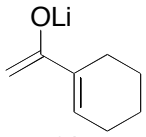
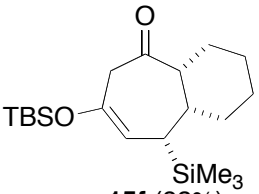
Scheme 4



In the [3 + 2] annulation,[4] the products and product distributions greatly depend upon the β-substituent of the acryloylsilane. Consequently, we examined the annulation using β-trimethylsilyl derivatives **11**. When lithium enolate **13a** (generated with LDA) was added to (*E*)-(β-trimethylsilyl)acryloyl)silane (*E*)-**11** in THF at -80 °C and then the solution (0.02 M) was allowed to warm to -30 °C, *cis*-6-propyl-5-trimethylsilyl-3-cycloheptenone **15a** was obtained in 73% yield (Table 1, entry 1). This annulation was successfully applied to enolates of both alkenyl and cycloalkenyl methyl ketones (Table 1). It should be noted that only the 5,6-cis isomer was obtained in all cases except for **15d.** The relative stereochemistries for **15a**-**c** were assigned on the basis of $J_{5,6}$ (3.8 - 4.5 Hz) and NOESY experiments. The stereostructure of **15f** was determined by X-ray analysis, and the all-cis structure of **15e** was derived from a NOESY experiment.

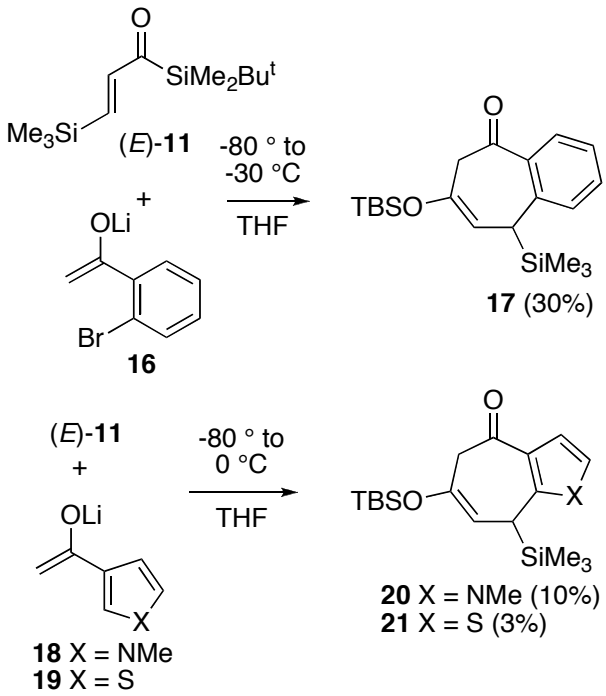
Table 1. [3 + 4] Annulation of (*E*)-11 with Ketone Enolates



entry	ketone enolate	product
1	 **13a**	 **15a** (73%)
2	 **13b**	 **15b** (84%)
3	 **13c**	 **15c** (84%)
4	 **13d**	 **15d** (67%)
5	 **13e**	 **15e** (73%)
6	 **13f**	 **15f** (82%)

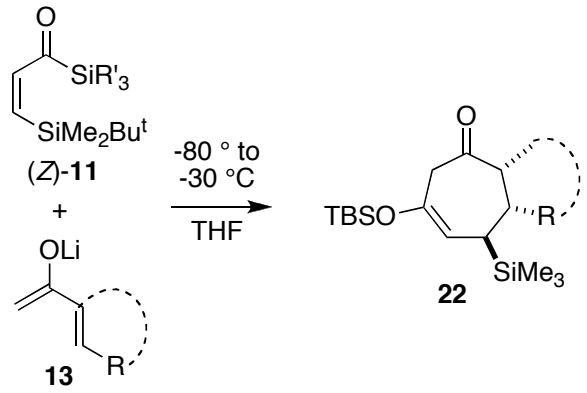
It is particularly noteworthy that aromatic double bonds can also participate in the annulation. Thus, although the reaction with acetophenone enolate resulted in recovery of the starting materials, reaction with the lithium enolate of 2'-bromoacetophenone **16** provided benzocycloheptenone **17** in 30% yield. Interestingly, in the case of heteroaromatics, even on substrates lacking a leaving group, lithium enolates of 3-acetyl-N-methylpyrrole and 3-acetylthiophene **18**, **19**, the reaction proceeded albeit in poor yields, affording seven-membered ring fused heterocycles **20**, **21** after the spontaneous aromatization.

Scheme 5



In sharp contrast to the cases of (*E*)-**11**, the reaction of (*Z*)-**11** proceeded considerably more slowly and produced 5,6-*trans* derivatives **22** as the only isomer in lower yields, together with substantial recovery of the starting materials (Scheme 6). Moreover, no reaction was observed with 2'-bromoacetophenone enolate **16**. The assignment of the 5,6-trans stereochemistry of **22** is based on the $J_{5,6}$ (6.4-7.9 Hz) and NOESY experiments. We will later discuss a possible mechanism that can explain the stereospecificity.

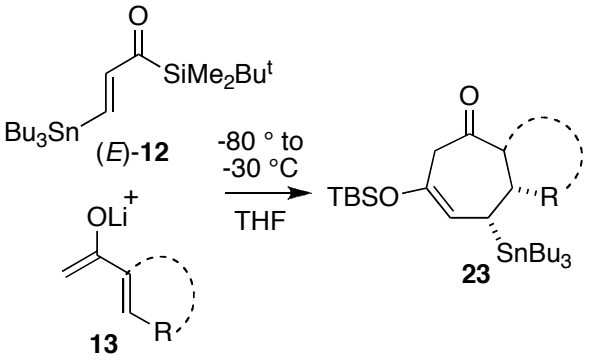
Scheme 6



entry	ketone enolate	yield (%)	
		22	recovered (*Z*)-**11**
1	**13a**	31	56
2	**13b**	29	55
3	**13c**	11	59
4	**13d**	18	31
5	**13e**	24	51
6	**13f**	32	48
7	**16**	0	48

The same stereospecificity was observed in the reaction of β-tributylstannyl derivatives (*E*)- and (*Z*)-**12**. Thus, when (*E*)-**12** were subjected to the same reaction conditions as (*E*)-**11**, the cycloheptenones **23** with 5,6-cis stereochemistry were obtained in comparable yields (Scheme 7). On the other hand, reaction of (*Z*)-**12** was slow even in comparison with (*Z*)-**11** and required higher concentration and temperatures (0.1 M, -30 ° to 0 °C), affording 5,6-trans derivatives **24** in lower yields probably because of the increased steric bulk of the tributylstannyl group (Scheme 8).

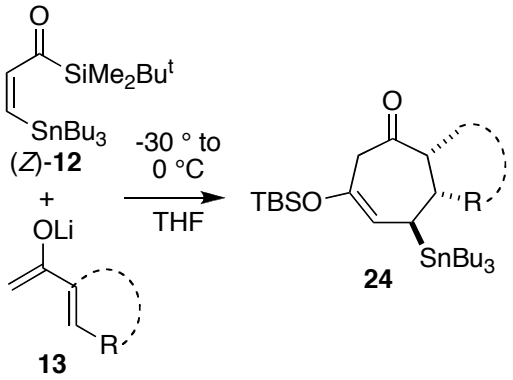
Scheme 7



ketone enolate	yield (%)
13b	72
13c	72
13d	69
13e	42
13f	63
16	26 [a]

a Only 5-protodestannylated compound was obtained.

Scheme 8

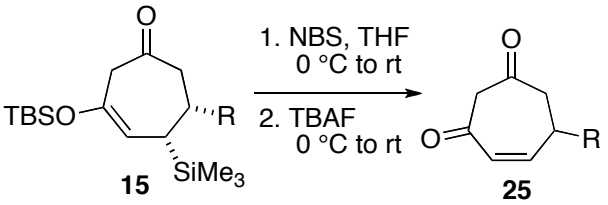


ketone enolate	yield (%)	
	24	recovered (*Z*)-**12**
13b	14	60
13c	18	26
13e	15[a]	52
13f	11	62

a Both 5,6,7-cis isomer and its C-7 epimer were obtained in a ratio of 1:2.

Synthetic Elaboration of the Annulation Products 15 and 23 The annulation products **15** and **23** can be readily transformed into synthetically valuable systems. One useful transformation involves the conversion of the siloxycycloheptenones **15** to enediones **25**. Treatment of **15** in THF with NBS[8] followed by tetra-*n*-butylammonium fluoride (TBAF) afforded enediones **25** in good-to-excellent yields (Scheme 9).

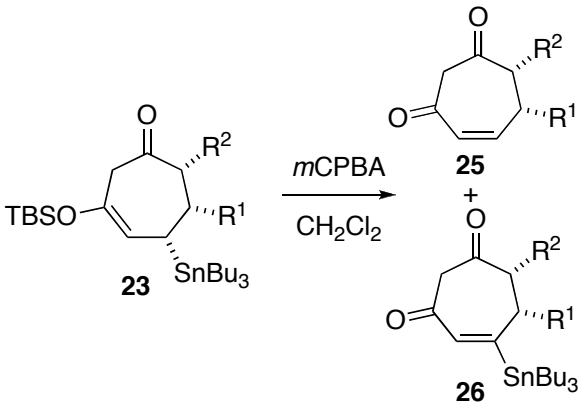
Scheme 9



25b R = $CHMe_2$ 89%
25c R = $(CH_2)_4Me$ 97%
25d R = Me, Me 75%

In the case of tri-*n*-butystannyl derivatives **23**, more facile transformation into the enedione **25** was realized by treatment of **23** with *m*-chloroperbenzoic acid (mCPBA)[9] in CH_2Cl_2 at 0 °C. The formation of vinylstannane derivative **26** in the cases of **23d** and **23f** can be interpreted as the result of a less favorable *anti*-periplanar relationship between the stannyl group and the epoxy group owing to the nonbonding interactions involving the stannyl group.

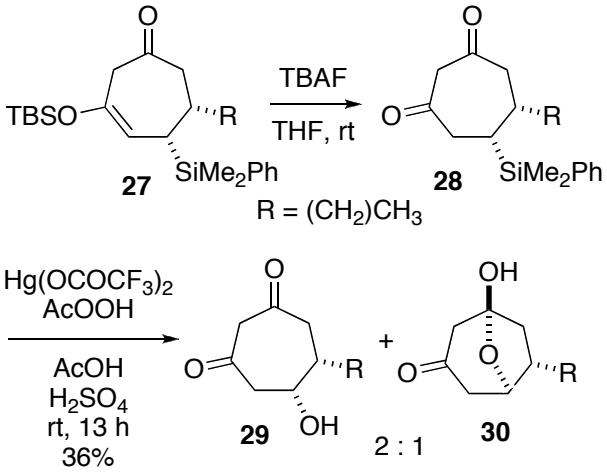
Scheme 10



	R^1	R^2	**25**	**26**
b	$CHMe_2$	H	84%	-
c	$(CH_2)_4Me$	H	89%	-
d	Me, Me	H	76%	11%
e	- $(CH_2)_3$ -		89%	-
f	- $(CH_2)_4$ -		57%	10%

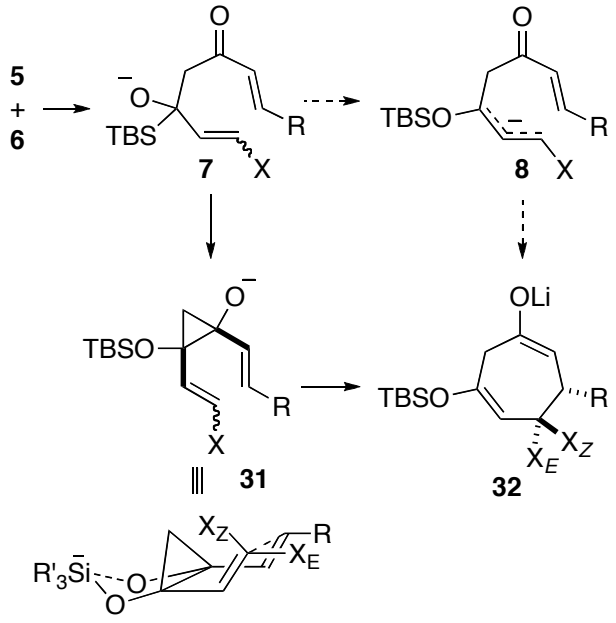
The attempted Fleming's oxidative desilylation[10] of 5-dimethylphenylsilyl derivative **28**, derived from **27** which was prepared from (β-(dimethylphenylsilyl)acryloyl)silane, resulted in the formation of a mixture of 5-hydroxy derivative **29** and hemiketal **30** in low yield.

Scheme 11



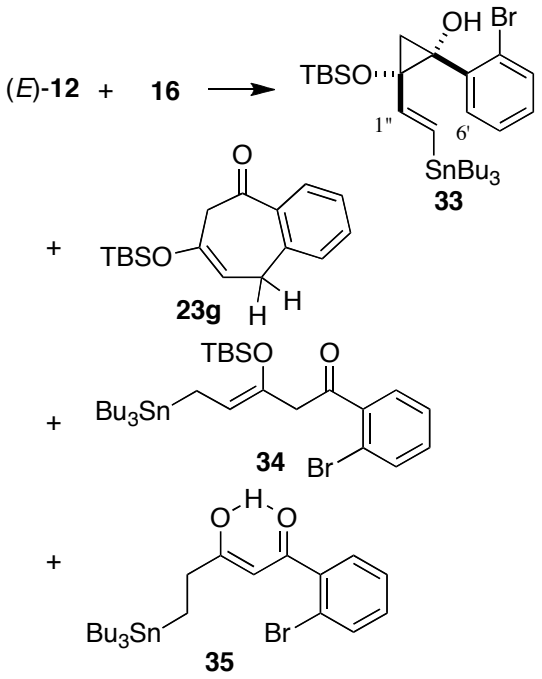
Reaction Mechanism of the [3 + 4] Annulation. The observed stereospecificity and the participation of the aromatic double bond in the [3 + 4] annulation are incompatible with a pathway involving intramolecular Michael addition of delocalized allylic anion (**8**→**32**). A reasonable mechanism to explain these observations seems to be a pathway involving a concerted anionic oxy-Cope rearrangement of the *cis*-1,2-divinylcyclopropandiolate intermediate **31** (**31**→**32**)[11] which was stereoselectively derived from the 1,2-adduct **7** by the Brook rearrangement, followed by internal trapping of the generated carbanion by the ketone carbonyl (Scheme 12). The observed stereospecificity can be rationalized by a concerted pathway of the Cope rearrangement via a boat-like transition state, and the high reactivity can be interpreted as result of the rate acceleration of the rearrangement by the oxyanion.[12,13] The stereoselective formation of the *cis*-1,2-divinyl derivative **31** can be explained by invoking the internally O-Si coordinated structure.[14]

Scheme 12



To obtain support for the proposed mechanism, we decided to trap the cyclopropanolate intermediate **31** by low-temperature quenching of the reaction of the β-tributylstannyl derivative (*E*)-**12** with 2'-bromoacetophenone enolate **16** which appeared to be the slowest [3 + 4] annulation examined so far. While treatment of (*E*)-**12** with **16** at -80 °C for 60 min afforded **34**, the addition/Brook rearrangement product, together with recovery of the starting ketone, upon warming to -45 °C, cyclopropanol **33** was isolated in 24% yield, in addition to cycloheptenone **23g** and **34**. The cyclopropanol structure of **33** was ascertained by ^{1}H and ^{13}C NMR in which the H-3 proton and C-3 carbon appeared at 1.21 and 1.75 ppm (each doublet, J = 7.5 Hz, H-3) and at 23.5 ppm, respectively. The 1,2-cis stereochemistry of **33** was indicated by the presence of cross peaks between H-1" and H-6' in NOESY experiments.

Scheme 13

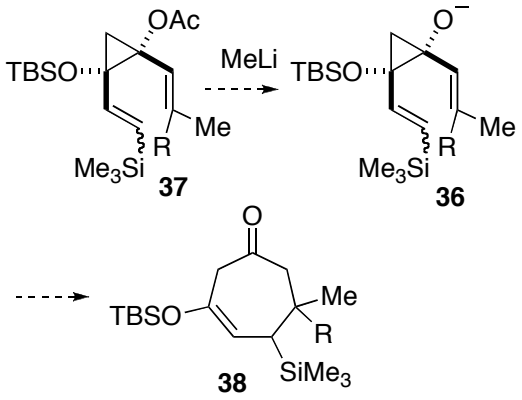


conditions	yield (%)				recovery of ketone
	33	**23g**	**34**	**35**	
-80 °C, 60 min	0	0	31	0	69
-80 °C to -45 °C 40 min	24	5	16	0	32
-80 °C to -40 °C 60 min	17	7	33	7	9
-80 °C to -30 °C 60 min	8	26	31	3	8

The yield of **33** decreased, and that of **23g** increased with rising temperature, suggesting that the alkoxide of cyclopropanol **33** is the precursor to **23g**. In fact, treatment of **33** with LDA in THF at -30 °C for 10 min afforded **23g** in 18% yield along with **34** and **35**. These observations provide strong support for the proposed mechanism, but this is a rather specific case because an aromatic double bond is involved in the reaction, and no stereochemical information on the anionic oxy-Cope rearrangement is available. Although the stereocontrolled process of the Cope rearrangement of divinylcyclopropanes is well known and the fact that the anionic reaction is qualitatively faster than the neutral counterpart is fully expected from other anion-accelerated rearrangements,[12] anionic oxy-Cope rearrangement have never been previously reported for any divinylcyclopropanes. Therefore, to gain further support for the mechanism, we decided to synthesize independently 1,2-divinylcyclopropanolates **36** and explore the reactivity and stereochemical aspect of their anionic oxy-Cope rearrangement. First, to gain insight into

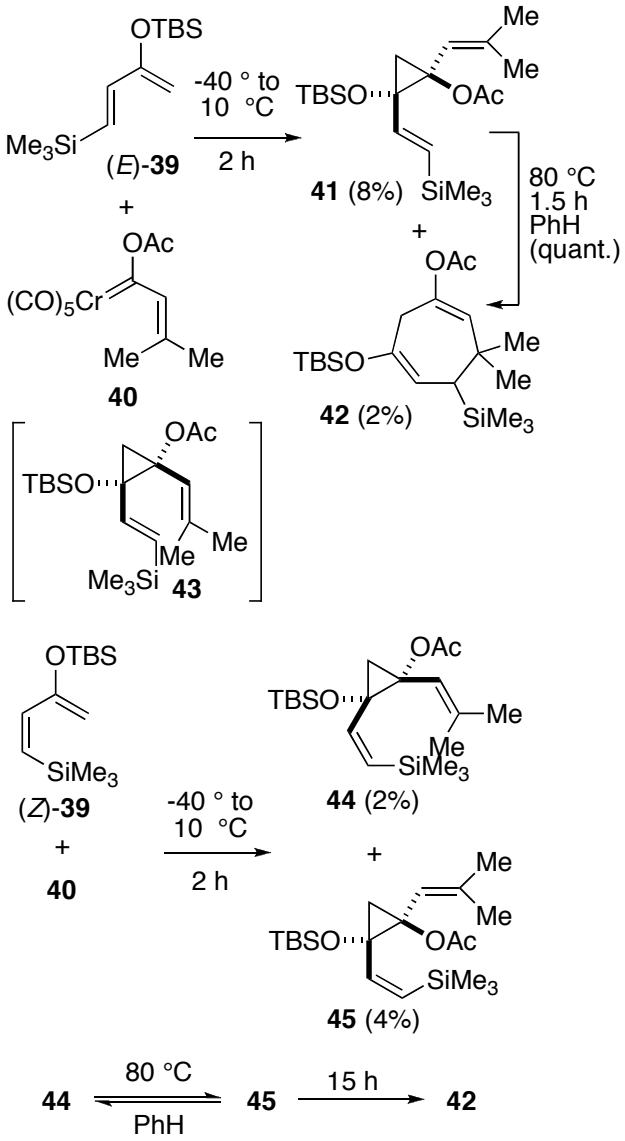
the reactivity, we investigated the rearrangement of 1-(2-methylpropenyl)-2-(2-(trimethylsilyl)ethenyl)cyclopropanolates **36** (R = Me), derived from the reaction of the corresponding cyclopropyl acetates **37** with two equivalents of MeLi, to cycloheptenone **38**, creating no stereogenic center.

Scheme 14



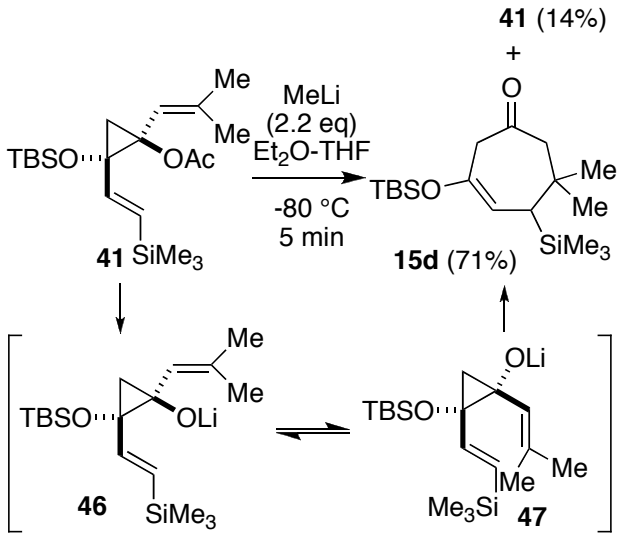
Reaction of (*E*)-**39**[15] with in situ generated **40**[16] at -40 ° to 10 °C for 2 h afforded *trans*-divinylcyclopropyl acetate **41** and cycloheptadiene **42**, while (*Z*)-**39** produced both *cis*- and *trans*-cyclopropyl acetates **44**, **45** under the same conditions. Cycloheptadiene **42** can arise from the thermal Cope rearrangement of *cis*-1,2-divinycyclopropyl acetate **43** below room temperature, because conversion of the trans derivative **41** into **42** via trans-to-cis isomerization required heating at 80 °C for 1.5 h.[17] On the other hand, separate heating of **44** and **45** in benzene resulted in equilibration between them, and complete transformation into **42** required refluxing in the solvent for 15 h.

Scheme 15



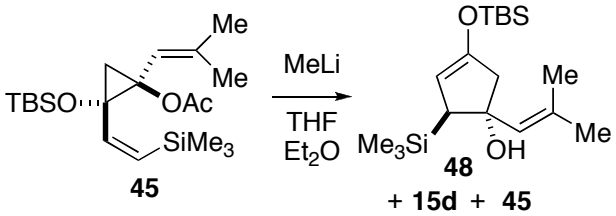
Because the desired *cis*-1,2-divinyl derivatives could not be obtained in the case of the (*E*)-derivative, the reaction with MeLi was performed using the *trans* derivatives **41** and **44**, in anticipation of fast trans-to-cis isomerization, and *cis*-derivative **45**. When **41** was treated with MeLi (2.2 equiv) at -80 °C for 5 min and then quenched with acetic acid (2.2 equiv), cycloheptenone **15d** was obtained in 71% yield. This observation suggests that the anionic oxy-Cope rearrangement from **47** to **15d** is a rapid process even at -80 °C because the overall transformation involving the acetyl cleavage, ring-opening/reclosure sequence and the anionic oxy-Cope rearrangement (**41** → **46** → **47** → **15d**) was almost completed within 5 min at -80 °C.

Scheme 16



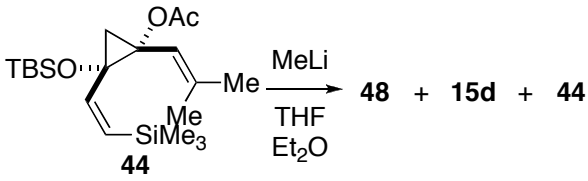
On the other hand, reactions of the (*Z*)-derivatives **45** and **44** proceeded more slowly and afforded cyclopentenol **48** as a major product in addition to the Cope product **15d**. The cyclopentenol **48** can be formed via competing oxyanion accelerated vinylcyclopropane-cyclopentene rearrangement.[15,18] The relative slowness of the anionic oxy-Cope rearrangement can be attributed to the steric repulsion between the (*Z*)-trimethylsilyl group and the hydrogen atom on the cyclopropane ring in the transition state from **44** leading to **15d**, which is well documented for the thermal Cope rearrangement of *cis*-1,2-divinylcyclopropanes.[11] The more predominant formation of **48** from **45** than from **44** at lower temperature can be explained by assuming that the 1,3-sigmatropic shift of internally Si-O coordinated bicycle **49**, generated from **45**, to **48** is much faster than the trans-to-cis isomerization required for the Cope rearrangement, presumably because of its fixed conformation suitable for the overlap of the orbitals required for the rearrangement.[15]

Scheme 17



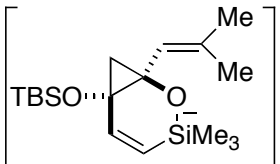
45 **48** + **15d** + **45**

	48	**15d**	**45**
-80 °C, 5 min	43%	11%	46%
-80 ° to -30 °C	68%	18%	13%



44 **48** + **15d** + **44**

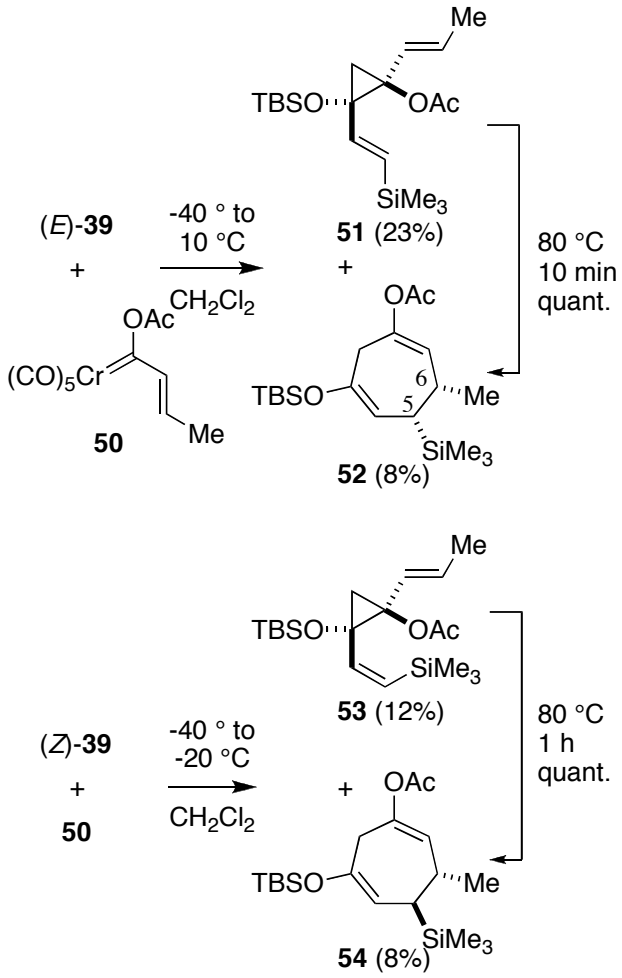
	48	**15d**	**44**
-80 °C, 5 min	8%	14%	73%
-80 ° to -30 °C	51%	32%	14%



49

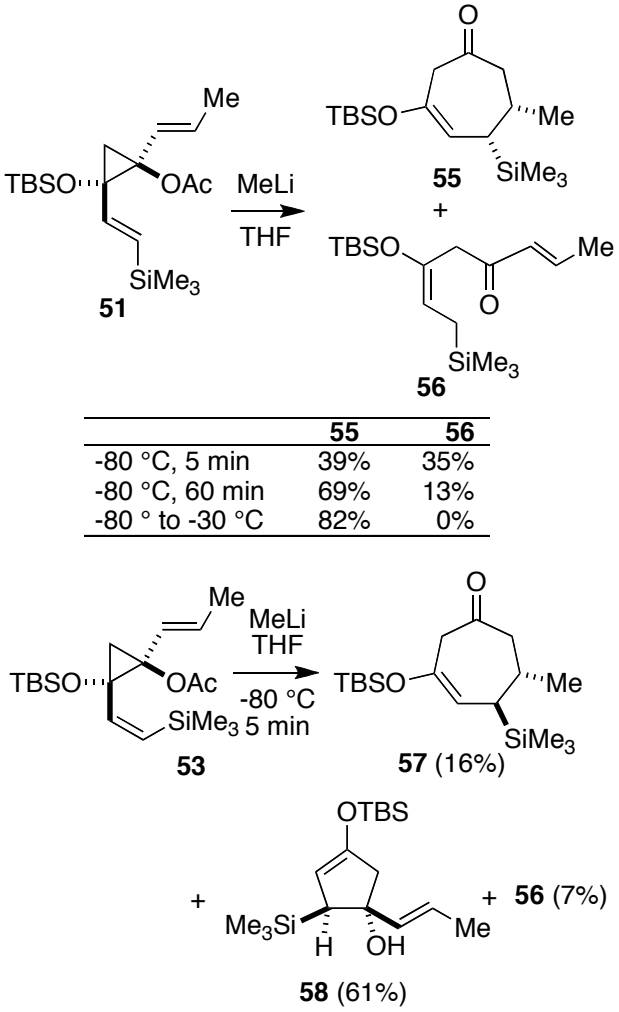
Having obtained results indicating very rapid process of the anionic oxy-Cope rearrangement of 1,2-divinylcyclopropanolates, we next proceeded to prepare propenyl derivative **36** (R = H) to examine the stereochemical course of the anionic oxy-Cope rearrangement. Not unexpectedly, the requisite *cis*-derivatives were not obtained from both reactions of (*E*)- and (*Z*)-**39** with **50**,[16] and *trans*-derivatives **51** and **53** formed together with thermal Cope products **52** and **54**.[19] The thermal Cope rearrangement of **51** into **52** was faster than those of **41**, **44**, **45** and **53**.

Scheme 18



Reaction of **51** with MeLi (2.2 equiv) afforded *cis*-6-methyl-5-(trimethylsilyl)cycloheptenone **55** as a single diastereomer and the ring-opening product **56**. The ratio of **55** to **56** increased with an increase in temperature and reaction time, suggesting that **56** can be formed from *trans*-divinylcyclopropanolate during the hydrolytic workup because the ring-closure of **56** to **55** seems unlikely.[20] The same reaction with **53** resulted in the formation of 5,6-trans derivative **57** and **56** in addition to the cyclopentenol **58**. The results indicated that the anionic oxy-Cope rearrangement of the 1,2-divinylcyclopropanolates is stereospecific. In these cases, the rate-determining step seems to be the trans-to-cis isomerization and not the Cope rearrangement, because even in the more congested system such as **41**, the overall transformation was completed within 5 min.

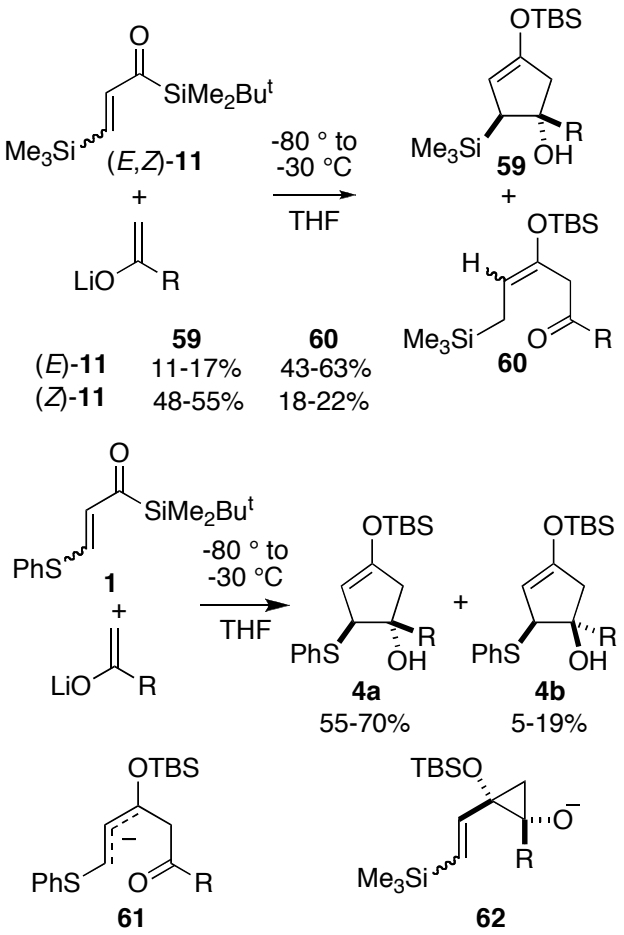
Scheme 19



The results obtained with **44**, **45**, **51**, and **53** have shown that the anionic oxy-Cope rearrangement of *cis*-1,2-divinylcyclopropanolates proceeds very rapidly at lower temperatures and stereospecifically, providing additional support for the proposed pathway involving the anionic oxy-Cope rearrangement of 1,2-divinylcyclopropanolate. Moreover, the intermediacy of the cyclopropanolate **31** can reasonably account for the unsuccessful [3 + 4] annulation in the case of (β-(phenylthio)acryloyl)silane **1** on the basis of our earlier studies on [3 + 2] annulation using **1**. Thus, we have found that the reaction of β-substituted acryloylsilanes with ketone enolates greatly depends upon the β-substituent.[4] The β-trimethylsilyl derivative **12** affords a single cyclopentenol **59** and uncyclized enol silyl ethers **60** in the different ratio depending on the vinylsilane geometry, in contrast to the observation with β-phenylthio derivative **12** in which isomeric cyclopentenols **4a** and **4b** are obtained in almost the same ratio irrespective of the

acylsilane geometry. We propose a reaction course either by way of delocalized allylic carbanion intermediate **61** or by way of cyclopropanolate intermediate **62** depending on the α-carbanion-stabilizing ability of the β-substituent; the former for more anion-stabilizing phenylthio derivative, and the latter for less anion-stabilizing trimethylsilyl group.[21] Consequently, the failure of the [3 + 4] annulation in the reaction of **1** can be attributed to the formation of delocalized allylic carbanion which does not lead to cycloheptenone.

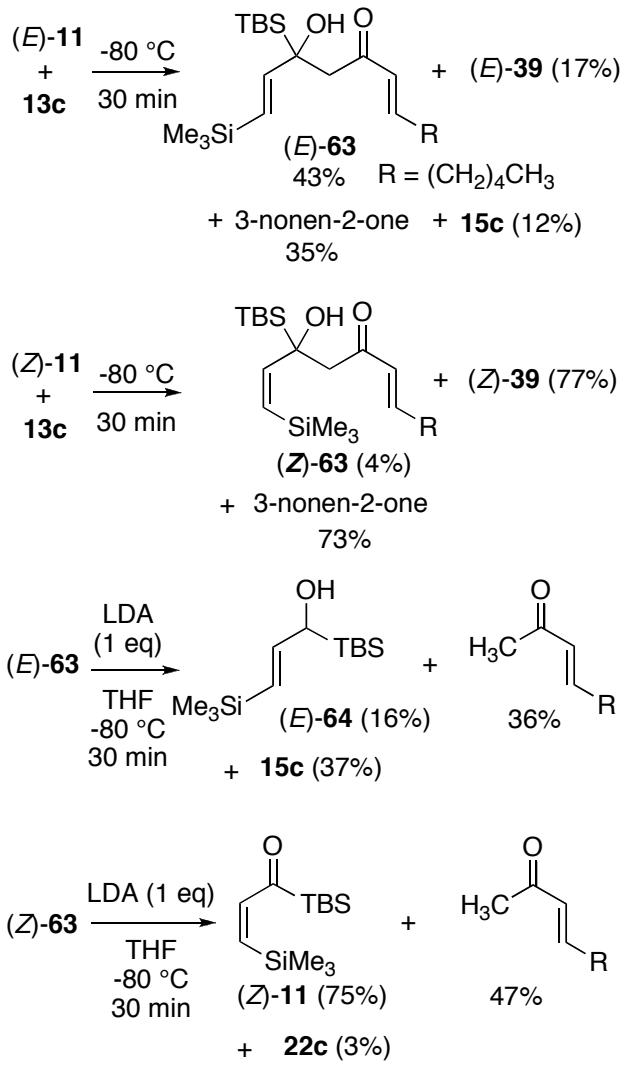
Scheme 20



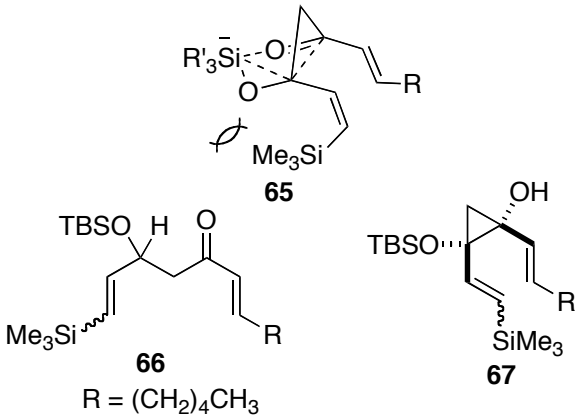
The relatively slow reaction of (*Z*)-**11** and (*Z*)-**12** in comparison with their *E* counterparts, at first glance, seems to be due to unfavorable steric interaction between the heteroatom substituents and ring hydrogen atom in the transition state leading to 5,6-trans derivatives as previously mentioned. This, however, is incompatible with the fact that a large amount of the starting acylsilanes was recovered, because the required retro Aldol/Brook sequence (**31** →**7** →**5**,**6**, Scheme 12) seems unlikely. Moreover, the fact that in the reaction of *cis*-1,2-

divinylcyclopropyl acetate **44** with MeLi acryloylsilane **11** could not be detected rules out the possibility of the reverse process. To obtain information about the relative reactivity of the (*E*)- and (*Z*)-acryloylsilanes toward ketone enolates, we conducted the low-temperature quenching of the reaction of the acryloylsilanes with the enolate **13c**. The reaction of (*Z*)-**11** with **13c** at -80 °C for 30 min resulted in the recovery of the starting acylsilane (*Z*)-**11** in 77% yield along with the formation of a trace amount of 1,2-adduct (*Z*)-**63**, in contrast to the reaction of (*E*)-**11** under the same conditions in which the 1,2-adduct (*E*)-**63** (43%), the annulation product **15c** (12%), and (*E*)-**11** (17%) were isolated. Treatment of the isolated 1,2-adduct (*E*)-**63** with LDA (1 equiv) afforded the cycloheptenone **15c** (37%), 3-nonen-2-one, and (*E*)-**64**, the reduction product of (*E*)-**11** with LDA. On the other hand, under the same conditions, (*Z*)-**63** produced (*Z*)-**11** (75%), 3-nonen-2-one and cycloheptenone **22c**.

Scheme 21



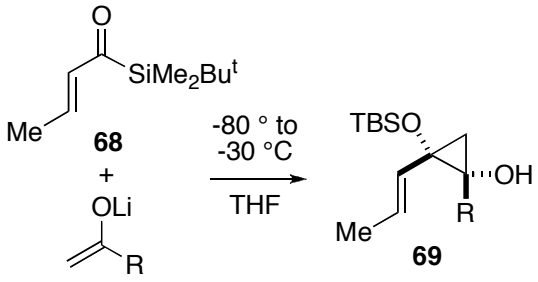
These results suggest that the lower reactivity of (*Z*)-acryloylsilanes is attributed in part to the slow formation of the 1,2-adduct due to an unfavorable equilibrium toward the starting materials. Although the origin of this unfavorable equilibrium in the *Z*-isomer remains unclear at this time, we assume that it may be ascribed to the relatively severe steric repulsions in the (*Z*)-1,2-adduct and in the transition state **65** leading to the divinylcyclopropanolate via the Brook rearrangement/cyclopropanation. The assumption that the Brook rearrangement/cyclopropanation sequence is a concerted process is based on the fact that the attempted isolation of Brook rearrangement product **66** and cyclopropanol derivative **67** was unsuccessful and the anionic oxy-Cope rearrangement is very rapid even at -80 °C as previously mentioned.



The precise mechanism of the [3 + 4] annulation is still unclear. Nonetheless, the available data are consistent with the proposed mechanism that involves the anionic oxy-Cope rearrangement of the *cis*-1,2-divinylcyclopropanolate.

[3 + 4] Annulation of β-Alkyl-Substituted Acryloylsilanes with the Lithium Enolates of Alkenyl Methyl Ketones. The previously discussed mechanistic consideration suggests that a requirement for the successful [3 + 4] annulation would be the formation of *cis*-1,2-divinylcyclopropanolates. In fact, very recently we have found that the reaction of *trans*-1-(3-methyl-(1*E*)-butenyl)-2-(1-propenyl)cyclopropyl acetate with MeLi (2.2 equiv) produced the cycloheptenone derivative.[22] Also, we have previously reported that the reaction of crotonoylsilane **68** with the lithium enolate of methyl ketones produced *cis*-2-vinyl-1,2-cyclopropanediol derivative **69**.[14]

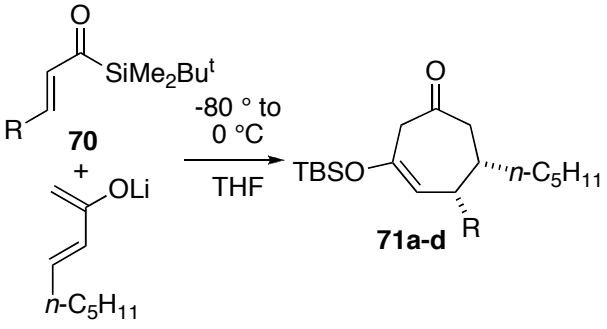
Scheme 22



This led us to examine the [3 + 4] annulation using β-alkyl-substituted acryloylsilanes which would allow stereoselective introduction of an alkyl group at the 5-position of cycloheptenones and constitute a general and stereoselective approach to the highly functionalized seven-membered carbocycles.

When lithium enolate of 3-nonen-2-one **13c** was added to a THF solution of 4-methyl-2-pentenoylsilane **70a** (R = *i*-Pr)[23] at -80 °C and then the solution was warmed to 0 °C, *cis*-5-isopropyl-6-pentyl-3-cycloheptenone **71a** was obtained as a single diastereomer in 75% yield.[24] The same results were obtained in the reaction of other β-alkyl-substituted acryloylsilanes **70b-d**, with stereochemistry determined on the basis of NOESY experiments (Scheme 23).

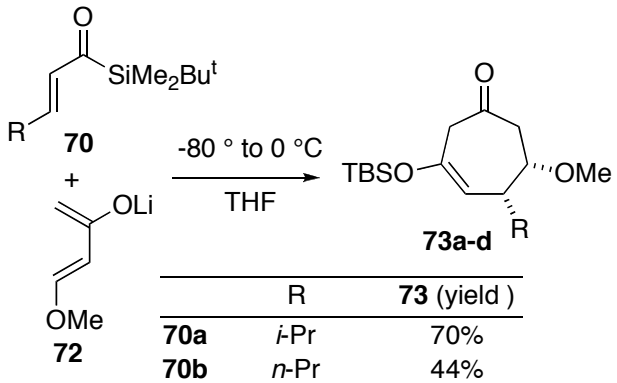
Scheme 23



	R	**71** (yield)
70a	*i*-Pr	75%
70b	*n*-Pr	69%
70c	*t*-Bu	65%
70d	cyclohexyl	77%

The use of the lithium enolate of 4-methoxy-3-buten-2-one **72** as the C4 unit allowed the introduction of an oxygen function at the 6-position to give 6-methoxy derivatives **73a-d**.

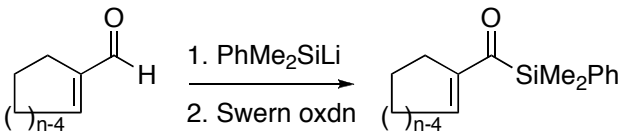
Scheme 24



	R	**73** (yield)
70a	*i*-Pr	70%
70b	*n*-Pr	44%
70c	*t*-Bu	65%
70d	cyclohexyl	57%

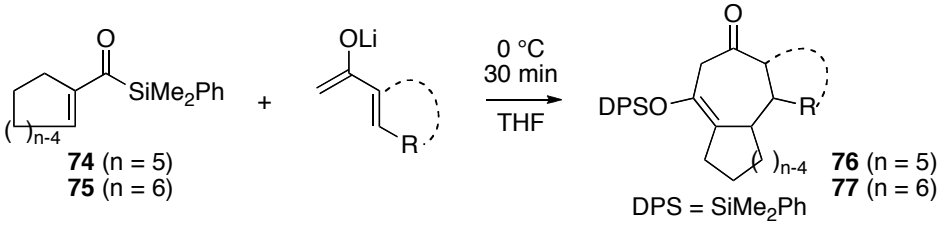
This procedure was also successfully applied to the synthesis of bi- and tricyclic systems **76** and **77** using cycloalkenylcarbonylsilanes **74** and **75** which were prepared by the reaction of 1-cyclopentenecarboxaldehyde and 1-cyclohexenecarboxaldehyde with dimethyl(phenyl)silyllithium[25] followed by Swern oxidation (Scheme 25, Table 2). In these cases, better yields were obtained when the reaction was performed at 0 °C rather than -80 °C to 0 °C, and a nonaqueous workup by the addition of acetic acid (1 equiv) was used. The stereochemistry of the products was determined on the basis of NOESY experiments and the X-ray analysis of **77f**. The stereochemistry at C-1 in **76e**,**f** and **77e**,**f** is interpreted as the result of kinetic protonation from the less-hindered side of the cycloheptenone enolate.

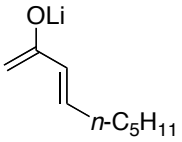
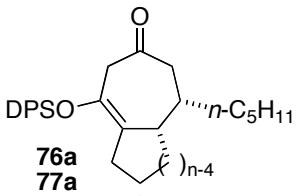
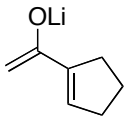
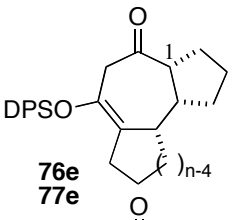
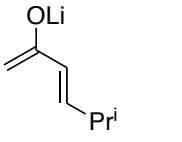
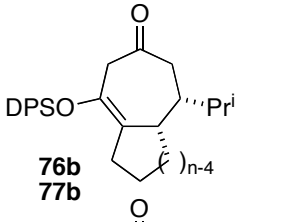
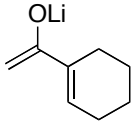
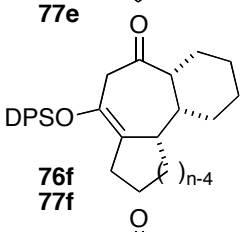
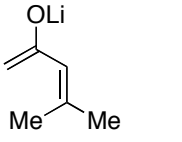
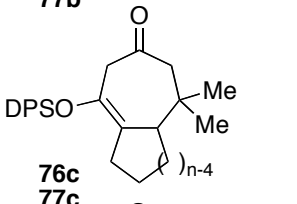
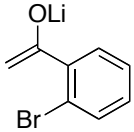
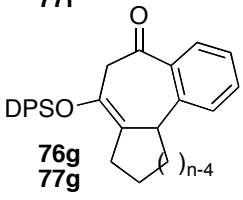
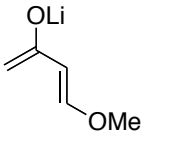
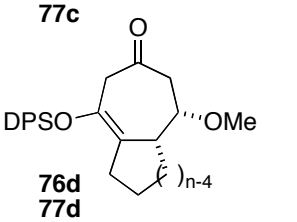
Scheme 25



74 (n = 5) (46%)
75 (n = 6) (34%)

Table 2



ketone enolate	n	product	yield	ketone enolate	n	product	yield
	5	 **76a** **77a**	82%		5	 **76e** **77e**	51%
	6		82%		6		65%[a]
	5	 **76b** **77b**	59%		5	 **76f** **77f**	68%
	6		70%		6		71%
	5	 **76c** **77c**	54%		5	 **76g** **77g**	23%
	6		68%		6		17%
	5	 **76d** **77d**	51%				
	6		73%				

a The C-1 epimer was isolated in 12% yield.

In conclusion, we have demonstrated synthetically useful and mechanistically interesting [3 + 4] annulation methodology which permits a rapid and stereocontrolled construction of highly functionalized cycloheptenone derivatives that are often difficult to make in other ways.

Experimental Section

General: All NMR spectra were measured at 500 MHz ^{1}H and 125 MHz ^{13}C and in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26) and the $CDCl_3$ triplet (δ 77.2) unless otherwise noted. Liquid chromatography under medium pressures (MPLC) was carried out by using prepacked columns (22 mm x 300 mm, 10 μ silica gel or 22 mm x 150 mm, 5 μ silica gel). For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325

mesh) for column chromatography; Merck precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures. Melting points were not corrected. Elemental combustion analysis was performed at the Microanalysis Laboratory of this University.

General Procedure for the [3 + 4] Annulation Using 11 and 12: Reaction of (*E*)-11 with Li Enolate of 3-Nonen-2-one (13c). To a cooled (-80°C) solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (139 μL, 100 mg, 0.99 mmol) and *n*-BuLi (1.32 M in hexane, 0.75 mL, 0.99 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (149 μL, 126 mg, 0.90 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of (*E*)-**11** (262 mg, 1.08 mmol) in THF (41 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (30 mL). The mixture was extracted with Et_2O (15 mL x 2), and the combined organic phases were washed with water (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 20:1 hexane-AcOEt) to give **15c** (289 mg, 84%). **15c (R = $(CH_2)_4CH_3$)**: a colorless oil, R_f = 0.48 (hexane:AcOEt = 15:1). IR (film) 1710, 1640, 1250 cm^{-1}. ^1H NMR δ0.01 (9H, s), 0.13 and 0.17 (each 3H, s), 0.93 (9H, s), 1.11-1.38 (8H, m), 0.88 (3H, t, J = 6.4 Hz), 1.64 (1H, dd, J = 8.1, 3.8 Hz), 2.29-2.37 (2H, m), 2.43 (1H, dd, J = 11.8, 6.4 Hz), 2.59 (1H, dd, J = 11.8, 9.8 Hz), 2.83 (1H, d, J = 18.4 Hz), 3.46 (1H, br m, J = 18.4 Hz), 4.94 (1H, dd, J = 8.1, 2.4 Hz). ^{13}C NMR δ-3.5, -3.9, -0.7, 14.8, 18.7, 23.4, 27.5, 32.5, 34.7, 26.4, 29.8, 41.5, 48.1, 51.7, 107.1, 149.3, 211.4. HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, found 382.2730.

General Procedure for Transformation of Cycloheptenones 15 into Cycloheptenediones 25. To a cooled (ice-water) solution of **15c** (100 mg, 260 μmol) in THF (2.6 mL) was added

NBS (50 mg, 270 μmol), and then the reaction mixture was stirred at room temperature for 10 min. The mixture was cooled in ice-water bath again before addition of TBAF (1.0 M in THF, 0.26 mL, 260 μmol). After stirring at the same temperature for 10 min, the mixture was allowed to warm to room temperature, and then diluted with Et_2O (20 mL) and water (30 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (20 mL x 2). The combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residue was subjected to column chromatography (silica gel, 3.3 g; elution with 1:2 hexane-Et_2O) to give **25c** (45 mg, 89%). **25c**: a pale yellow oil, R_f = 0.55 (hexane : AcOEt = 1 : 1). IR (film) 1715, 1670 cm^{-1}. ^1H NMR δ 0.89 (3H, t, *J* = 7.0 Hz), 1.28-1.44 (6H, m), 2.47 (1H, dd, *J* = 17.1, 14.1 Hz), 2.69 (1H, dd, *J* = 17.1, 3.4 Hz), 2.96-3.05 (1H, m), 3.58 (1H, dm, *J* = 14.3 Hz), 4.10 (1H, d, *J* = 14.3 Hz), 6.07 (1H, dm, *J* = 12.0 Hz), 6.66 (1H, ddm, *J* = 12.0, 4.3 Hz). ^{13}C NMR δ 14.1, 18.0, 22.7, 26.6, 31.7, 35.5, 35.7, 47.1, 61.4, 131.9, 152.8, 192.3, 203.3. HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1267.

General Procedure for Transformation of Cycloheptenones 23 into Cycloheptenediones 25. To a cooled (ice-water) solution of **23c** (54 mg, 90 μmol) in CH_2Cl_2 (0.45 mL) was added mCPBA (80%, 20 mg, 90 μmol), and then the solution was stirred at the same temperature for 15 min. The reaction mixture was concentrated, the residue was subjected to column chromatography (silica gel, 4 g, elution with 1:1 hexane-Et_2O) to give **25c** (16 mg, 89%).

Trapping Experiment of the Cyclopropanolate Intermediate. To a stirred and cooled (-80 °C) solution of LDA, prepared from diisopropylamine (124 μL, 882 μmol) and *n*-BuLi (1.45 M hexane solution, 610 μL, 882 μmol) in THF (1 mL), was added dropwise a solution of 2'-bromoacetophenone (176 mg, 882 μmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of (*E*)-**12** (405 mg, 882 μmol) in THF (41 mL) over 2 min. The reaction mixture was allowed to warm to -45 °C over 40 min, and then quenched by acetic acid (52 mg, 882 μmol) in THF (1 mL). The mixture

was extracted with Et_2O (30 mL x 2) after addition of saturated aqueous NH_4Cl solution (30 mL), and the combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 20:1 hexane-Et_2O) to give **33** (139 mg, 24%), **23g** (13 mg, 5%), **34** (93 mg, 16%), and 2'-bromoacetophenone (56 mg, 32%).

33: a pale yellow oil, R_f = 0.40 (hexane : Et_2O = 10 : 1). IR (film) 3530 cm^{-1}. ^1H NMR δ 0.15 and 0.18 (each 3H, s), 0.60-0.75 (6H, m), 0.84 (9H, t, *J* = 7.3 Hz), 0.97 (9H, s), 1.14-1.22 (6H, m), 1.25-1.32 (6H, m), 1.21 (1H, d, *J* =7.5 Hz), 1.75 (1H, d, *J* = 7.5 Hz), 3.66 (1H, s), 5.62 (1H, d, *J* = 19.2 Hz), 5.90 (1H, d, *J* = 19.2 Hz), 7.07 (1H, ddd, *J* = 7.7, 7.7, 1.7 Hz), 7.19 (1H, ddd, *J* = 7.7, 7.7, 1.1 Hz), 7.29 (1H, dd, *J* = 7.7, 1.7 Hz), 7.49 (1H, dd, *J* = 7.7, 1.1 Hz). ^{13}C NMR δ -3.5, -3.1, 9.5, 13.9, 27.4, 29.1, 18.3, 23.4, 26.1, 63.6 and 64.9, 126.2, 126.7, 126.9, 129.3, 131.5, 133.2, 138.6, 146.0. HRMS calcd for $C_{29}H_{51}O_2BrSiSn$ 658.1864, found 658.1847.

34: a colorless oil, R_f = 0.53 (hexane : Et_2O = 10 : 1). IR (film) 1700 cm^{-1}. ^1H NMR δ 0.13 (6H, s), 0.63-0.85 (6H, m), 0.87 (9H, t, *J* = 7.3 Hz), 0.92 (9H, s), 1.21-1.30 (6H, m), 1.35-1.43 (6H, m), 1.58 (2H, d, *J* = 8.8 Hz), 3.63 (2H, s), 4.74 (1H, t, *J* = 8.8 Hz), 7.25 (1H, ddd, *J* = 7.9, 7.9, 1.9 Hz), 7.32 (1H, ddd, *J* = 7.9, 7.9, 1.1 Hz), 7.39 (1H, dd, *J* = 7.9, 1.9 Hz), 7.57 (1H, dd, *J* = 7.9, 1.1 Hz). ^{13}C NMR δ -3.7, 7.9, 9.4, 13.9, 27.5, 29.3, 18.4, 26.0, 50.9, 112.6, 119.0, 127.4, 129.4, 131.5, 133.7, 139.5, 141.2, 201.5. HRMS calcd for $C_{25}H_{42}O_2BrSiSn$ (M^+-C_4H_9) 601.1159, Found 601.1120.

Reaction of 33 with LDA. To a cooled (-30 °C) solution of **33** (114 mg, 173 μmol) in THF (8 mL) was added dropwise LDA (0.5 M THF-hexane solution, 359 μL, 173 μmol). After stirring at the same temperature for 10 min, the reaction was quenched by acetic acid (11 mg, 173 μmol) in THF (0.2 mL). The reaction mixture was extracted with Et_2O (10 mL x 2) after addition of saturated aqueous NH_4Cl solution (10 mL). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g; elution with 20:1 hexane-Et_2O) to give **23g** (9 mg, 18%) and a mixture of **34** and **35** (65 mg, 48%; 11%).

35: a pale yellow oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1600 cm^{-1}. ^1H NMR δ 0.80-0.95 (15H, m), 0.98-1.11 (2H, m), 1.25-1.35 (6H, m), 1.40-1.60 (6H, m), 2.51-2.63 (2H, m), 5.98 (1H, s), 7.28 (1H, ddd, *J* = 8.1, 7.5 Hz), 7.37 (1H, ddd, *J* = 7.5, 1.1 Hz), 7.51 (1H, dd, *J* = 7.5, 1.9 Hz), 7.63 (1H, dd, *J* = 8.1, 1.1 Hz). ^{13}C NMR δ -4.4, 4.2, 9.2, 13.9, 27.6, 29.4, 36.4, 100.6, 120.3, 127.6, 130.1, 131.6, 134.0, 138.0, 185.4 and 198.5. HRMS calcd for $C_{23}H_{37}O_2BrSn$ 544.0999, Found 544.1025.

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*E*)-39). To a cooled (ice-water) solution of methyl phenyl sulfone (516 mg, 3.3 mmol) in THF (7 mL) was added dropwise *n*-BuLi (1.47 M hexane solution, 2.25 mL, 3.3 mmol). After stirring at the same temperature for 1 h, the mixture was added dropwise to a cooled (-80 °C) solution of (*E*)-**11** (728 mg, 3.0 mmol) in THF (7 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (15 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (10 mL x 2). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 36 g; elution with hexane) to give (*E*)-**39** (562 mg, 73%). a colorless oil, R_f = 0.39 (hexane). IR (neat) 1250 cm^{-1}. ^1H NMR δ 0.09 (9H, s), 0.17 (6H, s), 0.97 (9H, s), 4.35 and 4.37 (each 1H, br s), 6.18 (1H, d, *J* = 18.6 Hz), 6.34 (1H, d, *J* = 18.6 Hz). ^{13}C NMR δ -4.5, -1.1, 18.5, 26.0, 96.7, 130.1, 141.4, 155.8. HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1657.

(*Z*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*Z*)-39). (*Z*)-**39** was obtained from (*Z*)-**11** in 85% yield by the procedure described above for (*E*)-**39**. a colorless oil, R_f = 0.50 (hexane). IR (neat) 1250 cm^{-1}. ^1H NMR δ 0.14 (9H, s), 0.20 (6H, s), 0.95 (9H, s), 4.35 and 4.36 (each 1H, br s), 5.61 (1H, d, *J* = 15.2 Hz), 6.52 (1H, d, *J* = 15.2 Hz). ^{13}C NMR δ -3.6, 0.4, 19.0, 26.4, 95.8, 132.4, 143.9, 157.1. HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1643.

Reaction of enol silyl ether (*E*)-39 with Fischer carbene complex 40. To a suspension of $Cr(CO)_6$ (440 mg, 2.00 mmol) in Et_2O (40 mL) was added 2-methylpropen-1-yllithium,

prepared from 1-bromo-2-methyl-1-propene (270 mg, 2 mmol) and *t*-butyllithium (1.50 M pentane solution, 3 mL, 5 mmol), at room temperature over 10 min. After stirring at room temperature for 30 min, the mixture was concentrated. Water (20 mL) was added to the residue, and the insoluble material was filtered out through Celite. To the filtrate was added an aqueous solution (2 mL) of Me_4NBr (460 mg, 3.00 mmol). The mixture was extracted with CH_2Cl_2 (20 mL x 3), and the combined organic phases were washed with brine (10 mL), dried, concentrated to give the complex **40** (480 mg) as a red solid. To a solution of this compound (480 mg, 1.37 mmol) in CH_2Cl_2 (3 mL) was added acetyl bromide (115 μL, 1.51 mmol) at -40 °C. After stirring at the same temperature for 1 h, a solution of (*E*)-**39** (440 mg, 1.71 mmol) in CH_2Cl_2 (20 mL) over 10 min. The solution was allowed to warm to 10 °C over 2.5 h, and then poured into aqueous saturated $NaHCO_3$ (30 mL). The phases were separated, and the aqueous phase was extracted with hexane (30 mL x 3). The combined organic phases were washed with saturated brine (30 mL), dried, and then concentrated. The residue was subjected to column chromatography (silica gel, 25 g; elution with 20:1 hexane-Et_2O) followed by MPLC (10 μ silica gel; elution with 55:1 hexane-Et_2O) to give **41** (40 mg, 8%) and **42** (12 mg, 2%).

41: a colorless oil, R_f = 0.39 (hexane : Et_2O = 10 : 1). IR (film) 1750 cm^{-1}. ^1H NMR δ 0.06 (9H, s), -0.03 and 0.07 (each 3H, s), 0.84 (9H, s), 1.17 (1H, d, *J* = 7.4 Hz), 1.50 (1H, d, *J* = 7.4 Hz), 1.71 (3H, d, *J* = 1.4 Hz), 1.75 (3H, d, *J* = 1.4 Hz), 1.89 (3H, s), 5.68 (1H, br m), 5.80 (1H, d, *J* = 18.8 Hz), 5.98 (1H, d, *J* = 18.8 Hz). ^{13}C NMR δ -3.1, -2.1, -0.2, 19.0, 20.4, 22.0, 26.3, 26.7, 27.5, 64.3, 64.8, 121.4, 129.3, 142.1, 145.7, 171.1. HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2353.

42: a pale yellow oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1755 cm^{-1}. ^1H NMR δ 0.08 (9H, s), 0.14 (6H, s), 0.90 (9H, s), 1.09 (3H, s), 1.22 (3H, s), 1.55 (1H, d, *J* = 9.2 Hz), 2.08 (3H, s), 2.69 (1H, d, *J* = 20.6 Hz), 3.34 (1H, br d, *J* = 20.6 Hz), 4.97 (1H, d, *J* = 9.2 Hz), 5.20 (1H, d, *J* = 2.1 Hz). ^{13}C NMR δ -4.3, -4.2, 0.9, 18.1, 21.3, 25.9, 30.8, 32.3, 36.4, 37.6, 38.1, 109.3, 129.3, 135.3, 143.1, 170.0. HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2346.

Reaction of enol silyl ether (*Z*)-39 with Fischer carbene complex 40. To a solution of the **40** (1.20 g, 3.43 mmol) described above in CH_2Cl_2 (8 mL) was added acetyl bromide (305 μL, 4.10 mmol) at -40 °C. After stirring at the same temperature for 1 h, a solution of (*Z*)-**39** (1.75 g, 6.82 mmol) in CH_2Cl_2 (56 mL) over 35 min. The solution was allowed to warm to 10 °C over 2 h, and then poured into aqueous saturated $NaHCO_3$ (30 mL). The phases were separated, and the aqueous phase was extracted with hexane (100 mL x 1, 50 mL x 2). The combined organic phases were washed with saturated brine (100 mL), dried, and then concentrated. The residue was subjected to column chromatography (silica gel, 90 g; elution with 20:1 hexane-Et_2O) followed by MPLC (10 μ silica gel; elution with 55:1 hexane-Et_2O) to give **44** (28 mg, 2%) and **45** (53 mg, 4%).

44: a colorless oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1755 cm^{-1}. ^1H NMR δ 0.09 (9H, s), 0.07 and 0.10 (each 3H, s), 0.84 (9H, s), 1.34 (1H, d, *J* = 7.5 Hz), 1.41 (1H, d, *J* = 7.5 Hz), 1.65 (3H, d, *J* = 1.3 Hz), 1.76 (3H, d, *J* = 1.3 Hz), 2.00 (3H, s), 5.36 (1H, br m), 5.63 (1H, d, *J* = 15.2 Hz), 6.56 (1H, br d, *J* = 15.2 Hz). ^{13}C NMR δ -3.4, -2.9, 0.4, 18.1, 19.2, 21.2, 25.6, 25.8, 26.4, 61.0, 61.5, 121.0, 132.3, 140.5, 145.7, 170.4. HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2371.

45: a colorless oil, R_f = 0.46 (hexane : Et_2O = 10 : 1). IR (film) 1750 cm^{-1}. ^1H NMR δ 0.15 (9H, s), 0.03 and 0.12 (each 3H, s), 0.81 (9H, s), 1.14 (3H, dd, *J* = 7.3, 1.3 Hz), 1.56 (1H, d, *J* = 7.3 Hz), 1.71 (3H, d, *J* = 1.3 Hz), 1.77 (3H, d, *J* = 1.3 Hz), 1.90 (3H, s), 5.65 (1H, br s), 5.67 (1H, d, *J* = 15.0 Hz), 6.52 (1H, dd, *J* = 15.0, 1.3 Hz). ^{13}C NMR δ -3.2, -2.9, 0.6, 18.1, 19.4, 21.2, 25.7, 25.8, 26.9, 62.2, 62.4, 120.7, 133.6, 140.1, 144.6, 170.6. HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2402.

Thermal Cope rearrangement of 41, 44, and 45. This procedure is representative for the thermal Cope rearrangement of the cyclopropyl acetates. A solution of **41** (9.1 mg, 23.8 μmol) in benzene (2.4 mL) was refluxed for 1.5 h. Concentration of the solution gave pure **42** (9.1 mg, 100%).

Reaction of cyclopropyl acetates 41 with MeLi. To a cooled (-80 °C) solution of **41** (21.1 mg, 55.1 μmol) in THF (2.8 mL) was added dropwise MeLi (1.07 M in Et_2O, 114 μL, 122 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (7.4 mg, 123 μmol) in THF (0.5 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (5 mL), and then extracted with Et_2O (5 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residue was subjected to MPLC (5 μ silica gel, elution with 40:1 hexane-Et_2O) to give **15d** (13.4 mg, 71%) and **41** (2.9 mg, 14%).

Reaction of cyclopropyl acetates 44 and 45 with MeLi. The following procedure for **45** is representative: To a cooled (-80 °C) solution of **45** (12.6 mg, 32.9 μmol) in THF (1.6 mL) was added dropwise MeLi (1.00 M in Et_2O, 73 μL, 73.0 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (4.4 mg, 73.3 μmol) in THF (0.2 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (3 mL), and then extracted with Et_2O (3 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residue was filtered through a short pad of silica gel (120 mg) to give a mixture (12.1 mg) of **48**, **15d** and **45**. Attempted purification of this mixture by MPLC led to complete decomposition of **48**; the characterization was made by the comparison of its ^1H NMR with those of **58** and related compounds.

Reaction of enol silyl ether (*E*)-39 with Fischer carbene complex (50). To a suspension of $Cr(CO)_6$ (360 mg, 1.63 mmol) in Et_2O (10 mL) was added 1-propenyllithium (0.018 M Et_2O solution, 90 mL, 1.62 mmol), prepared from 1-bromo-1-propene with *t*-butyllithium, at room temperature over 10 min. After stirring at room temperature for 1 h, the mixture was concentrated. Water (20 mL) was added to the residue, and the insoluble material was filtered out through Celite. To the filtrate was added an aqueous solution (1.6 mL) of Me_4NBr (380 mg, 2.44 mmol). The mixture was extracted with CH_2Cl_2 (20 mL x 3), and the combined organic phases were washed with brine (10 mL), dried, concentrated. The residual solid was recrystallized from CH_2Cl_2-Et_2O to give tetramethylammonium

(propenyl(oxido)carbene)pentacarbonyl-chromium (320 mg, 59%). a red needles, mp 112-113 °C (dec), Anal. calcd for $C_{13}H_{17}O_6NCr$: C, 46.56; H, 5.11; N, 4.18; Found: C, 46.28; H, 4.98; N, 3.99.

To a cooled (-40 °C) solution of the above carbene complex (195 mg, 580 μmol) in CH_2Cl_2 (1.2 mL) was added dropwise acetyl bromide (48 μL, 640 μmol), and then the reaction mixture was stirred at the same temperature for 1 h. To this mixture was added dropwise a solution of (*E*)-**39** (300 mg, 1.16 mmol) in CH_2Cl_2 (9.4 mL) over 10 min. The reaction mixture was allowed to warm to 10 °C over 2 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution (15 mL), and extracted with hexane (10 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g; elution with 20 : 1 hexane-Et_2O) followed by MPLC (elution with 50:1 hexane-Et_2O) to give **51** (48 mg, 23%), a 1:1 mixture of **52** and **i** (35 mg, 16%), and 2-acetoxy-5-(*t*-butyldimethylsiloxy)-7-methyl-3-(trimethylsilyl)cyclohepta-1,4-diene (17 mg, 8%). The mixture of **52** and **i** was separated by resubjecting to the MPLC.

51: a colorless oil, R_f = 0.38 (hexane : Et_2O = 10 : 1). IR (film) 1760 cm^{-1}. ^1H NMR δ 0.06 (9H, s), 0.04 and 0.08 (each 3H, s), 0.87 (9H, s), 1.35 (1H, d, *J* = 7.7 Hz), 1.51 (1H, d, *J* = 7.7 Hz), 1.73 (3H, dd, *J* = 6.4, 1.5 Hz), 1.94 (3H, s), 5.55 (1H, dq, *J* = 15.6, 6.4 Hz), 5.66 (1H, dq, *J* = 15.6, 1.5 Hz), 5.73 (1H, d, *J* = 18.8 Hz), 6.04 (1H, d, *J* = 18.8 Hz). ^{13}C NMR δ -3.7, -2.9, -1.1, 18.2, 18.2, 21.2, 25.4, 25.9, 65.9, 66.1, 125.8, 126.5, 129.0, 144.0, 169.9. HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2178.

52: a colorless oil, R_f = 0.56 (hexane : Et_2O = 5 : 1). IR (film) 1755 cm^{-1}. ^1H NMR δ 0.04 (9H, s), 0.13 and 0.14 (each 3H, s), 0.91 (9H, s), 1.01 (3H, d, *J* = 7.3 Hz), 1.85 (1H, br d, *J* = 7.5 Hz), 2.09 (3H, s), 2.39 (1H, d, *J* = 19.5 Hz), 2.64-2.74 (1H, br s), 3.75 (1H, d, *J* = 19.5 Hz), 4.91 (1H, dd, *J* = 7.5, 1.7 Hz), 5.30 (1H, dd, *J* = 5.9, 2.5 Hz). ^{13}C NMR δ -4.4, -4.3, -1.1, 18.1, 21.2, 23.3, 25.9, 32.5, 29.4, 38.0, 107.2, 125.5, 144.0, 169.8. HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, found 368.2200.

2-acetoxy-5-(t-butyldimethylsiloxy)-7-methyl-3-(trimethylsilyl)cyclohepta-1,4-diene: a colorless oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1760 cm^{-1}. ^1H NMR δ 0.00 (9H, s), 0.12 and 0.12 (each 3H, s), 0.91 (9H, s), 1.11 (3H, d, *J* = 6.4 Hz), 1.88 (1H, dddd, *J* = 16.7, 11.8, 2.8, 2.1 Hz), 2.07 (1H, dd, *J* = 16.7, 5.8 Hz), 2.11 (3H, s), 2.42 (1H, dddd, *J* = 11.8, 6.4, 5.8, 1.9 Hz), 2.92 (1H, dd, *J* = 4.3, 2.8 Hz), 4.77 (1H, dd, *J* = 4.3, 2.1 Hz), 6.95 (1H, d, *J* = 1.9 Hz). ^{13}C NMR δ -4.2, -4.1, -2.1, 17.4, 18.2, 21.1, 25.9, 28.7, 30.9, 39.6, 102.9, 126.2, 127.2, 147.6, 168.3. HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, found 368.2193.

i: a colorless plates, mp 65 °C (petroleum), R_f = 0.56 (hexane : Et_2O = 5 : 1). IR (KBr) 1745 cm^{-1}. ^1H NMR δ -0.02 (9H, s), 0.11 and 0.11 (each 3H, s), 0.81 (1H, dd, *J* = 6.4, 4.3 Hz), 0.91 (9H, s), 1.08 (3H, d, *J* = 6.8 Hz), 1.80 (1H, ddd, *J* = 15.8, 8.6, 1.9 Hz), 1.86 (1H, dd, *J* = 15.8, 5.6 Hz), 1.99 (1H, dddd, *J* = 8.6, 6.8, 5.6, 4.3 Hz), 2.02 (3H, s), 3.88 (1H, d, *J* = 6.4 Hz), 4.57 (1H, d, *J* = 1.9 Hz). ^{13}C NMR δ -4.2, -4.2, -3.4, 18.2, 21.1, 23.0, 23.4, 25.7, 25.9, 37.3, 60.5, 98.3, 153.5, 171.9. Anal. Calcd for $C_{19}H_{36}O_3Si_2$: C, 61.92; H, 9.85. Found: C, 62.07; H, 9.93.

Reaction of enol silyl ether (*Z*)-39 with Fischer carbene complex (50). To a cooled (-40 °C) solution of the above carbene complex (160 mg, 477 μmol) in CH_2Cl_2 (1.2 mL) was added dropwise acetyl bromide (39 μL, 525 μmol), and then the reaction mixture was stirred at the same temperature for 1 h. To this mixture was added dropwise a solution of (*Z*)-**39** (245 mg, 954 μmol) in CH_2Cl_2 (7.6 mL) over 6 min. The reaction mixture was allowed to warm to -20 °C over 2 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution (10 mL), and extracted with hexane (10 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 15 g; elution with 20 : 1 hexane-Et_2O) followed by MPLC (elution with 50:1 hexane-Et_2O) to give **53** (21 mg, 12%), **54** (16 mg, 8%), and **i** (36 mg, 21%).

53: a colorless oil, R_f = 0.57 (hexane : Et_2O = 5 : 1). IR (film) 1760 cm^{-1}. ^1H NMR δ 0.14 (9H, s), 0.07 and 0.09 (each 3H, s), 0.84 (9H, s), 1.36 (1H, d, *J* = 7.7 Hz), 1.41 (1H, d, *J* = 7.7 Hz), 1.73 (3H, dd, *J* = 6.4, 1.5 Hz), 2.00 (3H, s), 5.48 (1H, dq, *J* = 15.6, 6.4 Hz), 5.58 (1H, dq, *J* =

15.6, 1.5 Hz), 5.80 (1H, d, *J* = 14.7 Hz), 6.52 (1H, d, *J* = 14.7 Hz). ^{13}C NMR δ -3.0, -2.9, -1.1, 18.1, 18.2, 21.4, 25.9, 25.9, 63.4, 64.9, 125.3, 126.8, 136.7, 143.8, 170.3. HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2234.

54: a colorless oil, R_f = 0.58 (hexane : Et_2O = 5 : 1). IR (film) 1755 cm^{-1}. ^{1}H NMR δ 0.04 (9H, s), 0.13 and 0.15 (each 3H, s), 0.91 (9H, s), 1.21 (3H, d, *J* = 7.1 Hz), 1.42 (1H, dd, *J* = 8.9, 3.5 Hz), 2.08 (3H, s), 2.41-2.49 (1H, m), 2.88 (1H, d, *J* = 21.6 Hz), 3.16 (1H, d, *J* = 21.6 Hz), 5.02 (1H, dd, *J* = 8.9, 0.5 Hz), 5.53 (1H, dd, *J* = 8.6, 1.9 Hz). ^{13}C NMR δ -4.3 and -4.2, -1.6, 18.1, 21.3, 22.9, 25.9, 30.2, 32.9, 39.0, 108.0, 123.0, 143.4, 144.7, 169.7. HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2175.

Reaction of 51 with MeLi. This procedure is representative of reactions of **51** and **53** with MeLi: To a cooled (-80 °C) solution of **24** (21 mg, 55.6 μmol) in THF (2.8 mL) was added dropwise MeLi (1.07 M in Et_2O, 115 μL, 123 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (7.4 mg, 123 μmol) in THF (0.5 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (5 mL), and then extracted with Et_2O (5 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residue was subjected to MPLC (5 μ silica gel, elution with 50:1 hexane-Et_2O) to give **55** (7.0 mg, 39%) and **56** (6.5 mg, 35%).

55: a colorless oil, R_f = 0.48 (hexane : Et_2O = 5 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.02 (9H, s), 0.14 and 0.17 (each 3H, s), 0.92 (9H, s), 0.95 (3H, d, *J* = 6.6 Hz), 1.60 (1H, dd, *J* = 7.9, 3.2 Hz), 2.37 (1H, dd, *J* = 11.1, 6.2 Hz), 2.44-2.50 (1H, m), 2.62 (1H, dd, *J* = 11.1, 9.8 Hz), 2.82 (1H, d, *J* = 18.6 Hz), 3.43 (1H, dm, *J* = 18.6 Hz), 4.92 (1H, dd, *J* = 7.9, 2.4 Hz). ^{13}C NMR δ -4.4, -4.1, -1.6, 18.2, 19.3, 25.8, 28.7, 36.1, 50.4, 51.0, 105.5, 149.6, 208.9. HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2069.

56: a pale yellow oil, R_f = 0.53 (hexane : Et_2O = 5 : 1). IR (film) 1700 cm^{-1}. ^{1}H NMR δ 0.00 (9H, s), 0.12 (6H, s), 0.88 (9H, s), 1.31 (2H, d, *J* = 8.5 Hz), 1.88 (3H, dd, *J* = 6.8, 1.7 Hz), 3.21 (2H, s), 4.79 (1H, t, *J* = 8.5 Hz), 6.25 (1H, dq, *J* = 15.6, 1.7 Hz), 6.90 (1H, dq, *J* = 15.6, 6.8 Hz).

^{13}C NMR δ -4.3, -1.6, 16.7, 18.2, 18.4, 25.9, 44.7, 106.4, 130.7, 143.0, 143.8, 197.0. HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2076.

57: a colorless oil, R_f = 0.47 (hexane : Et_2O = 5 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.07 (9H, s,), 0.12 (6H, s), 0.90 (9H, s), 1.05 (3H, d, *J* = 6.8 Hz), 1.35 (1H, ddd, *J* = 9.2, 7.5, 1.0 Hz), 2.52 (1H, dd, *J* = 14.1, 8.1 Hz), 2.16-2.24 (1H, m), 2.62 (1H, dd, *J* = 14.1, 4.1 Hz), 2.95 (1H, d, *J* = 17.5 Hz), 3.35 (1H, ddd, *J* = 17.5, 1.3, 1.1 Hz), 4.99 (1H, dd, *J* = 7.5, 1.3 Hz). ^{13}C NMR δ -4.2, -4.2, -1.4, 18.1, 23.9, 25.8, 33.3, 31.5, 50.4, 49.9, 109.3, 144.2, 209.2. HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2118.

58: a colorless oil, R_f = 0.27 (hexane : Et_2O = 5 : 1). IR (film) 1720 cm^{-1}. ^{1}H NMR δ -0.03 (9H, s), 0.16 and 0.17 (each 3H, s), 0.93 (9H, s), 1.72 (3H, dd, *J* = 6.0, 1.3 Hz), 1.89 (2H, dd, *J* = 2.8, 0.9 Hz), 2.15 (1H, d, *J* = 16.2 Hz), 2.23 (1H, s), 2.67 (1H, ddd, *J* = 16.2, 2.4, 1.5 Hz), 4.64 (1H, ddd, *J* = 2.8, 2.4, 0.9 Hz), 5.65 (1H, dd, *J* = 15.4, 1.3 Hz), 5.72 (1H, dq, *J* =15.4, 6.0 Hz). HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2100.

Low-Temperature Quenching of Reactions of (*E*)- and (*Z*)-11 with 13c. To a stirred and cooled (-80°C) solution of lithium diisopropylamide prepared from diisopropylamine (572 μL, 413 mg, 4.08 mmol) and *n*-BuLi (1.28 M in hexane, 3.19 mL, 4.08 mmol) in THF (2 mL) was added dropwise a solution of 3-nonen-2-one (614 μL, 521 mg, 3.71 mmol) in THF (2 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **(*E*)-11** (900 mg, 3.71 mmol) in THF (170 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (234 μL, 245 mg, 4.08 mmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (40 mL), and then extracted with Et_2O (40 mL x 3). The combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g; elution with 30:1 hexane-AcOEt) to give **(*E*)-63** (613 mg, 43%), **(*E*)-11** (155 mg, 17%), 3-none-2-one (182 mg, 35%), and **15c** (172 mg, 12%). **(*E*)-63**: a colorless oil, R_f = 0.29 (hexane : Et_2O = 15 : 1). IR (film) 3645, 1665 (weak) cm^{-1}. ^{1}H NMR δ -

0.01 (9H, s), 0.01 (6H, s), 0.89 (3H, t, *J* = 6.8 Hz), 0.95 (9H, s), 1.26-1.35 (4H, m), 1.46 (2H, br tt, *J* = 6.8, 6.8 Hz), 2.20 (2H, dt, *J* = 6.8, 6.8 Hz), 2.72 (1H, d, *J* = 15.4 Hz), 3.04 (1H, d, *J* = 15.4 Hz), 3.79 (1H, s), 5.67 (1H, d, *J* = 19.0 Hz), 6.02 (1H, dt, *J* = 15.0, 1.5 Hz), 6.12 (1H, d, *J* = 19.0 Hz), 6.77 (1H, dt, *J* = 15.8, 6.8 Hz). ^{13}C NMR δ -7.7, -7.4, -1.0, 14.1, 18.5, 28.0, 22.6, 29.9, 31.6, 32.6, 44.9, 73.9, 124.9, 131.6, 148.9, 150.1, 202.1. HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, Found 382.2710.

To a stirred and cooled (-80°C) solution of lithium diisopropylamide prepared from diisopropylamine (191 μL, 138 mg, 1.36 mmol) and *n*-BuLi (1.28 M in hexane, 1.06 mL, 1.36 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (205 μL, 174 mg, 1.24 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **(*Z*)-11** (300 mg, 1.24 mmol) in THF (58 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (78 μL, 82 mg, 1.36 mmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (10 mL), and then extracted with Et_2O (20 mL x 3). The combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g; elution with 20:1 hexane-AcOEt) to give **(*Z*)-63** (20 mg, 4%), **(*Z*)-11** (231 mg, 77%), 3-none-2-one (127 mg, 73%). **(*Z*)-63**: a colorless oil, R_f = 0.59 (hexane : AcOEt = 10 : 1). IR (film) 3435, 1655 (weak) cm^{-1}. ^{1}H NMR δ -0.07 and 0.02 (each 3H, s), 0.11 (9H, s), 0.89 (3H, t, *J* = 6.2 Hz), 0.99 (9H, s), 1.25-1.40 (4H, m), 1.46 (2H, br tt, *J* = 7.5, 7.5 Hz), 2.21 (2H, dt, *J* = 7.1, 7.1 Hz), 2.72 (1H, d, *J* = 15.0 Hz), 2.99 (1H, d, *J* = 15.0 Hz), 3.91 (1H, s), 5.36 (1H, d, *J* = 14.3 Hz), 6.02 (1H, dd, *J* = 15.8, 0.9 Hz), 6.25 (1H, dd, *J* = 14.3, 0.6 Hz), 6.78 (1H, dt, *J* = 15.8, 7.1 Hz). ^{13}C NMR δ -6.9, -6.8, 2.2, 14.1, 18.6, 28.1, 22.6, 31.5, 27.9, 32.7, 45.0, 75.9, 125.8, 131.5, 149.5, 150.6, 202.2. HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, Found 382.2730.

Reactions of (*E*)- and (*Z*)-63 with LDA. To a cooled (-80°C) solution of **(*E*)-63** (186 mg, 486 μmol) in THF (21 mL) was added dropwise a solution of lithium diisopropylamide prepared from diisopropylamine (68 μL, 49 mg, 486 μmol) and *n*-BuLi (1.28 M in hexane, 380

μL, 486 μmol) in THF (3 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (28 μL, 29 mg, 483 μmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (8 mL), and then extracted with Et_2O (20 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 18 g; elution with 15:1 hexane-Et_2O) to give **15c** (69 mg, 37%), **(*E*)-64** (19 mg, 16%), and 3-nonen-2-one (25 mg, 36%). **(*E*)-64:** a colorless oil, $R_f = 0.34$ (hexane : AcOEt = 15 : 1). IR (film) 3435 cm^{-1}. ^1H NMR δ -0.05 and -0.02 (each 3H, s), 0.06 (9H, s), 0.95 (9H, s), 4.21 (1H, dd, *J* = 4.7, 2.1 Hz), 5.67 (1H, dd, *J* = 18.8, 2.1 Hz), 6.28 (1H, dd, *J* = 18.8, 4.7 Hz). ^{13}C NMR δ -8.7, -7.4, -0.9, 17.3, 27.1, 69.6, 122.9, 148.6. HRMS calcd for $C_{12}H_{28}OSi_2$ 244.1679, Found 244.1654.

To a cooled (-80°C) solution of **(*Z*)-63** (57 mg, 149 μmol) in THF (6.5 mL) was added dropwise a solution of lithium diisopropylamide prepared from diisopropylamine (21 μL, 15 mg, 149 μmol) and *n*-BuLi (1.28 M in hexane, 116 μL, 149 μmol) in THF (1 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (9 μL, 9 mg, 149 μmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (3 mL), and then extracted with Et_2O (7 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 6.5 g; elution with 30:1 hexane-AcOEt) to give **22c** (1.7 mg, 3%), **(*Z*)-11** (27 mg, 75%), and 3-nonen-2-one (9.8 mg, 47%).

General Procedure for the Reaction of 70 with Lithium Enolate of 3-Nonen-2-one (13c). This procedure is representative of reactions of **70** with lithium enolate of 3-nonen-2-one. To a stirred and cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (122 μL, 88 mg, 0.870 mmol) and *n*-BuLi (1.44 M in hexane, 605 μL, 0.871 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (131 μL, 111 mg, 0.792 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via

a cannula to a cooled (-80 °C) solution of **70a** (168 mg, 0.791 mmol) in THF (36 mL). The reaction mixture was allowed to warm to 0 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (30 mL). The mixture was extracted with Et_2O (20 mL x 2), and the combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 28 g; elution with 10:1 hexane-AcOEt) to give **71a** (207 mg, 75% as a colorless oil).

71c: a colorless oil, R_f = 0.38 (hexane:AcOEt = 15:1). IR (film) 1710, 1655, 1250 cm^{-1}. ^1H NMR δ 0.14 and 0.17 (each 3H, s, $SiMe_2$), 0.86 (3H, t, *J* = 7.1 Hz, H-5"), 0.92 and 0.93 (each 9H, s), 1.10-1.48 (8H, m), 2.14 (1H, dd, *J* = 7.7, 2.8 Hz), 2.31-2.38 (1H, m), 2.44 (1H, dd, *J* = 11.3, 6.4 Hz), 2.58 (1H, dd, *J* = 11.3, 7.1 Hz), 2.77 (1H, d, *J* = 16.9 Hz), 3.52 (1H, dd, *J* = 16.9, 2.1 Hz), 4.96 (1H, dd, *J* = 7.7, 2.1 Hz). ^{13}C NMR δ -4.3, -4.0, 14.3, 18.1, 22.9, 27.2, 30.8, 32.2, 25.8, 29.2, 33.5, 42.2, 49.1, 49.8, 51.3, 108.2, 147.2, 209.4. HRMS calcd for $C_{22}H_{42}O_2Si$: 366.2954, Found: 366.2964.

General procedure for the [3 + 4] annulation using acylsilanes 74. This procedure is representative of reactions of **74** with lithium enolate of 3-none-2-one (**13c**): To a stirred and cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (84 μL, 61 mg, 0.603 mmol) and *n*-BuLi (1.41 M in hexane, 426 μL, 0.600 mmol) in THF (0.5 mL) was added dropwise a solution of 3-nonen-2-one (99 μL, 84 mg, 0.600 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (0 °C) solution of **74** (125 mg, 0.542 mmol) in THF (24 mL). The reaction mixture was stirred at 0 °C for 30 min, and then quenched by acetic acid (36 mg, 0.600 mmol). The mixture was concentrated, and then the residue was subjected to column chromatography (silica gel, 10 g; elution with 10:1 hexane-AcOEt) to give **76a** (164 mg, 82%).

76a: a colorless oil, R_f = 0.26 (hexane:AcOEt = 20:1). IR (film) 1705, 1685, 1250 cm^{-1}. ^1H NMR δ 0.47 and 0.46 (each 3H, s), 0.89 (3H, t, *J* = 7.1 Hz), 0.08-1.42 (9H, m), 1.42-1.52 (1H, m), 1.62-1.65 (1H, m), 1.80-1.87 (1H, m), 1.94-2.00 (1H, m), 1.99-2.08 (1H, br m), 2.35-2.42 (1H, m), 2.47 (2H, d, *J* = 5.8 Hz), 2.81-2.86 (1H, br m), 2.82 (1H, d, *J* = 15.0 Hz), 3.53 (1H,

dm, J = 15.0 Hz), 7.35-7.42 (3H, m, Ar), 7.52-7.62 (2H, m, Ar). ^{13}C NMR δ-0.6, 14.3, 22.8, 25.3, 27.4, 29.0, 31.2, 31.3, 32.2, 41.1, 44.5, 48.4, 51.5, 125.7, 128.0, 130.0, 133.6, 136.0, 137.4, 207.4. HRMS calcd for $C_{23}H_{34}O_2Si$: 370.2328, Found: 370.2330.

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Supporting Information Available: Full experimental detail and characterization data for all new compounds described in the text, and X-ray structural information on **15f** and **77f** (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

† Rigaku Corporation.

References and Notes

(1) For general reviews, see: (a) Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*, VCH, New York, 1988. (b) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavac, F.; White, C. T. In *The Total Synthesis of Natural Products*; ApSimon, J. Ed.; John Wiley & Sons: New York, 1983; Vol. 5, pp 333-390.

(2) (a) Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203-5223. (b) Hudlicky, T.; Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org. React.* **1992**, *41*, 1-133. (c) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 593-615. (d) Piers, E. *ibid* Vol. 5, pp 971-998. (e) Mann, J. *Tetrahedron* **1986**, *42*, 4611-4659. (f) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23,* 1-88. (g) Noyori, R.; Hayakawa, Y. *Org. React.* **1983**, *29*, 163-344.

(3) (a) Lee, J.; Kim, H.; Cha, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 9919-9920 and references cited therein. (b) Barluenga, J.; Aznar, F.; Martín, A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 9419-9426 and references cited therein. (c) Trost, B. M.; Yamazaki, S. *Chem. Lett.* **1994**, 2245-2248 and references cited therein. (d) Hudlicky, T.; Fleming, A.; Radesca, L. *J. Am. Chem. Soc.* **1989**, *111*, 6691-6707 and references cited therein. (e) Wulff, W. D.; Yang, D. C.; Murray, C. K. *J. Am. Chem. Soc.* **1989**, *110*, 2653-2655. (f) Molander, G. A.; Eastwood, P. R. *J. Org. Chem.* **1996**, *61*, 1910-1911 and references cited therein. (g) Harmata, M.; Elomari, S.; Barnes, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 2860-2871.

(4) Takeda, K.; Fujisawa, M.; Makino, T.; Yoshii, E.; Yamaguchi, K. *J. Am. Chem. Soc.* **1993**, *115*, 9351-9352.

(5) (a) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 149-221. (b) Brook, A. G. *Acc. Chem. Res.*, **1974**, *7*, 77-84.

(6) (a) Takeda, K.; Takeda, M.; Nakajima, A.; Yoshii, E. *J. Am. Chem. Soc.* **1995**, *117*, 6400-6401. (b) Takeda, K.; Nakajima, A.; Yoshii, E. *Synlett* **1996**, 753-754.

(7) (a) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949-960. For reviews on acylsilanes, see: (a) Qi, H.; Curran, D. P. In *Comprehensive Organic Functional Group Transformations*, Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W.; Moody, C. J., Eds.; Pergamon, Oxford, 1995, pp 409-431. (b) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proc. Int.*, **1992**, *24*, 553-582. (c) Bulman Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147-195. (d) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647-660.

(8) Reuss, R. H.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 1785-1787.

(9) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4186-4187.

(10) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc. Perkin 1*, **1995**, 317-337.

(11) For reviews on rearrangement of divinylcyclopropanes, see: ref. (2b) and (a) Piers, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 971-998. (b) Hill, R. K. *ibid* Vol. 5, pp 785-826.

(12) (a) Wilson, S. R. *Org. React.* **1993**, *43*, 93-250. For related charge accelerated rearrangements, see: (b) Bronson, J. J.; Danheiser, R. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 999-1036.

(13) For thermal Cope rearrangement of *cis*-1-aryl-2-vinylcyclopropanes, see: Marvell, E. N.; Lin, C. *J. Am. Chem. Soc.* **1978**, *100*, 877-883. and ref. (11b).

(14) Takeda, K.; Nakatani, J.; Nakamura, H.; Sako, K.; Yoshii, E.; Yamaguchi, K. *Synlett* **1993**, 841-843.

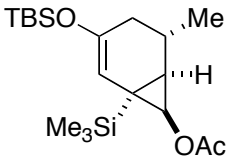
(15) Takeda, K.; Sakurama, K.; Yoshii, E. *Tetrahedron Lett.* **1997**, *38*, 3257-3260.

(16) This compound was prepared according to Wulff's procedure. Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660-5662.

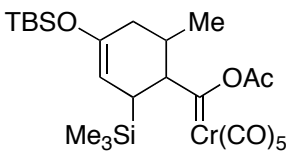
(17) Similar results have been reported for the reaction of Danishefsky's diene and cyclohexenyl methoxy chromium carbene complex by Wulff and coworkers. Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642-3659. The relatively facile cis-to-trans isomerization of **41** involving ring-opening/reclosure and the fast thermal Cope rearrangement of the *cis*-derivative of **41** may be interpreted in terms of the push-pull effect by the siloxy and acetoxy groups.

(18) For an oxyanion-accelerated vinylcyclopropane rearrangement, see: (a) Danheiser, R. L.; Martinez-Davila, C.; Morin, Jr., J. M. *J. Org. Chem.* **1980**, *45*, 1340-1341. (b) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443-2446. and ref. (12b).

(19) The major side product of the reaction was bicyclo[4.1.0]heptene **i** (X-ray) which was an intramolecular C-H insertion product of Diels-Alder adduct **ii**. see: Takeda, K.; Okamoto, Y.; Nakajima, A.; Yoshii, E.; Koizumi, T. *Synlett* **1997**, 1181-1183.



i



ii

(20) We believe that the slower trans-to-cis isomerization of **51** relative to more congested **41** would be due to lower ground state energy of the *trans*-1,2-divinylcyclopropropanolate from **51** than that of **41**.

(21) We will report the mechanistic details of the [3 + 2] annulation including the comparison of α-carbanion-stabilizing ability between the phenylthio and trimethylsilyl groups elsewhere.

(22) Takeda, K,; Okamoto, Y.; Koizumi, T. unpublished results. Also, see ref (19).

(23) Nowick, J. S.; Danheiser, R. L. *J. Org. Chem.* **1989**, *54*, 2798-2802.

(24) Reaction with crotonoylsilane **70** (R = Me) gave a poor yield of the cycloheptenone presumably because of decomposition caused by enolate-mediated deprotonation of the β-methyl group of **70**.

(25) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc. Perkin I* **1981**, 2520-2526.

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[3 + 4] Annulation of α,β-Unsaturated Acylsilanes with Enolates of α,β-Unsaturated Methyl Ketones: Scope and Mechanism

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Supporting Information

General: IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer. ^{1}H NMR spectra were taken on Varian UnityPlus 500 (500 MHz) in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26) unless otherwise noted. ^{13}C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2) unless otherwise noted. Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. Low- and high-resolution mass spectra (EI-MS) were obtained with a JEOL JMS-D-300 spectrometer combined with a JEOL JMA-2000 data processing system. Liquid chromatography under medium pressures (MPLC) was carried out with a JASCO PU-980 pump system by using prepacked columns (22 mm x 300 mm, 10 μ silica gel or 22 mm x 150 mm, 5 μ silica gel) (Kusano Kagakukikai Co.). For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; Merck precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures. Melting points (uncorrected) were determined by using a Yanagimoto micro-melting point apparatus. Elemental combustion analysis was performed at the Microanalysis Laboratory of this University.

(*Z*)- and (*E*)-*tert*-Butyldimethylsilyl 2-(Phenylthio)ethenyl Ketones (*Z*)-1 and (*E*)-1. A solution of *n*-BuLi (1.66 M in hexane, 6.33 mL, 10.5 mmol) was added to a solution of 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethoxy)-1,2-propadiene **10** (2.42 g, 10.0 mmol) in THF (20 mL) at -80 °C, and then the solution was stirred at the same temperature for 20 min. To the reaction mixture was a solution of diphenyl disulfide (2.18 g, 10 mmol) in THF (10 mL) over 5 min. After stirring at the same temperature for 10 min, the reaction mixture was diluted with pentane (100 mL) and water (50 mL). The phases were separated and the aqueous phase was extracted with pentane (50 mL x 2). The combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was dissolved in THF-H_2O (5:1, 18 mL) before addition of CF_3COOH (8.5 mL). After stirring at room temperature for 5 min, the reaction mixture was diluted with pentane (50 mL). The mixture was successively washed with water (50 mL x 2), saturated aqueous $NaHCO_3$ (50 mL x 2) and brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g; elution with 15:1 hexane-Et_2O) to give **1** (2.60 g, 93%) in a 7.6:1 *Z*/*E* ratio. The diastereomeric mixture was separated by MPLC (elution with 18:1 hexane-Et_2O). (*Z*)-**1**: orange needles, mp 50-51 °C (hexane), R_f = 0.32 (15:1 hexane-Et_2O), IR (KBr) 1595, 1480 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.23 (6H, s, $SiMe_2$), 0.97 (9H, s, *t*-Bu), 6.86 (1H, d, *J* = 9.5 Hz, H-2), 7.08 (1H, d, *J* = 9.5 Hz, H-3), 7.30-7.50 (5H, m, Ar-H). ^{13}C NMR ($CDCl_3$) -7.1 ($SiMe_2$), 26.6 (*t*-Bu), 16.8 (SiC), 123.5 (C-2), 143.9 (C-3), 128.2, 129.3, 130.6, 137.8 (Ar). MS *m*/*e* 278.1129 (calcd for $C_{15}H_{22}OSSi$ 278.1159). Anal. Calcd for $C_{15}H_{22}OSSi$: C, 64.69; H,

7.96, Found: C, 64.42; H, 7.89. (*E*)-**1** an orange oil, R_f = 0.32 (15:1 hexane-Et_2O), IR (neat) 1595, 1480 cm^{-1}; ^1H NMR ($CDCl_3$) 0.17 (6H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 6.46 (1H, d, *J* = 15.1 Hz, H-2), 7.35-7.52 (5H, m, Ar-H), 7.59 (1H, d, *J* = 15.1 Hz, H-3). ^{13}C NMR ($CDCl_3$) -6.5 ($SiMe_2$), 26.5 (*t*-Bu), 132.5 (C-2), 144.0 (C-3), 129.0, 129.6, 129.6, 131.1 (Ar). MS *m/e* 278.1127 (calcd for $C_{15}H_{22}OSSi$ 278.1159).

(*Z*)- and (*E*)-*tert*-Butyldimethylsilyl 2-(tri-*n*-Butylstannyl)ethenyl Ketones (*Z*)-12 and (*E*)-12. A solution of *n*-BuLi (1.54 M in hexane, 13.4 mL, 20.6 mmol) was added to a solution of **10** (5.00 g, 20.6 mmol) in THF (25 mL) at -80 °C, and then the solution was stirred at the same temperature for 40 min. This solution was added to a cooled (-80 °C) solution of *n*-Bu_3SnCl (5.6 mL, 20.6 mmol) and HMPA (3.6 mL, 20.6 mmol) in THF (20 mL). After stirring at the same temperature for 20 min, the reaction mixture was allowed to warm to 0 °C before addition of NEt_3 (2.1 mL). The reaction mixture was partitioned between pentane (50 mL) and saturated aqueous $NaHCO_3$ (50 mL). The aqueous phase was extracted with pentane (50 mL x 2), and then the combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residue was dissolved in MeOH (680 mL), and then stirred at room temperature for 20 min after addition of *p*-TsOH·H_2O (630 mg, 3.31 mmol). After addition of a solution of K_2CO_3 (300 mg, 3.31 mmol) in water (2 mL), the mixture was concentrated. The residue was partitioned between Et_2O (100 mL) and water (100 mL), the aqueous phase was extracted with Et_2O (100 mL x 2). The combined organic phases were successively washed with water (100 mL) and saturated brine (100 mL), dried, and concentrated. The residue was subjected to column chromatography (silica gel, 150 g; elution with 30:1 hexane-Et_2O) to give (*E*)-**12** (4.35 g, 46%) and (*Z*)-**12** (4.16 g, 44%). (*E*)-**12**: a dark orange oil, a dark orange oil, R_f = 0.56 (hexane: Et_2O = 10 : 1). IR (film) 1655 cm^{-1}. ^1H NMR δ 0.22 (6H, s, $SiMe_2$), 0.87 (9H, t, *J* = 6.8 Hz, $SnCH_2$), 0.91 (9H, s, *t*-Bu), 0.90-1.04 (6H, m, $SnCH_2$), 1.24-1.33 (6H, m, $SnCH_2CH_3$), 1.40-1.56 (6H, m, $SnCH_2CH_2$), 6.75 (1H, d, *J* = 19.9 Hz, H-2), 7.41 (1H, d, *J* = 19.9 Hz, H-3). ^{13}C NMR δ -5.8 ($SiMe_2$), 9.6, 13.6, 27.1, 29.0 (SnBu), 16.6 (CMe_3), 26.5 (*t*-Bu), 149.5 (C-2), 151.4 (C-3), 234.6 (C-1). HRMS calcd for $C_{21}H_{44}OSiSn$ 460.2183, found 460.2184. (*Z*)-**12**: a dark yellow oil, R_f = 0.73 (hexane: Et_2O = 10 : 1). IR (film) 1655 cm^{-1}. ^1H NMR δ 0.21 (6H, s, $SiMe_2$), 0.86 (9H, t, *J* = 6.8 Hz, $SnCH_2$), 0.91 (6H, t, *J* = 6.8 Hz, $SnCH_2$), 0.93 (9H, s, *t*-Bu), 1.23-1.33 (6H, m, $SnCH_2CH_3$), 1.38-1.54 (6H, m, $SnCH_2CH_2$), 6.80 (1H, d, *J* = 12.4 Hz, H-2), 7.64 (1H, d, *J* = 12.4 Hz, H-3). ^{13}C NMR δ -7.1 ($SiMe_2$), 11.4, 14.0, 27.6, 29.4 (SnBu), 17.0 (CMe_3), 26.7 (*t*-Bu), 144.1 (C-2), 150.7 (C-3), 234.6 (C-1). HRMS calcd for $C_{21}H_{44}OSiSn$ 460.2183, found 460.2193.

Reaction of 1 with 13c. To a cooled (-80 °C) solution of LDA, prepared from diisopropylamine (142 μL, 1.02 mmol) and *n*-BuLi (1.50 M hexane solution, 677 μL, 1.02 mmol) in THF (1 mL), was added dropwise a solution of 3-nonen-2-one (129 mg, 923 μmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of (*E*)-(β-(phenylthio)acryloyl)silane **1** (*E*/*Z* mixture) (308 mg, 1.11 mmol) in THF (43 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by a solution of AcOH (58 μL, 61 mg, 1.02 mmol) in THF (1 mL) and of saturated aqueous NH_4Cl (30 mL). The mixture was extracted with Et_2O (30 mL x 3), and the combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 44 g; elution with 35:1 hexane-AcOEt) to give **14a** (119 mg, 31%) and impure **14b** (68 mg). The latter was purified by MPLC (10 μ silica gel; elution with 50:1 hexane-AcOEt) to give **14b** (12 mg, 3%). **14a**: a colorless oil, R_f = 0.19 (hexane: AcOEt = 20 : 1). ^1H NMR δ 0.18, 0.18 (each 3H, s, $SiMe_2$), 0.86 (3H, t, *J* = 6.8 Hz, C-7'), 0.93 (9H, s, *t*-Bu), 1.18-1.32 (6H, m, H-4', H-5' and H-6'), 1.88-1.98 (2H, m, H-3'), 2.23 (1H, s, OH), 2.22 (1H, d, *J* = 16.5 Hz, H-5), 2.82 (1H, ddd, *J* = 16.5, 2.1, 1.3 Hz, H-5), 4.17 (1H, d, *J* = 2.4 Hz, H-2), 4.71-4.73 (1H, br m, H-3), 5.72 (1H, dt, *J* = 15.6, 6.6 Hz, H-2'), 5.81 (1H, dm, *J* = 15.6 Hz, H-1'), 7.15 (1H, tm, *J* = 7.3 Hz, Ar-H), 7.23 (2H, t, *J* = 7.3 Hz, Ar-H), 7.34 (2H, d, *J* = 7.3 Hz, Ar-H). ^{13}C NMR δ -4.5, -4.3 ($SiMe_2$), 14.2 (C-7'), 18.3 (CMe_3), 22.7, 28.8, 31.6 (C-4', C-5' and C-6'), 25.7 (*t*-Bu), 32.4 (C-3'),

46.8 (C-5), 62.6 (C-2), 81.2 (C-1), 101.8 (C-3), 126.2, 128.7, 130.4 (Ar), 130.7 (C-2'), 131.9 (C-1'), 136.7 (Ar), 156.0 (C-4). **14b**: a colorless oil, R_f = 0.36 (hexane: AcOEt = 20 : 1). ^{1}H NMR δ 0.16, 0.17 (each 3H, s, $SiMe_2$), 0.88 (3H, t, *J* = 7.1 Hz, C-7'), 0.91 (9H, s, *t*-Bu), 1.20-1.36 (6H, m, H-4', H-5' and H-6'), 2.02 (2H, br dt, *J* = 6.6, 6.6 Hz, H-3'), 2.43 (1H, br d, *J* = 16.5 Hz, H-5), 2.53 (1H, ddd, *J* = 16.5, 1.7, 1.7 Hz, H-5), 3.40 (1H, s, OH), 4.16 (1H, dd, *J* = 2.4, 2.4 Hz, H-2), 4.64-4.67 (1H, br m, H-3), 5.66 (1H, d, *J* = 15.4 Hz, H-1'), 5.82 (1H, dt, *J* = 15.4, 6.6 Hz, H-2'), 7.16-7.20 (1H, m, Ar-H), 7.22-7.28 (2H, m, Ar-H), 7.39 (2H, d, *J* = 7.3 Hz, Ar-H). ^{13}C NMR δ -4.4 ($SiMe_2$), 14.3 (C-7'), 18.3 (CMe_3), 22.7, 29.1, 31.6 (C-4', C-5' and C-6'), 25.8 (*t*-Bu), 32.3 (C-3'), 47.3 (C-5), 65.4 (C-2), 76.7 (C-1), 101.5 (C-3), 126.7, 128.8, 130.8 (Ar), 128.9 (C-2'), 134.3 (C-1'), 136.1 (Ar), 155.4 (C-4).

General Procedure for the [3 + 4] Annulation Using 11 and 12: Reaction of (*E*)-11 with Li Enolate of 3-Nonen-2-one (13c). To a cooled (-80°C) solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (139 μL, 100 mg, 0.99 mmol) and *n*-BuLi (1.32 M in hexane, 0.75 mL, 0.99 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (149 μL, 126 mg, 0.90 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of (*E*)-**11** (262 mg, 1.08 mmol) in THF (41 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (30 mL). The mixture was extracted with Et_2O (15 mL x 2), and the combined organic phases were washed with water (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 20:1 hexane-AcOEt) to give **15c** (289 mg, 84%).

15a (R = $(CH_2)_2CH_3$): a colorless oil, R_f = 0.53 (hexane:AcOEt = 10:1). IR (film) 1710, 1645, 1250 cm^{-1}. ^{1}H NMR δ0.02 (9H, s, $SiMe_3$), 0.13 and 0.16 (each 3H, s, $SiMe_2$), 0.86 (3H, t, *J* = 7.1 Hz, H-3'), 0.91 (9H, s, *t*-Bu), 1.10-1.39 (4H, m, H-1'and H-2'), 1.63 (1H, dd, *J* = 8.1, 3.9 Hz, H-5), 2.30-2.39 (1H, m, H-6), 2.41 (1H, dd, *J* = 11.5, 6.4 Hz, H-7), 2.57 (1H, dd, *J* = 11.5, 11.5 Hz, H-7), 2.81 (1H, d, *J* = 18.4 Hz, H-2), 3.44 (1H, d, *J* = 18.4 Hz, H-2), 4.93 (1H, dd, *J* = 8.1, 2.4 Hz, H-4). ^{13}C NMR δ -4.1 and -4.4 ($SiMe_2$), -1.3 ($SiMe_3$), 14.1 (C-3'), 18.2 (*C*Me_3), 20.3, 36.4 (C-1' and 2'), 25.8 (*t*-Bu), 29.1 (C-5), 40.6 (C-6), 47.4 (C-7), 51.1 (C-2), 106.6 (C-4), 148.8 (C-3), 210.8 (C-1). HRMS calcd for $C_{19}H_{37}O_2Si_2$ (M^+-1) 324.2485, found 324.2498.

15b (R = $CHMe_2$): a colorless oil, R_f = 0.45 (hexane:AcOEt = 15:1). IR (film) 1715, 1645, 1250 cm^{-1}. ^{1}H NMR δ0.03 (9H, s, $SiMe_3$), 0.13 and 0.16 (each 3H, s, $SiMe_2$), 0.87, 0.89 (each 3H, d, *J* = 6.8 Hz, CH*Me*$_2$), 0.91 (9H, s, *t*-Bu), 1.80-1.89 (1H, m, C*H*Me_2), 1.72 (1H, dd, *J* = 8.1, 4.5 Hz, H-5), 2.25-2.31 (2H, m, H-6 and H-7), 2.80 (1H, br dd, *J* = 13.0, 13.0 Hz, H-7), 2.84 (1H, d, *J* = 18.8 Hz, H-2), 3.41 (1H, br d, *J* = 18.8 Hz, H-2), 4.93 (1H, dd, *J* = 8.1, 2.4 Hz, H-4). ^{13}C NMR δ -4.1 and -4.4 ($SiMe_2$), -1.5 ($SiMe_3$), 18.6 (*C*Me_3), 18.1, 22.1 (CH*Me*$_2$), 25.8 (*t*-Bu), 28.6 (C-5), 41.3 (C-7), 47.4 (C-6), 50.9 (C-2), 107.3 (C-4), 148.2 (C-3), 211.8 (C-1). HRMS calcd for $C_{19}H_{38}O_2Si_2$ 354.2410, found 354.2413.

15c (R = $(CH_2)_4CH_3$): a colorless oil, R_f = 0.48 (hexane:AcOEt = 15:1). IR (film) 1710, 1640, 1250 cm$^{-1.}$ ^{1}H NMR δ0.01 (9H, s, $SiMe_3$), 0.13 and 0.17 (each 3H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 1.11-1.38 (8H, m, H-1', H-2', H-3', and H-4'), 0.88 (3H, t, *J* = 6.4 Hz, H-5'), 1.64 (1H, dd, *J* = 8.1, 3.8 Hz, H-5), 2.29-2.37 (2H, m, H-6), 2.43 (1H, dd, *J* = 11.8, 6.4 Hz, H-7), 2.59 (1H, dd, *J* = 11.8, 9.8 Hz, H-7), 2.83 (1H, d, *J* = 18.4 Hz, H-2), 3.46 (1H, br m, *J* = 18.4 Hz, H-2), 4.94 (1H, dd, *J* = 8.1, 2.4 Hz, H-4). ^{13}C NMR δ -3.5 and -3.9 ($SiMe_2$), -0.7 ($SiMe_3$), 14.8 (C-5'), 18.7 (*C*Me_3), 23.4, 27.5, 32.5, 34.7 (C-1', C-2', C-3', and C-4'), 26.4 (*t*-Bu), 29.8 (C-5), 41.5 (C-6), 48.1 (C-7), 51.7 (C-2), 107.1 (C-4), 149.3 (C-3), 211.4 (C-1). HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, found 382.2730.

15d (R = Me, Me): a colorless oil, R_f = 0.47 (hexane:AcOEt = 15:1). IR (film) 1710, 1645, 1250 cm^{-1}. ^{1}H NMR δ0.07 (9H, s, $SiMe_3$), 0.14 and 0.17 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 1.00-1.09 (each 3H, s, Me_2), 1.32 (1H, d, *J* = 8.5 Hz, H-5), 1.85 (1H, d, *J* = 10.5 Hz, H-7), 2.79 (1H, d, *J* = 19.9 Hz, H-2), 2.98 (1H, d, *J* =

10.5 Hz, H-7), 3.28 (1H, dm, J = 19.9 Hz, H-2), 5.00 (1H, dd, J = 8.5, 2.4 Hz, H-4). ^{13}C NMR δ -4.1 and -4.4 ($SiMe_2$), 0.3 ($SiMe_3$), 18.1 (CMe_3), 25.8 (*t*-Bu), 27.6, 29.4 (Me), 35.1 (C-5), 42.9 (C-6), 56.6 (C-7), 50.1 (C-2), 107.3 (C-4), 150.8 (C-3), 209.9 (C-1). HRMS calcd for $C_{18}H_{36}O_2Si_2$ 340.2254, found 340.2251.

15e (R = $(CH_2)_3$): a colorless oil, R_f = 0.54 (hexane:AcOEt = 10:1). IR (film) 1710, 1645, 1250 cm^{-1}. ^{1}H NMR δ -0.01 (9H, s, $SiMe_3$), 0.13 and 0.15 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 1.39-1.49 (1H, m, H-2'), 1.54-1.64 (1H, m, H-1'), 1.69 (1H, ddd, J = 12.4, 7.9, 6.2 Hz, H-1'), 1.72-1.79 (1H, m, H-3'), 1.82-1.90 (1H, m, H-2'), 1.84 (1H, dm, J = 6.4 Hz, H-5), 1.97 (1H, dddd, J = 12.0, 12.0, 10.0, 6.6 Hz, H-3'), 2.67 (1H, dddd, J = 10.0, 10.0, 7.9, 2.4 Hz, H-6), 2.86 (1H, ddd, J = 10.0, 10.0, 10.0 Hz, H-7), 3.05 (1H, d, J = 17.1 Hz, H-2), 3.40 (1H, d, J = 17.1 Hz, H-2), 4.81 (1H, dd, J = 6.4, 1.9 Hz, H-4). ^{13}C NMR δ -4.4 and -4.2 ($SiMe_2$), -2.2 ($SiMe_3$), 18.2 (CMe_3), 24.9 (C-5), 25.8 (*t*-Bu), 27.0 (C2'), 28.6 (C-1'), 30.0 (C-3'), 46.2 (C-6), 49.3 (C-2), 60.0 (C-7), 106.5 (C-4), 149.2 (C-3), 211.2 (C-1). HRMS calcd for $C_{19}H_{36}O_2Si_2$ 352.2253, found 352.2261.

15f (R = $(CH_2)_4$): a colorless prisms, mp 74 °C (hexane-Et_2O). R_f = 0.47 (hexane:AcOEt = 15:1). IR (KBr) 1705, 1645, 1250 cm^{-1}. ^{1}H NMR (C_6D_6) δ 0.08 (9H, s, $SiMe_3$), 0.21 and 0.26 (each 3H, s, $SiMe_2$), 1.00 (9H, s, *t*-Bu), 1.06 (1H, dddd, J = 13.5, 13.0, 4.3, 4.3 Hz, H-4'), 1.14-1.24 (1H, m, H-2'), 1.40-1.49 (1H, m, H-1'), 1.54 (1H, br d, J = 13.5, 2.05 Hz, H-3'), 1.71 (1H, br d, H-2'), 1.79 (1H, d, J = 7.1 Hz, H-5), 2.04-2.16 (2H, m, H-3' and H-6), 2.13 (1H, br ddd, J = 11.5, 3.9, 3.9 Hz, H-6), 2.27 (1H, br d, J = 13.0 Hz, H-4'), 2.38 (1H, br dd, J = 3.9, 3.9 Hz, H-7), 2.85 (1H, dd, J = 12.2, 1.9 Hz, H-2), 3.67 (1H, dd, J = 12.2, 1.9 Hz, H-2), 5.00 (1H, ddd, J = 7.1, 1.9, 1.9 Hz, H-4). ^{13}C NMR (C_6D_6) δ -4.3 and -4.2 ($SiMe_2$), -1.8 ($SiMe_3$), 18.2 (CMe_3), 22.2 (C-3'), 25.8 (*t*-Bu), 26.9 (C-1'), 27.6 (C-2'), 28.8 (C-4'), 31.3 (C-5), 46.3 (C-6), 51.3 (C-2), 57.7 (C-7), 106.0 (C-4), 149.9 (C-3), 203.3 (C-1). Anal Calcd for $C_{20}H_{38}O_2Si_2$: C, 65.51; H, 10.45. Found: C, 65.26; H, 10.56.

17: a colorless oil, R_f = 0.63 (hexane:AcOEt = 5:1). IR (KBr) 1680, 1600, 1250 cm^{-1}. ^{1}H NMR δ 0.01 (9H, s, $SiMe_3$), 0.14 and 0.16 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 3.05 (1H, d, J = 9.0 Hz, H-5), 3.37 (1H, d, J = 17.3 Hz, H-2), 3.67 (1H, dm, J = 17.3 Hz, H-2), 5.33 (1H, dd, J = 9.0, 1.1 Hz, H-4), 7.00 (1H, dd, J = 7.7, 0.4 Hz, H-1'), 7.19 (1H, ddm, J = 7.7, 7.7 Hz, H-3'), 7.33 (1H, ddd, J = 7.7, 7.7, 1.5 Hz, H-2'), 7.70 (1H, dd, J = 7.7, 1.3 Hz, H-4'). ^{13}C NMR δ -3.8 and -3.7 ($SiMe_2$), -0.5 ($SiMe_3$), 18.6 (CMe_3), 26.3 (*t*-Bu), 38.2 (C-5), 51.4 (C-2), 108.5 (C-4), 125.7 (C-3'), 130.5 (C-1'), 130.6 (C-4'), 132.1 (C-2'), 138.2 (C-6), 143.8 (C-7), 144.4 (C-3), 198.2 (C-1). HRMS calcd for $C_{20}H_{32}O_2Si_2$ 360.1941, found 360.1936.

20: pale yellow oil, R_f = 0.19 (hexane:AcOEt = 5:1). IR (film) 1640, 1550 cm^{-1}. ^{1}H NMR δ 0.10 (9H, s, $SiMe_3$), 0.13 and 0.14 (each 6H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 3.03 (1H, d, J = 9.4 Hz, H-5), 3.11 (1H, dd, J = 18.4, 1.9 Hz, H-2), 3.48 (3H, s, NMe), 3.73 (1H, ddd, J = 18.4, 1.9 Hz, H-4), 5.29 (1H, ddd, J = 9.4, 1.9, 1.9 Hz, H-4), 6.43 (1H, d, J = 3.2 Hz, H-2'), 6.62 (1H, d, J = 3.2 Hz, H-3'). ^{13}C NMR δ -4.3 and -4.2 ($SiMe_2$), -0.4 ($SiMe_3$), 18.1 (CMe_3), 25.8 (*t*-Bu), 27.4 (C-5), 34.4 (NMe), 49.9 (C-2), 105.4 (C-4), 108.8 (C-3), 122.0 (C-2), 142.1 and 146.8 (C-6 and C-7), 189.7 (C-1).

21: pale yellow oil, R_f = 0.59 (hexane:AcOEt = 5:1). IR (film) 1655, 1250 cm^{-1}. ^{1}H NMR δ 0.13 and 0.14 (each 3H, s, $SiMe_2$), 0.16 (9H, s, $SiMe_3$), 0.92 (9H, s, *t*-Bu), 3.12 (1H, dd, J = 16.0, 1.9 Hz, H-2), 3.34 (1H, d, J = 9.0 Hz, H-5), 3.81 (1H, dd, J = 16.0, 1.9 Hz, H-2), 5.38 (1H, ddd, J = 9.0, 1.9, 1.9 Hz, H-4), 6.87 (1H, dd, J = 5.6, 0.4 Hz, H-2'), 7.41 (1H, d, J = 5.6 Hz, H-3'). ^{13}C NMR δ -4.3 ($SiMe_2$), -0.6 ($SiMe_3$), 18.1 (CMe_3), 25.8 (*t*-Bu), 33.1 (C-5), 50.3 (C-2), 107.9 (C-4), 119.7 (C-2'), 129.1 (C-3'), 136.9 and 145.2 (C-6 and C-7), 188.2 (C-1).

22a (R = $(CH_2)_2CH_3$): a colorless oil, R_f = 0.50 (hexane:AcOEt = 10:1). IR (film) 1710, 1655, 1250 cm^{-1}. ^{1}H NMR δ 0.05 (9H, s, $SiMe_3$), 0.11 and 0.11 (each 3H, s, $SiMe_2$), 0.87 (2H, br t, H-3'), 0.89 (3H, s, *t*-Bu), 1.21-1.42 (4H, m, H-1' and H-2'), 1.47 (1H, dd, J = 7.9, 7.9 Hz, H-5), 1.94-2.02 (1H, br m, H-6), 2.58 (2H, d, J = 5.8 Hz, H-7), 2.96 (1H, d, J = 17.9 Hz, H-2), 3.31 (1H, ddd, J = 17.9, 1.3, 1.3 Hz, H-2), 5.00 (1H, dd, J = 7.9, 1.3 Hz, H-4). ^{13}C NMR δ -4.3 and -4.2 ($SiMe_2$), -1.5 ($SiMe_3$), 14.3 (C-3'), 18.0 (CMe_3), 20.4, 39.2 (C-1' and

C-2'), 25.8 (*t*-Bu), 31.4 (C-5), 36.0 (C-6), 47.0 (C-7), 50.4 (C-2), 109.0 (C-4), 143.8 (C-3), 209.2 (C-1). HRMS calcd for $C_{19}H_{38}O_2Si_2$ 324.2485, found 324.2498.

22b (R = $CHMe_2$): a colorless oil, R_f = 0.38 (hexane:AcOEt = 16:1). IR (film) 1710, 1655, 1250 cm^{-1}. ^1H NMR δ 0.01 (9H, s, $SiMe_3$), 0.10 and 0.12 (each 3H, s, $SiMe_2$), 0.89 (each 3H, s, *t*-Bu), 0.80, 0.90 (each 3H, d, J = 6.8 Hz, $CHMe_2$), 1.52 (1H, dd, J = 8.3, 6.4 Hz, H-5), 1.82-1.88 (1H, m, $CHMe_2$), 2.24 (1H, dd, J = 12.4, 3.0 Hz, H-7), 2.74 (1H, dd, J = 12.4, 10.9 Hz, H-7), 2.91 (1H, d, J = 18.6 Hz, H-2), 3.31 (1H, br d, J = 18.8 Hz, H-2), 5.09 (1H, dd, J = 8.3, 1.9 Hz, H-4). ^{13}C NMR δ -4.3 and -4.1 ($SiMe_2$), -1.7 ($SiMe_3$), 18.0 (CMe_3), 16.8, 21.2 ($CHMe_2$), 25.8 (*t*-Bu), 29.5 (C-5), 42.3 (C-7), 42.7 (C-6), 50.5 (C-2), 109.6 (C-4), 143.3 (C-3), 210.5 (C-1). HRMS calcd for $C_{19}H_{38}O_2Si_2$ 354.2410, found 354.2392.

22c R = $(CH_2)_4CH_3$: a colorless oil, R_f = 0.42 (hexane:AcOEt = 15:1). IR (film) 1710, 1655, 1250 cm^{-1}. ^1H NMR δ 0.06 (9H, s, $SiMe_3$), 0.12 and 0.12 (each 3H, s, $SiMe_2$), 0.87 (3H, t, 7.3, H-5'), 0.90 (9H, s, *t*-Bu), 1.19-1.44 (8H, m, H1', H-2', H-3', and H-4'), 1.47 (1H, dd, J = 7.9, 7.9 Hz, H-5), 1.93-2.00 (2H, m, H-6), 2.57-2.63 (2H, m, H-7), 2.97 (1H, d, J = 17.7 Hz, H-2), 3.32 (1H, dm, J = 17.7 Hz, H-2), 5.01 (1H, dd, J = 7.9, 1.3 Hz, H-4). ^{13}C NMR δ -4.3 and -4.2 ($SiMe_2$), -1.4 ($SiMe_3$), 18.1 (CMe_3), 22.8, 27.0, 32.1, 37.0 (C-1', C-2', C-3', and C-4'), 14.2 (C-5'), 25.8 (*t*-Bu), 31.5 (C-5), 36.3 (C-6), 47.0 (C-7), 50.4 (C-2), 109.1 (C-4), 143.8 (C-3), 209.3 (C-1). HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, found 382.2740.

22e: a colorless oil, R_f = 0.25 (hexane:AcOEt = 10:1). IR (film) 1710, 1650, 1250 cm^{-1}. ^1H NMR δ 0.01 (9H, s, $SiMe_3$), 0.12, 0.16 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 1.08 (1H, dddd, J = 12.4, 12.4, 12.4, 7.7 Hz, H-1'), 1.25 (1H, dd, J = 12.4, 7.7 Hz, H-5), 1.42-1.55 (2H, m, H-2' and H-3'), 1.82-1.90 (1H, br dd, H-2'), 2.12 (ddd, J = 17.3, 8.6, 4.3 Hz, H-3'), 2.47 (1H, dddd, J = 12.4, 12.4, 9.6, 6.0, H-6), 2.87 (1H, d, J = 19.2 Hz, H-2), 3.33 (1H, dm, J = 19.2 Hz, H-2), 3.44 (1H, ddd, J = 9.6, 8.6, 3.6 Hz, H-7), 5.00 (1H, dd, J = 7.7, 2.4 Hz, H-4). ^{13}C NMR δ -4.4 and -4.0 ($SiMe_2$), -1.8 ($SiMe_3$), 18.2 (CMe_3), 24.0 (C-3'), 25.8 (*t*-Bu), 26.1 (C-2'), 26.9 (C-5), 32.2 (C-1'), 51.0 (C-2), 52.0 (C-6), 53.0 (C-7), 109.5 (C-4), 149.4 (C-3), 212.7 (C-1). HRMS calcd for $C_{19}H_{36}O_2Si_2$ 352.2253, found 352.2243

22f: a colorless oil, R_f = 0.44 (hexane:AcOEt = 15:1). IR (film) 1705, 1645, 1250 cm^{-1}. ^1H NMR δ0.05 (9H, s, $SiMe_3$), 0.11, 0.13 (each 3H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 1.15-1.29 (2H, m, H-1' and H-3'), 1.30-1.40 (1H, m, H-4'), 1.43 (1H, br ddd, J = 12.8, 3.9, 3.9 Hz, H-2'), 1.57-1.63 (1H, m, H-1'), 1.63-1.70 (1H, m, H-3'), 1.70-1.78 (1H, m, H-2'), 1.90-1.96 (1H, m, H-4'), 1.99-2.06 (1H, m, H-6), 2.97 (1H, d, J = 17.9 Hz, H-2), 3.05-3.10 (1H, br m, H-7), 3.20 (1H, d, J = 17.9 Hz, H-2), 4.88 (1H, dd, J = 7.5, 1.3 Hz, H-4). ^{13}C NMR δ -4.4 and -4.1 ($SiMe_2$), -1.3 ($SiMe_3$), 18.1 (CMe_3), 22.8 (C-2'), 25.6 (C-3'), 25.8 (*t*-Bu), 25.9 (C-4'), 27.4 (C-5), 29.6 (C-1'), 40.5 (C-6), 49.2 (C-7), 50.6 (C-2), 107.3 (C-4), 148.7 (C-3), 211.7 (C-1). HRMS calcd for $C_{20}H_{38}O_2Si_2$ 366.2410, Found 366.2416.

23b: a pale yellow oil, R_f = 0.43 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^1H NMR δ 0.11 and 0.12 (each 3H, s, $SiMe_2$), 0.89 (9H, s, *t*-Bu), 0.80-0.95 (18H, m, Me_2 and SnBu), 1.26-1.37 (7H, m, SnBu), 1.38-1.52 (6H, m, SnBu), 1.59-1.66 (1H, m, $CHMe_2$), 2.16 (1H, dd, J = 14.3, 14,3 Hz, H-7), 2.22-2.26 (1H, m, H-6), 2.48 (1H, br d, J = 7.7 Hz, H-5), 2.67 (1H, ddd, J = 14.3, 2.6, 2.6 Hz, H-7), 2.79 (1H, d, J = 15.6 Hz, H-2), 3.76 (1H, ddd, J = 15.6, 2.2, 2.2 Hz, H-2), 5.12 (1H, dd, J = 7.7, 2.6 Hz, H-4). ^{13}C NMR δ -4.2 and -4.3 ($SiMe_2$), 10.6 (SnBu), 13.8 (SnBu), 18.0 (CMe_3), 20.8 and 22.0 (Me_2), 25.8 (*t*-Bu), 27.7 (SnBu), 29.4 (SnBu), 31.4 (C-5), 33.2 ($CHMe_2$), 49.4 (C-2), 49.5 (C-7), 113.3 (C-4), 141.0 (C-3), 207.8 (C-1). HRMS calcd for $C_{28}H_{56}O_2SiSn$ 572.3072, found 572.3097.

23c: a pale yellow oil, R_f = 0.47 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^1H NMR δ 0.10 and 0.12 (each 3H, s, $SiMe_2$), 0.89 (9H, s, *t*-Bu), 0.72-0.95 (18H, m, CH_3 and SnBu), 1.17-1.33 (14H, m, $(CH_2)_4$ and SnBu), 1.35-1.50 (6H, m, SnBu), 2.17 (1H, dd, J = 14.8, 10.5 Hz, H-7), 2.31 (1H, br dm, J = 7.5 Hz, H-5), 2.49-2.55 (1H, m, H-6), 2.56 (1H, dm, J = 14.8 Hz, H-7), 2.82 (1H, d, J = 15.8 Hz, H-2), 3.73 (1H, ddd, J = 15.8, 2.1, 2.1

Hz, H-2), 5.10 (1H, dd, *J* = 7.5, 2.1 Hz, H-4). ^{13}C NMR δ -4.3 and -4.3 ($SiMe_2$), 10.5 (SnBu), 13.8 (SnBu), 14.2 (Me), 18.0 (CMe_3), 22.8, 27.3, 32.8, and 37.3 (C-1', C-2', C-3' and C-4'), 25.8 (*t*-Bu), 27.7 (SnBu), 29.4 (SnBu), 32.0 (C-5), 38.7 (C-6), 49.9 (C-2), 51.4 (C-7), 112.7 (C-4), 141.5 (C-3), 207.6 (C-1). HRMS calcd for $C_{30}H_{60}O_2SiSn$ 600.3385, found 600.3351.

23d: a colorless oil, R_f = 0.41 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.13 and 0.15 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 0.80-0.95 (15H, m, SnBu), 0.99 and 1.03 (each 3H, s, Me), 1.27-1.35 (6H, m, SnBu), 1.37-1.52 (6H, m, SnBu), 1.88 (d, *J* = 8.5 Hz, H-5), 2.04 (1H, dd, *J* = 10.8, H-7), 2.88 (1H, d, *J* = 10.8 Hz, H-7), 2.93 (1H, d, *J* = 18.8 Hz, H-2), 3.20 (1H, ddd, *J* = 18.8 Hz, H-2), 5.13 (1H, dd, *J* = 8.5, 1.3 Hz, H-4). ^{13}C NMR δ -4.5 and -4.1 ($SiMe_2$), 10.8 (SnBu), 13.8 (SnBu), 18.1 (CMe_3), 25.8 (*t*-Bu), 27.7 (SnBu), 29.4 (SnBu), 29.7 and 30.5 (Me_2), 36.7 (C-5), 42.4 (C-6), 50.5 (C-2), 56.1 (C-7), 109.7 (C-4), 148.7 (C-3), 208.9 (C-1). HRMS calcd for $C_{27}H_{54}O_2SiSn$ 558.2915, found 558.2939.

23e: a pale yellow oil, R_f = 0.52 (hexane : Et_2O = 10 : 1). IR (film) 1700 cm^{-1}. ^{1}H NMR δ 0.11 and 0.13 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 0.75-0.92 (15H, m, SnBu), 1.26-1.35 (6H, m, SnBu), 1.37-1.50 (7H, m, H-1' and SnBu), 1.54-1.62 (1H, m, H-2'), 1.66-1.72 (1H, m, H-2'), 1.72-1.79 (1H, m, H-3'), 1.82-1.90 (1H, m, H-1'), 1.99-2.07 (1H, m, H-3'), 2.33 (dd, *J* = 6.7, 3.2 Hz, H-5), 2.78 (1H, dddd, *J* = 10.0, 10.0, 7.7, 3.2 Hz, H-6), 2.90 (1H, ddd, *J* = 10.0, 10,0, 10.0 Hz, H-7), 3.03 (1H, d, *J* = 17.0 Hz, H-2), 3.38 (1H, ddd, *J* = 17.0 Hz, H-2), 5.04 (1H, dd, *J* = 6.7, 1.6 Hz, H-4). ^{13}C NMR δ -4.4 and -4.3 ($SiMe_2$), 9.6 (SnBu), 13.8 (SnBu), 18.1 (CMe_3), 23.7 (C-5), 25.8 (*t*-Bu), 26.4 (C-1'), 27.7 (SnBu), 29.4 (SnBu), 29.4 (C-3'), 31.1 (C-2'), 48.8 (C-6), 49.5 (C-2), 59.5 (C-7), 110.1 (C-4), 148.0 (C-3), 210.3 (C-1). HRMS calcd for $C_{28}H_{54}O_2SiSn$ 570.2915, found 570.2916.

23f: a colorless oil, R_f = 0.50 (hexane : Et_2O = 10 : 1). IR (film) 1705 cm^{-1}. ^{1}H NMR δ 0.11 and 0.13 (each 3H, s, $SiMe_2$), 0.80-0.95 (15H, m, SnBu), 0.90 (9H, s, *t*-Bu), 1.24-1.40 (8H, m, H-1' and SnBu), 1.40-1.56 (7H, m, H-2' and SnBu), 1.57-1.68 (1H, m), 1.73 (1H, br d, *J* = 10.9 Hz, H-3'), 2.07 (1H, br d, *J* = 15.0 Hz, H-4'), 2.18 (1H, br d, *J* = 12.4 Hz, H-6), 2.45 (1H, dd, *J* = 6.4, 1.6 Hz, H-5), 2.73 (1H, dd, *J* = 12.5, 0.9 Hz, H-2), 2.82-2.86 (1H, br m, H-7), 3.91 (1H, dd, *J* = 12.5, 1.8 Hz, H-2), 4.95 (1H, ddd, *J* = 6.4, 1.5, 1.5 Hz, H-4). ^{13}C NMR δ -4.3 ($SiMe_2$), 9.3 (SnBu), 13.9 (SnBu), 18.1 (CMe_3), 22.0 (C-2'), 25.8 (*t*-Bu), 26.8 (C-3'), 27.7 (SnBu), 29.1 (C-1'), 29.2 (C-5), 29.4 (SnBu), 48.2 (C-6), 51.3 (C-2), 58.0 (C-7), 109.7 (C-4), 148.1 (C-3), 205.8 (C-1). HRMS calcd for $C_{29}H_{56}O_2SiSn$ 584.3072, found 584.3111.

23g: a colorless oil, R_f = 0.36 (hexane : Et_2O = 10 : 1). IR (film) 1665 cm^{-1}. ^{1}H NMR δ 0.10 (6H, s, $SiMe_2$), 0.90 (9H, s, *t* -Bu), 3.52 (2H, d, *J* = 6.8 Hz, H-7), 3.68 (2H, s, H-4), 5.38 (1H, t, *J* = 6.8 Hz, H-6), 7.16 (1H, d, *J* = 7.5 Hz, H-6'), 7.31 (1H, ddm, *J* = 7.5, 7.5 Hz, H-4'), 7.40 (1H, ddd, *J* = 7.5, 7.5, 1.5 Hz, H-5'), 8.08 (1H, dd, *J* = 7.5, 1.5 Hz, H-3'). ^{13}C NMR δ -4.7 ($SiMe_2$), 17.9 (*C*Me_3), 25.5 (*t*-Bu), 33.1 (C-7), 50.8 (C-4), 106.5 (C-6), 126.6 (C-4'), 129.4 (C-6'), 130.2 (C-3'), 132.5 (C-5'), 135.1 (C-1), 144.2 (C-2), 149.5 (C-6), 192.8 (C-3). HRMS calcd for $C_{17}H_{24}O_2Si$ 288.1546, found 288.1539.

24b: a colorless oil, R_f = 0.53 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.09, 0.10 (each 3H, s, SiMe2), 0.79 (3H, d, *J* = 6.6 Hz, Me), 0.82-1.00 (18H, SnBu and Me), 0.89 (9H, s, *t*-Bu), 1.25-1.37 (6H, m, SnBu), 1.40-1.54 (6H, m, SnBu), 1.60-1.67 (1H, m, C*H*Me_2), 2.02 (1H, ddd, *J* = 10.5, 10.5, 2.1 Hz, H-6), 2.19 (1H, ddd, *J* = 7.1, 7.1, 1.5 Hz, H-5), 2.37 (1H, dd, *J* =15.2, 2.1 Hz, H-7), 2.57 (1H, dd, *J* = 15.2, 10.5 Hz, H-7), 2.82 (1H, d, *J* = 17.1 Hz, H-2), 3.65 (1H, ddd, *J* = 17.1, 1.8, 1.8 Hz, H-2), 5.12 (1H, dm, *J* = 7.1 Hz, H-4). ^{13}C NMR δ -4.3, -4.3 ($SiMe_2$), 10.0, 13.9, 27.7, 29.4 (SnBu), 16.5 (Me), 21.9 (Me), 18.0 (CMe_3), 25.8 (*t*-Bu), 30.4 (C-5), 32.5 ($CHMe_2$), 43.0 (C-6), 44.0 (C-7), 49.7 (C-2), 112.4 (C-4), 139.8 (C-3), 209.7 (C-1). HRMS calcd for $C_{28}H_{56}O_2SiSn$ 572.3072, found 572.3064.

24c: a colorless oil, R_f = 0.47 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.10, 0.10 (each 3H, s, $SiMe_2$), 0.85-0.95 (18H, SnBu and 5'-CH_3), 0.90 (9H, s, *t*-Bu), 1.18-1.40 (14H, m, SnBu and H-2', H-3', and

H-4'), 1.44-1.53 (6H, m, SnBu), 2.03 (1H, ddm, J = 6.8, 6.8 Hz, H-5), 2.07-2.15 (1H, m, H-6), 2.53 (1H, dd, J =15.4, 8.8 Hz, H-7), 2.60 (1H, dd, J = 15.4, 3.0 Hz, H-7), 2.85 (1H, d, J = 16.7 Hz, H-2), 3.62 (1H, dm, J = 16.7 Hz, H-2), 5.08 (1H, dm, J = 6.8 Hz, H-4). ^{13}C NMR δ -4.3 ($SiMe_2$), 10.0, 13.9, 27.8, 29.5 (SnBu), 14.2 (C-5'), 18.0 (CMe_3), 22.8, 27.0, 32.2, 36.8 (C1', C-2', C3', and C-4'), 25.8 (*t*-Bu), 32.0 (C-5), 37.7 (C-6), 48.6 (C-7), 49.9 (C-2), 112.0 (C-4), 140.3 (C-3), 208.7 (C-1). HRMS calcd for $C_{30}H_{60}O_2SiSn$ 600.3385, found 600.3428.

24e: a colorless oil, R_f = 0.47 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.12 and 0.16 (each 3H, s, $SiMe_2$), 0.75-1.0 (15H, m, SnBu), 1.13 (1H, dddd, J = 11.9, 11.9, 11.9, 7.9 Hz, H-1'), 1.25-1.35 (6H, m, SnBu), 1.53-1.62 (3H, m, H-1' and H-2'), 1.71 (1H, dd, J = 13.0, 7.7 Hz, H-5), 1.79-1.87 (1H, m, H-3'), 2.17 (1H, dddd, J = 13.2, 13.2, 9.6, 4.5 Hz, H-3'), 2.68 (1H, dddd, J =13.0, 9.6, 6.0 Hz, H-6), 2.86 (1H, d, J = 18.8 Hz, H-2), 3.43 (1H, ddd, J = 9.6, 9.6, 4.5 Hz, H-7), 5.18 (1H, dd, J = 7.7, 2.1 Hz, H-4). ^{13}C NMR δ -4.5 and -4.0 ($SiMe_2$), 9.4, 13.9, 27.7, 29.4 (SnBu), 18.2 (CMe_3), 24.4 (C-5), 24.9 (C-3'), 25.5 (C-2'), 25.8 (*t*-Bu), 33.4 (C-1'), 51.0 (C-2), 53.6 (C-7), 53.7 (C-6), 111.4 (C-4), 149.1 (C-3), 211.9 (C-1). HRMS calcd for $C_{28}H_{54}O_2SiSn$ 570.2915, found 570.2938.

24e' (C-7 epimaer of **24e**): a colorless oil, R_f = 0.40 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.09, 0.11 (each 3H, s, $SiMe_2$), 0.85-0.96 (15H, m, SnBu), 0.90 (9H, s, *t*-Bu), 1.15-1.23 (1H, m, H-3'), 1.27-1.36 (6H, m, SnBu), 1.40-1.56 (7H, m, SnBu and H-2'), 1.64-1.72 (1H, m, H-2'), 1.70-1.79 (1H, m, H-1'), 1.90-1.97 (1H, m, H-3'), 2.04-2.12 (2H, m, H-5 and H-1'), 2.12-2.22 (1H, m, H-7), 2.87 (1H, d, J =19.0 Hz, H-2), 2.93 (1H, ddd, J = 9.6, 9.6, 6.2 Hz, H-6), 3.67 (1H, dm, J = 19.0, H-2), 5.13-5.19 (1H, m, H-4). ^{13}C NMR δ -4.4 and -4.1 ($SiMe_2$), 9.7, 13.9, 27.7, 29.5 (SnBu), 18.0 (CMe_3), 25.6 (C-2'), 25.8 (*t*-Bu), 26.2 (C-1'), 33.2 (C-5), 36.4 (C-3'), 45.1 (C-7), 48.5 (C-2), 59.1 (C-6), 113.7 (C-4), 139.7 (C-3), 209.9 (C-1). HRMS calcd for $C_{28}H_{54}O_2SiSn$ 570.2915, found 570.2952.

24f: a colorless oil, R_f = 0.49 (hexane : Et_2O = 10 : 1). IR (film) 1705 cm^{-1}. ^{1}H NMR δ 0.11 and 0.12 (each 3H, s, $SiMe_2$), 0.82-0.95 (15H, m, SnBu), 1.25-1.52 (16H, m, SnBu), 1.72-1.80 (2H, m), 2.10 (1H, dd, J = 10.9, 7.3 Hz, H-5), 2.28-2.36 (1H, m, H-6), 2.82-2.87 (1H, m, H-7), 2.98 (1H, d, J = 16.0 Hz, H-2), 3.39 (1H, d, J = 16.0 Hz, H-2), 5.05 (1H, d, J = 7.3 Hz, H-4). ^{13}C NMR δ -4.4 and -4.2 ($SiMe_2$), 9.9, 13.9, 27.7, 29.4 (SnBu), 18.1 (CMe_3), 24.0, 24.1, 26.2, 32.3 (C-1', C-2', C-3', and C-4'), 28.2 (C-5), 41.0 (C-6), 50.0 (C-2), 52.1 (C-7), 110.5 (C-4), 149.7 (C-3), 209.5 (C-3). HRMS calcd for $C_{29}H_{56}O_2SiSn$ 584.3072, found 584.2996.

General Procedure for Transformation of Cycloheptenones 15 into Cycloheptenediones 25. To a cooled (ice-water) solution of **15c** (100 mg, 260 μmol) in THF (2.6 mL) was added NBS (50 mg, 270 μmol), and then the reaction mixture was stirred at room temperature for 10 min. The mixture was cooled in ice-water bath again before addition of TBAF (1.0 M in THF, 0.26 mL, 260 μmol). After stirring at the same temperature for 10 min, the mixture was allowed to warm to room temperature, and then diluted with Et_2O (20 mL) and water (30 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (20 mL x 2). The combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residue was subjected to column chromatography (silica gel, 3.3 g; elution with 1:2 hexane-Et_2O) to give **25c** (45 mg, 89%).

25b: a pale yellow oil, R_f = 0.43 (hexane : AcOEt = 1 : 1). IR (film) 1715, 1670 cm^{-1}. ^{1}H NMR δ 0.97 (3H, d, J = 6.8 Hz, Me), 0.98 (3H, d, J = 6.8 Hz, Me), 1.83-1.93 (1H, m, C*H*Me_2), 2.46 (1H, dd, J = 16.9, 14.2 Hz, H-7), 2.61 (1H, dd, J = 16.9, 3.4 Hz, H-7), 2.86-2.92 (1H, m, H-6), 3.54 (1H, dm, J = 14.6 Hz, H-2), 4.10 (1H, d, J = 14.6, Hz, H-2), 6.09 (1H, ddd, J = 12.2, 2.6, 1.7 Hz, H-4), 6.70 (1H, ddd, J = 12.2, 4.3, 1.3 Hz, H-5). ^{13}C NMR δ 19.2 and 19.4 (Me), 32.4 (*C*HMe_2), 41.5 (C-6), 44.4 (C-7), 61.2 (C-2), 132.4 (C-4), 151.3 (C-5), 192.4 (C-3), 203.6 (C-1). HRMS calcd for $C_{10}H_{14}O_2$ 166.0994, found 166.0961.

25c: a pale yellow oil, R_f = 0.55 (hexane : AcOEt = 1 : 1). IR (film) 1715, 1670 cm^{-1}. ^{1}H NMR δ 0.89 (3H, t, J = 7.0 Hz, Me), 1.28-1.44 (6H, m, H-2', H-3' and H-4'), 2.47 (1H, dd, J = 17.1, 14.1 Hz, H-7), 2.69 (1H, dd, J = 17.1, 3.4 Hz, H-7), 2.96-3.05 (1H, m, H-6), 3.58 (1H, dm, J = 14.3 Hz, H-2), 4.10 (1H, d, J = 14.3, Hz, H-2),

6.07 (1H, dm, J = 12.0 Hz, H-4), 6.66 (1H, ddm, J = 12.0, 4.3 Hz, H-5). ^{13}C NMR δ 14.1 (Me), 18.0 (CMe_3), 22.7, 26.6, 31.7 (C-2', C-3' and C-4'), 35.5 (C-1'), 35.7 (C-6), 47.1 (C-7), 61.4 (C-2), 131.9 (C-4), 152.8 (C-5), 192.3 (C-3), 203.3 (C-1). HRMS calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1267.

25d: a colorless plates, mp 88 °C (CH_2Cl_2-hexane). R_f = 0.61 (AcOEt). IR (film) 1650, 1615 cm^{-1}. ^{1}H NMR δ 1.21 (6H, s, Me), 2.71 (2H, s, H-7), 3.64 (2H, s, H-2), 5.96 (1H, dm, J = 12.4, H-4), 6.33 (1H, dm, J = 12.4 Hz, H-5). ^{13}C NMR δ 29.3 (Me_2), 36.9 (C-6), 55.3 (C-7), 60.4 (C-2), 128.0 (C-4), 153.7 (C-5), 195.4 (C-3), 203.2 (C-1). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.78; H, 7.96.

General Procedure for Transformation of Cycloheptenones 23 into Cycloheptenediones 25. To a cooled (ice-water) solution of **23c** (54 mg, 90 μmol) in CH_2Cl_2 (0.45 mL) was added mCPBA (80%, 20 mg, 90 μmol), and then the solution was stirred at the same temperature for 15 min. The reaction mixture was concentrated, the residue was subjected to column chromatography (silica gel, 4 g, elution with 1:1 hexane-Et_2O) to give **25c** (16 mg, 89%).

26d: a colorless oil, R_f = 0.29 (hexane : Et_2O = 5 : 1). IR (film) 1720, 1655 cm^{-1}. ^{1}H NMR δ0.89 (9H, t, J = 7.3 Hz, SnBu), 0.91-1.05 (6H, m, SnBu), 1.16 (6H, s, Me), 1.27-1.35 (6H, m, SnBu), 1.42-1.52 (6H, m, SnBu), 2.65 (2H, s, H-7), 3.54 (2H, s, H-2), 6.09 (1H, s, H-4). ^{13}C NMR δ 10.8, 13.9, 27.4, 29.1 (SnBu), 29.4 (Me), 40.6 (C-6), 55.1 (C-7), 60.4 (C-2), 144.5 (C-5), 157.1 (C-4), 201.6 (C-3), 204.3 (C-1). HRMS calcd for $C_{21}H_{38}O_2Sn$ 442.1894, found 442.1876.

26f: a colorless oil, R_f = 0.54 (hexane : Et_2O = 1 : 1). IR (film) 1710, 1655 cm^{-1}. ^{1}H NMR δ0.92-1.02 (15H, m, SnBu), 1.24-1.42 (8H, m, H-10 and SnBu), 1.42-1.55 (7H, m, H-9 and SnBu), 1.60-1.74 (2H, m, H-8 and H-9), 1.78-1.87 (2H, m, H-8 and H-11), 1.91 (1H, m, H-11), 2.53-2.58 (1H, m, H-1), 3.36-3.42 (1H, m, H-7), 3.53 (1H, d, J = 14.1 Hz, H-3), 4.08 (1H, d, J = 14.1 Hz, H-3), 6.60 (1H, d, J = 4.9 Hz, H-5). ^{13}C NMR δ 10.5, 13.9, 27.4, 29.2 (SnBu), 22.3 (C-9), 25.0 (C-11), 25.3 (C-10), 31.0 (C-8), 39.0 (C-7), 52.1 (C-1), 60.2 (C-3), 149.9 (C-6), 158.1 (C-5), 196.7 (C-4), 205.6 (C-2). HRMS calcd for $C_{23}H_{40}O_2Sn$ 468.2050, found 468.2071.

1-(*t*-Butyldimethylsilyl)-3-(dimethyl(phenyl)silyl)-2-propen-1-ones. To a cooled (-80 °C) solution of **10** (98.6 g, 0.769 mol) and 4,4'-thiobis(2-*t*-butyl-*m*-cresol) (200 mg) in THF (85 mL) was added dropwise *n*-BuLi (1.41 M in hexane, 30.0 mL, 43.3 mmol) over 5 min. The mixture was stirred at -80 °C for 30 min, and dimethyl(phenyl)silylchloride (7.50 mL, 45.3 mmol) was added over 10 min. After stirring at the same temperature 10 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature whereupon triethylamine (4.1 mL) was added. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (100 mL), and extracted with Et_2O (50 mL x 2). The combined organic phases were washed successively with water (50 mL) and saturated brine (50 mL), dried (K_2CO_3), concentrated. The residue was dissolved in THF-H_2O (1:1, 72 mL), and stirred in an ice-water bath for 14 h after addition of CF_3COOH (20 mL). The mixture was diluted with water (100 mL), and then extracted with pentane (50 mL x 3). The combined organic phases were washed thoroughly with saturated aqueous $NaHCO_3$ to remove CF_3COOH, and then saturated brine (50 mL). The pentane solution was dried, and concentrated. The residue was subjected to column chromatography (silica gel 760 g; elution with 15:1 hexane-Et_2O) to give (*E*)-derivative (4.05 g, 32%) and (*Z*)-derivative (4.53 g, 36%).

(***E***): a dark orange oil, R_f = 0.45 (hexane: Et_2O = 10 : 1). IR (film) 1595 cm^{-1}. ^{1}H NMR δ 0.25 (6H, s, $SiMe_2Bu$), 0.43 (6H, s, $SiMe_2Ph$), 0.94 (9H, s, *t*-Bu), 6.76 (1H, d, J = 19.2 Hz, H-2), 6.98 (1H, d, J = 19.2 Hz, H-3), 7.36-7.42 (3H, m, Ar-H), 7.51-7.54 (2H, m, Ar-H). ^{13}C NMR δ -5.8 ($SiMe_2Bu$), -2.9 ($SiMe_2Ph$), 16.8 (CMe_3), 26.7 (*t*-Bu), 142.8 (C-3), 148.3 (C-2), 128.1, 129.6, 133.9 and 136.8 (Ar), 236.4 (C-1).

(***Z***): a dark yellow oil, R_f = 0.74 (hexane: Et_2O = 10 : 1). IR (film) 1620 cm^{-1}. ^{1}H NMR δ 0.17 (6H, s, $SiMe_2Bu$), 0.34, 0.43 (each 3H, s, $SiMe_2Ph$), 0.89 (9H, s, *t*-Bu), 6.19 (1H, d, J = 14.3 Hz, H-2), 7.41 (1H, d, J = 14.3 Hz, H-3), 7.30-7.39 (3H, m, Ar-H), 7.52-7.59 (2H, m, Ar-H).

(5*R,6*R**)-3-(*t*-Butyldimethylsiloxy)-5-(dimethyl(phenyl)silyl)-6-pentyl-3-cyclohepten-1-one (27).** To a cooled (-80°C) solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (170 μL, 1.22 mmol) and *n*-BuLi (1.50 M in hexane, 0.81 mL, 1.22 mmol) in THF (2 mL) was added dropwise a solution of 3-nonen-2-one (156 mg, 1.11 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of the above (*E*)-derivative (405 mg, 1.33 mmol) in THF (50 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (50 mL). The mixture was extracted with Et_2O (50 mL x 2), and the combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g; elution with 10:1 hexane-Et_2O) to give **27** (370 mg, 75%). a pale yellow oil, R_f = 0.38 (hexane : Et_2O = 10 : 1). IR (film) 1710 cm^{-1}. ^1H NMR δ 0.06 and 0.12 (each 3H, s, $SiMe_2Bu$), 0.32, 0.34 (each 3H, s, $SiMe_2Ph$), 0.84 (3H, t, *J* = 7.0 Hz, CH_3), 0.90 (9H, s, *t*-Bu), 1.05-1.32 (8H, m, $(CH_2)_4$),1.95 (1H, dd, *J* = 8.1, 3.8 Hz, H-5), 2.30 (1H, m, H-6), 2.41 (1H, dd, *J* = 11.8, 6.2 Hz, H-7), 2.59 (1H, dd, *J* = 11.8, 9.8 Hz, H-7), 2.82 (1H, d, *J* = 18.4 Hz, H-2), 3.46 (1H, dd, *J* = 18.4, 1.0 Hz, H-2), 4.99 (1H, dd, *J* = 8.1, 2.3 Hz, H-4), 7.30-7.37 (3H, m, Ar-H), 7.46-7.50 (2H, m, Ar-H). ^{13}C NMR δ -4.6 and -4.1 ($SiMe_2Bu$), -3.0 and -2.7 ($SiMe_2Ph$), 18.1 (CMe_3), 22.7, 26.8, 31.7, and 34.1 (C-1', C-2', C-3' and C-4'), 25.8 (*t*-Bu), 29.0 (C-5), 40.9 (C-6), 47.7 (C-7), 51.1 (C-2), 106.3 (C-4), 148.9 (C-3), 210.5 (C-1), 128.0, 129.2, 134.0 and 138.1 (Ar). HRMS calcd for $C_{26}H_{44}O_2Si_2$ 444.2880, found 444.2865.

(5*R,6*R**)-5-(Dimethyl(phenyl)silyl)-6-pentylcyclohepta-1,3-dione (28)**. To a solution of **27** (365 mg, 0.82 mmol) in THF (8 mL) was added TBAF (1.0 M in THF, 0.82 mL, 0.82 mmol). After stirring at room temperature for 25 min, the reaction mixture was diluted with water (20 mL), and extracted with Et_2O (20 mL x1, 10 mL x 3). The combined organic phases were washed with saturate brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 15 g; 1:2 hexane-Et_2O) to give **28** (240 mg, 89%). a pale yellow oil, R_f = 0.31 (hexane : Et_2O = 1 : 2). IR (film) 1715, 1695 cm^{-1}. ^1H NMR δ 0.36 (6H, s, $SiMe_2Ph$), 0.63 (3H, t, *J* = 7.3 Hz, Me), 1.00-1.40 (8H, m, $(CH_2)_4$), 1.82 (1H, ddd, *J* = 13.5, 3.2, 3.2 Hz, H-5), 2.14 (1H, m, H-6), 2.44 (1H, dd, *J* = 16.2, 3.2 Hz, H-4), 2.54 (1H, dd, *J* = 12.8, 6.6 Hz, H-7), 2.58 (1H, dd, *J* = 12.8, 5.8 Hz, H-7), 2.60 (1H, dd, *J* = 16.2, 13.5 Hz, H-4), 3.33 (1H, d, *J* = 14.7 Hz, H-2), 3.81 (1H, d, *J* = 14.7 Hz, H-2), 7.34-7.40 (3H, m, Ar-H), 7.47-7.50 (2H, m, Ar-H). ^{13}C NMR δ -3.7 and -3.5 ($SiMe_2Ph$), 14.1 (Me), 22.6, 27.1, 31.6 and 30.8 (C-2', C-3', C-4' and C-1'), 29.5 (C-5), 35.6 (C-6), 40.4 (C-4), 49.7 (C-7), 59.8 (C-2), 128.2, 129.6, 133.9 and 136.7 (Ar), 204.2 (C-3), 206.4 (C-1). HRMS calcd for $C_{20}H_{30}O_2Si$ 330.2015, found 330.2013.

Oxidative desilylation of 28. 28 (100 mg, 300 μmol) was dissolved in 15% acetic acid solution of AcOOH (3.5 mL, 6.6 mmol) and silver trifluoroacetate (385 mg, 900 μmol), and stirred at room temperature for 13 h. The solution was diluted with Et_2O (50 mL), and washed successively with aqueous sodium thiocarbonate solution (5 mL) and saturated aqueous $NaHCO_3$ (5 mL x 4), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g; elution with 1:2 hexane-Et_2O) to give a 2:1 mixture of **29** and **30** (20 mg, 31%), along with **28** (39 mg, 39%). The mixture was separated by MPLC (5 μ silica gel, 22 x 150 mm; elution with 3:1 hexane-AcOEt).

29: a pale yellow oil, R_f = 0.26 (hexane : Et_2O = 1 : 2). IR (film) 3385, 1720 cm^{-1}. ^1H NMR δ 0.87 (3H, t, *J* = 7.0 Hz, Me), 1.20-1.35 (6H, m, H-2', H-3' and H-4'), 1.35-1.42 (1H, m, H-1'), 1.49-1.56 (1H, m, H-1'), 1.45 (1H, dd, *J* = 13.1, 4.4 Hz, H-7), 1.82 (1H, ddd, *J* = 14.1, 7.5, 7.5 Hz, H-6), 2.25 (1H, dd, *J* = 13.1, 8.9 Hz, H-7), 2.27 (1H, d, *J* = 15.8 Hz, H-4), 2.63 (1H, dd, *J* = 15.8, 5.3 Hz, H-4), 2.69 (2H, s, H-2), 3.62 (1H, m, OH), 4.29 (1H, d, *J* = 5.3 Hz, H-5). ^{13}C NMR δ -3.7 and -3.5 ($SiMe_2Ph$), 14.1 (Me), 22.6, 27.1, 31.6 and 30.8 (C-2', C-3', C-4' and C-1'), 29.5 (C-5), 35.6 (C-6), 40.4 (C-4), 49.7 (C-7), 59.8 (C-2), 204.2 (C-3), 206.4 (C-1). HRMS calcd for $C_{12}H_{20}O_3$ 212.1412, found 211.9876.

30: a pale yellow oil, R_f = 0.26 (hexane : Et_2O = 1 : 2). ^{1}H NMR δ 0.87 (3H, t, *J* = 7.0 Hz, Me), 1.20-1.33 (6H, m, H-2', H-3' and H-4'), 1.37-1.43 (1H, m, H-1'), 1.50-1.57 (1H, m, H-1'), 1.44 (1H, ddd, *J* = 13.3, 5.8, 5.8 Hz, H-7), 1.83 (1H, ddd, *J* = 14.1, 7.5, 7.5 Hz, H-6), 2.27 (1H, dd, *J* = 16.3, 1.3 Hz, H-4), 2.27 (1H, dd, *J* = 13.3, 8.8 Hz, H-7), 2.63 (1H, dd, *J* = 16.3, 5.6 Hz, H-4), 2.66 (1H, dd, *J* = 16.5, 2.8 Hz, H-2), 2.71 (1H, dd, *J* = 16.5, 1.3 Hz, H-2), 3.12 (1H, br d, *J* = 3.2 Hz, OH), 4.29 (1H, d, *J* = 5.6 Hz, H-5). ^{13}C NMR δ 14.2 (Me), 22.7, 27.4 and 31.8 (C-2', C-3' and C-4'), 36.7 (C-1'),42.6 (C-6), 43.8 (C-7), 48.0 (C-4), 54.5 (C-2), 76.8 (C-5), 104.5 (C-1), 206.3 (C-3).

Trapping Experiment of the Cyclopropanolate Intermediate. To a stirred and cooled (-80 °C) solution of LDA, prepared from diisopropylamine (124 μL, 882 μmol) and *n*-BuLi (1.45 M hexane solution, 610 μL, 882 μmol) in THF (1 mL), was added dropwise a solution of 2'-bromoacetophenone (176 mg, 882 μmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of (*E*)-**12** (405 mg, 882 μmol) in THF (41 mL) over 2 min. The reaction mixture was allowed to warm to -45 °C over 40 min, and then quenched by acetic acid (52 mg, 882 μmol) in THF (1 mL). The mixture was extracted with Et_2O (30 mL x 2) after addition of saturated aqueous NH_4Cl solution (30 mL), and the combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 20:1 hexane-Et_2O) to give **33** (139 mg, 24%), **23g** (13 mg, 5%), **34** (93 mg, 16%), and 2'-bromoacetophenone (56 mg, 32%).

33: a pale yellow oil, R_f = 0.40 (hexane : Et_2O = 10 : 1). IR (film) 3530 cm^{-1}. ^{1}H NMR δ 0.15 and 0.18 (each 3H, s, $SiMe_2$), 0.60-0.75 (6H, m, SnBu), 0.84 (9H, t, *J* = 7.3 Hz, SnBu), 0.97 (9H, s, *t*-Bu), 1.14-1.22 (6H, m, SnBu), 1.25-1.32 (6H, m, SnBu), 1.21 (1H, d, *J* =7.5 Hz, H-3), 1.75 (1H, d, *J* = 7.5 Hz, H-3), 3.66 (1H, s, OH), 5.62 (1H, d, *J* = 19.2 Hz, H-1"), 5.90 (1H, d, *J* = 19.2 Hz, H-2"), 7.07 (1H, ddd, *J* = 7.7, 7.7, 1.7 Hz, H-4'), 7.19 (1H, ddd, *J* = 7.7, 7.7, 1.1 Hz, H-5'), 7.29 (1H, dd, *J* = 7.7, 1.7 Hz, H-6'), 7.49 (1H, dd, *J* = 7.7, 1.1 Hz, H-3'). ^{13}C NMR δ -3.5 and -3.1 ($SiMe_2$), 9.5, 13.9, 27.4, 29.1 (SnBu), 18.3 (*C*Me_3), 23.4 (C-3), 26.1 (*t*-Bu), 63.6 and 64.9 (C-1 and C-2), 126.2 (C-2'), 126.7 (C-5'), 126.9 (C-1"), 129.3 (C-4'), 131.5 (C-6'), 133.2 (C-3'), 138.6 (C-1'), 146.0 (C-2"). HRMS calcd for $C_{29}H_{51}O_2BrSiSn$ 658.1864, found 658.1847.

34: a colorless oil, R_f = 0.53 (hexane : Et_2O = 10 : 1). IR (film) 1700 cm^{-1}. ^{1}H NMR δ 0.13 (6H, s, $SiMe_2$), 0.63-0.85 (6H, m, SnBu), 0.87 (9H, t, *J* = 7.3 Hz, SnBu), 0.92 (9H, s, *t*-Bu), 1.21-1.30 (6H, m, SnBu), 1.35-1.43 (6H, m, SnBu), 1.58 (2H, d, *J* = 8.8 Hz, H-5), 3.63 (2H, s, H-2), 4.74 (1H, t, *J* = 8.8 Hz, H-4), 7.25 (1H, ddd, *J* = 7.9, 7.9, 1.9 Hz, H-5'), 7.32 (1H, ddd, *J* = 7.9, 7.9, 1.1 Hz, H-4'), 7.39 (1H, dd, *J* = 7.9, 1.9 Hz, H-3'), 7.57 (1H, dd, *J* = 7.9, 1.1 Hz, H-6'). ^{13}C NMR δ -3.7 ($SiMe_2$), 7.9 (C-5), 9.4, 13.9, 27.5, 29.3 (SnBu), 18.4 (*C*Me_3), 26.0 (*t*-Bu), 50.9 (C-2), 112.6 (C-4), 119.0 (C-2'), 127.4 (C-4'), 129.4 (C-3'), 131.5 (C-5'), 133.7 (C-6'), 139.5 (C-1'), 141.2 (C-3), 201.5 (C-1). HRMS calcd for $C_{25}H_{42}O_2BrSiSn$ (M^+-C_4H_9) 601.1159, Found 601.1120.

Reaction of 33 with LDA. To a cooled (-30 °C) solution of **33** (114 mg, 173 μmol) in THF (8 mL) was added dropwise LDA (0.5 M THF-hexane solution, 359 μL, 173 μmol). After stirring at the same temperature for 10 min, the reaction was quenched by acetic acid (11 mg, 173 μmol) in THF (0.2 mL). The reaction mixture was extracted with Et_2O (10 mL x 2) after addition of saturated aqueous NH_4Cl solution (10 mL). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g; elution with 20:1 hexane-Et_2O) to give **23g** (9 mg, 18%) and a mixture of **34** and **35** (65 mg, 48%; 11%).

35: a pale yellow oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1600 cm^{-1}. ^{1}H NMR δ 0.80-0.95 (15H, m, SnBu), 0.98-1.11 (2H, m, H-5), 1.25-1.35 (6H, m, SnBu), 1.40-1.60 (6H, m, SnBu), 2.51-2.63 (2H, m, H-4), 5.98 (1H, s, H-2), 7.28 (1H, ddd, *J* = 8.1, 7.5 Hz, H-5'), 7.37 (1H, ddd, *J* = 7.5, 1.1, H-4'), 7.51 (1H, dd, *J* = 7.5, 1.9 Hz, H-3'), 7.63 (1H, dd, *J* = 8.1, 1.1 Hz, H-6'). ^{13}C NMR δ -4.4 ($SiMe_2$), 4.2 (C-5), 9.2, 13.9, 27.6, 29.4

(SnBu), 36.4 (C-4), 100.6 (C-2), 120.3 (C-2'), 127.6 (C-4'), 130.1 (C-3'), 131.6 (C-5'), 134.0 (C-6'), 138.0 (C-1'), 185.4 and 198.5 (C-1 and C-3). HRMS calcd for $C_{23}H_{37}O_2BrSn$ 544.0999, Found 544.1025.

(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*E*)-39). To a cooled (ice-water) solution of methyl phenyl sulfone (516 mg, 3.3 mmol) in THF (7 mL) was added dropwise *n*-BuLi (1.47 M hexane solution, 2.25 mL, 3.3 mmol). After stirring at the same temperature for 1 h, the mixture was added dropwise to a cooled (-80 °C) solution of (*E*)-**11** (728 mg, 3.0 mmol) in THF (7 mL). The reaction mixture was allowed to warm to -30 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (15 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (10 mL x 2). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 36 g; elution with hexane) to give (*E*)-**39** (562 mg, 73%). a colorless oil, R_f = 0.39 (hexane). IR (neat) 1250 cm^{-1}. ^1H NMR δ 0.09 (9H, s, $SiMe_3$), 0.17 (6H, s, $SiMe_2$), 0.97 (9H, s, *t*-Bu), 4.35 and 4.37 (each 1H, br s, H-1), 6.18 (1H, d, *J* = 18.6 Hz, H-3), 6.34 (1H, d, *J* = 18.6 Hz, H-4). ^{13}C NMR δ -4.5 ($SiMe_2$), -1.1 ($SiMe_3$), 18.5 (CMe_3), 26.0 (*t*-Bu), 96.7 (C-1), 130.1 (C-3), 141.4 (C-4), 155.8 (C-2). HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1657.

(*Z*)-3-(*tert*-Butyldimethylsiloxy)-1-(trimethylsilyl)buta-1,3-diene ((*Z*)-39). (*Z*)-**39** was obtained from (*Z*)-**11** in 85% yield by the procedure described above for (*E*)-**39**. a colorless oil, R_f = 0.50 (hexane). IR (neat) 1250 cm^{-1}. ^1H NMR δ 0.14 (9H, s, $SiMe_3$), 0.20 (6H, s, $SiMe_2$), 0.95 (9H, s, *t*-Bu), 4.35 and 4.36 (each 1H, br s, H-1), 5.61 (1H, d, *J* = 15.2 Hz, H-3), 6.52 (1H, d, *J* = 15.2 Hz, H-4). ^{13}C NMR δ -3.6 ($SiMe_2$), 0.4 ($SiMe_3$), 19.0 (CMe_3), 26.4 (*t*-Bu), 95.8 (C-1), 132.4 (C-3), 143.9 (C-4), 157.1 (C-2). HRMS calcd for $C_{13}H_{28}OSi_2$ 256.1679, Found 256.1643.

Reaction of enol silyl ether (*E*)-39 with Fischer carbene complex 40. To a suspension of $Cr(CO)_6$ (440 mg, 2.00 mmol) in Et_2O (40 mL) was added 2-methylpropen-1-yllithium, prepared from 1-bromo-2-methyl-1-propene (270 mg, 2 mmol) and *t*-butyllithium (1.50 M pentane solution, 3 mL, 5 mmol), at room temperature over 10 min. After stirring at room temperature for 30 min, the mixture was concentrated. Water (20 mL) was added to the residue, and the insoluble material was filtered out through Celite. To the filtrate was added an aqueous solution (2 mL) of Me_4NBr (460 mg, 3.00 mmol). The mixture was extracted with CH_2Cl_2 (20 mL x 3), and the combined organic phases were washed with brine (10 mL), dried, concentrated to give the complex **40** (480 mg) as a red solid. To a solution of this compound (480 mg, 1.37 mmol) in CH_2Cl_2 (3 mL) was added acetyl bromide (115 μL, 1.51 mmol) at -40 °C. After stirring at the same temperature for 1 h, a solution of (*E*)-**39** (440 mg, 1.71 mmol) in CH_2Cl_2 (20 mL) over 10 min. The solution was allowed to warm to 10 °C over 2.5 h, and then poured into aqueous saturated $NaHCO_3$ (30 mL). The phases were separated, and the aqueous phase was extracted with hexane (30 mL x 3). The combined organic phases were washed with saturated brine (30 mL), dried, and then concentrated. The residue was subjected to column chromatography (silica gel, 25 g; elution with 20:1 hexane-Et_2O) followed by MPLC (10 μ silica gel; elution with 55:1 hexane-Et_2O) to give **41** (40 mg, 8%) and **42** (12 mg, 2%).

41: a colorless oil, R_f = 0.39 (hexane : Et_2O = 10 : 1). IR (film) 1750 cm^{-1}. ^1H NMR δ 0.06 (9H, s, $SiMe_3$), -0.03 and 0.07 (each 3H, s, $SiMe_2$), 0.84 (9H, s, *t*-Bu), 1.17 (1H, d, *J* = 7.4 Hz, H-3), 1.50 (1H, d, *J* = 7.4 Hz, H-3), 1.71 (3H, d, *J* = 1.4 Hz, 2'-Me), 1.75 (3H, d, *J* = 1.4 Hz, 2'-Me), 1.89 (3H, s, $OCOCH_3$), 5.68 (1H, br m, H-1'), 5.80 (1H, d, *J* = 18.8 Hz, H-1"), 5.98 (1H, d, *J* = 18.8 Hz, H-2"). ^{13}C NMR δ -3.1 and -2.1 ($SiMe_2$), -0.2 ($SiMe_3$), 19.0 (CMe_3), 20.4 (2'-Me), 22.0 ($OCOCH_3$), 26.3 (2'-Me), 26.7 (*t*-Bu), 27.5 (C-3), 64.3 and 64.8 (C-1 and C-2), 121.4 (C-1'), 129.3 (C-1"), 142.1 (C-2'), 145.7 (C-2"), 171.1 (CO). HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2353.

42: a pale yellow oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1755 cm^{-1}. ^1H NMR δ 0.08 (9H, s, $SiMe_3$), 0.14 (6H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 1.09 (3H, s, 7-Me), 1.22 (3H, s, 7-Me), 1.55 (1H, d, *J* = 9.2 Hz, H-6),

2.08 (3H, s, $OCOCH_3$), 2.69 (1H, d, *J* = 20.6 Hz, H-3), 3.34 (1H, br d, *J* = 20.6 Hz, H-3), 4.97 (1H, d, *J* = 9.2 Hz, H-5), 5.20 (1H, d, *J* = 2.1 Hz, H-1). ^{13}C NMR δ -4.3 and -4.2 ($SiMe_2$), 0.9 ($SiMe_3$), 18.1 (CMe_3), 21.3 ($OCOCH_3$), 25.9 (*t*-Bu), 30.8 (7-Me), 32.3 (7-Me), 36.4 (C-7), 37.6 (C-6), 38.1 (C-3), 109.3 (C-5), 129.3 (C-1), 135.3 and 143.1 (C-2 and C-4), 170.0 (CO). HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2346.

Reaction of enol silyl ether (*Z*)-39 with Fischer carbene complex 40. To a solution of the **40** (1.20 g, 3.43 mmol) described above in CH_2Cl_2 (8 mL) was added acetyl bromide (305 μL, 4.10 mmol) at -40 °C. After stirring at the same temperature for 1 h, a solution of (*Z*)-**39** (1.75 g, 6.82 mmol) in CH_2Cl_2 (56 mL) over 35 min. The solution was allowed to warm to 10 °C over 2 h, and then poured into aqueous saturated $NaHCO_3$ (30 mL). The phases were separated, and the aqueous phase was extracted with hexane (100 mL x 1, 50 mL x 2). The combined organic phases were washed with saturated brine (100 mL), dried, and then concentrated. The residue was subjected to column chromatography (silica gel, 90 g; elution with 20:1 hexane-Et_2O) followed by MPLC (10 μ silica gel; elution with 55:1 hexane-Et_2O) to give **44** (28 mg, 2%) and **45** (53 mg, 4%).

44: a colorless oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1755 cm^{-1}. ^{1}H NMR δ 0.09 (9H, s, $SiMe_3$), 0.07 and 0.10 (each 3H, s, $SiMe_2$), 0.84 (9H, s, *t*-Bu), 1.34 (1H, d, *J* = 7.5 Hz, H-3), 1.41 (1H, d, *J* = 7.5 Hz, H-3), 1.65 (3H, d, *J* = 1.3 Hz, 2'-Me), 1.76 (3H, d, *J* = 1.3 Hz, 2'-Me), 2.00 (3H, s, $OCOCH_3$), 5.36 (1H, br m, H-1'), 5.63 (1H, d, *J* = 15.2 Hz, H-1"), 6.56 (1H, br d, *J* = 15.2 Hz, H-2"). ^{13}C NMR δ -3.4 and -2.9 ($SiMe_2$), 0.4 ($SiMe_3$), 18.1 (CMe_3), 19.2 (2'-Me), 21.2 ($OCOCH_3$), 25.6 (2'-Me), 25.8 (*t*-Bu), 26.4 (C-3), 61.0 and 61.5 (C-1 and C-2), 121.0 (C-1'), 132.3 (C-1"), 140.5 (C-2'), 145.7 (C-2"), 170.4 (CO). HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2371.

45: a colorless oil, R_f = 0.46 (hexane : Et_2O = 10 : 1). IR (film) 1750 cm^{-1}. ^{1}H NMR δ 0.15 (9H, s, $SiMe_3$), 0.03 and 0.12 (each 3H, s, $SiMe_2$), 0.81 (9H, s, *t*-Bu), 1.14 (3H, dd, *J* = 7.3, 1.3 Hz, H-3), 1.56 (1H, d, *J* = 7.3 Hz, H-3), 1.71 (3H, d, *J* = 1.3 Hz, 2'-Me), 1.77 (3H, d, *J* = 1.3 Hz, 2'-Me), 1.90 (3H, s, $OCOCH_3$), 5.65 (1H, br s, H-1'), 5.67 (1H, d, *J* = 15.0 Hz, H-1"), 6.52 (1H, dd, *J* = 15.0, 1.3 Hz, H-2"). ^{13}C NMR δ -3.2 and -2.9 ($SiMe_2$), 0.6 ($SiMe_3$), 18.1 (CMe_3), 19.4 (2'-Me), 21.2 ($OCOCH_3$), 25.7 (2'-Me), 25.8 (*t*-Bu), 26.9 (C-3), 62.2 and 62.4 (C-1 and C-2), 120.7 (C-1'), 133.6 (C-1"), 140.1 (C-2'), 144.6 (C-2"), 170.6 (CO). HRMS calcd for $C_{20}H_{38}O_3Si_2$ 382.2360, found 382.2402.

Thermal Cope rearrangement of 41, 44, and 45. This procedure is representative for the thermal Cope rearrangement of the cyclopropyl acetates. A solution of **41** (9.1 mg, 23.8 μmol) in benzene (2.4 mL) was refluxed for 1.5 h. Concentration of the solution gave pure **42** (9.1 mg, 100%).

Reaction of cyclopropyl acetates 41 with MeLi. To a cooled (-80 °C) solution of **41** (21.1 mg, 55.1 μmol) in THF (2.8 mL) was added dropwise MeLi (1.07 M in Et_2O, 114 μL, 122 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (7.4 mg, 123 μmol) in THF (0.5 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (5 mL), and then extracted with Et_2O (5 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residue was subjected to MPLC (5 μ silica gel, elution with 40:1 hexane-Et_2O) to give **15d** (13.4 mg, 71%) and **41** (2.9 mg, 14%).

Reaction of cyclopropyl acetates 44 and 45 with MeLi. The following procedure for **45** is representative: To a cooled (-80 °C) solution of **45** (12.6 mg, 32.9 μmol) in THF (1.6 mL) was added dropwise MeLi (1.00 M in Et_2O, 73 μL, 73.0 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (4.4 mg, 73.3 μmol) in THF (0.2 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (3 mL), and then extracted with Et_2O (3 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residue was filtered through a short pad of silica gel (120 mg) to give a mixture (12.1 mg) of **48**, **15d** and **45**. Attempted purification of this mixture by MPLC led

to complete decomposition of **48**; the characterization was made by the comparison of its ^{1}H NMR with those of **58** and related compounds.

Reaction of enol silyl ether (*E*)-39 with Fischer carbene complex (50). To a suspension of $Cr(CO)_6$ (360 mg, 1.63 mmol) in Et_2O (10 mL) was added 1-propenyllithium (0.018 M Et_2O solution, 90 mL, 1.62 mmol), prepared from 1-bromo-1-propene with *t*-butyllithium, at room temperature over 10 min. After stirring at room temperature for 1 h, the mixture was concentrated. Water (20 mL) was added to the residue, and the insoluble material was filtered out through Celite. To the filtrate was added an aqueous solution (1.6 mL) of Me_4NBr (380 mg, 2.44 mmol). The mixture was extracted with CH_2Cl_2 (20 mL x 3), and the combined organic phases were washed with brine (10 mL), dried, concentrated. The residual solid was recrystallized from CH_2Cl_2-Et_2O to give tetramethylammonium (propenyl(oxido)carbene)pentacarbonyl-chromium (320 mg, 59%). a red needles, mp 112-113 °C (dec), Anal. calcd for $C_{13}H_{17}O_6NCr$: C, 46.56; H, 5.11; N, 4.18; Found: C, 46.28; H, 4.98; N, 3.99.

To a cooled (-40 °C) solution of the above carbene complex (195 mg, 580 μmol) in CH_2Cl_2 (1.2 mL) was added dropwise acetyl bromide (48 μL, 640 μmol), and then the reaction mixture was stirred at the same temperature for 1 h. To this mixture was added dropwise a solution of (*E*)-**39** (300 mg, 1.16 mmol) in CH_2Cl_2 (9.4 mL) over 10 min. The reaction mixture was allowed to warm to 10 °C over 2 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution (15 mL), and extracted with hexane (10 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g; elution with 20 : 1 hexane-Et_2O) followed by MPLC (elution with 50:1 hexane-Et_2O) to give **51** (48 mg, 23%), a 1:1 mixture of **52** and **i** (35 mg, 16%), and 2-acetoxy-5-(*t*-butyldimethylsiloxy)-7-methyl-3-(trimethylsilyl)cyclohepta-1,4-diene (17 mg, 8%). The mixture of **52** and **i** was separated by resubjecting to the MPLC.

51: a colorless oil, R_f = 0.38 (hexane : Et_2O = 10 : 1). IR (film) 1760 cm^{-1}. ^{1}H NMR δ 0.06 (9H, s, $SiMe_3$), 0.04 and 0.08 (each 3H, s, $SiMe_2$), 0.87 (9H, s, *t*-Bu), 1.35 (1H, d, *J* = 7.7 Hz, H-3), 1.51 (1H, d, *J* = 7.7 Hz, H-3), 1.73 (3H, dd, *J* = 6.4, 1.5 Hz, 2'-Me), 1.94 (3H, s, $OCOCH_3$), 5.55 (1H, dq, *J* = 15.6, 6.4 Hz, H-2'), 5.66 (1H, dq, *J* = 15.6, 1.5 Hz, H-1'), 5.73 (1H, d, *J* = 18.8 Hz, H-1"), 6.04 (1H, d, *J* = 18.8 Hz, H-2"). ^{13}C NMR δ -3.7 and -2.9 ($SiMe_2$), -1.1 ($SiMe_3$), 18.2 (CMe_3), 18.2 (2'-Me), 21.2 ($OCOCH_3$), 25.4 (C-3), 25.9 (*t*-Bu), 65.9 and 66.1 (C-1 and C-2), 125.8 (C-2'), 126.5 (C-1'), 129.0 (C-1"), 144.0 (C-2"), 169.9 (CO). HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2178.

52: a colorless oil, R_f = 0.56 (hexane : Et_2O = 5 : 1). IR (film) 1755 cm^{-1}. ^{1}H NMR δ 0.04 (9H, s, $SiMe_3$), 0.13 and 0.14 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 1.01 (3H, d, *J* = 7.3 Hz, 7-Me), 1.85 (1H, br d, *J* = 7.5 Hz, H-6), 2.09 (3H, s, $OCOCH_3$), 2.39 (1H, d, *J* = 19.5 Hz, H-3), 2.64-2.74 (1H, br s, H-7), 3.75 (1H, d, *J* = 19.5 Hz, H-3), 4.91 (1H, dd, *J* = 7.5, 1.7 Hz, H-5), 5.30 (1H, dd, *J* = 5.9, 2.5 Hz, H-1). ^{13}C NMR δ -4.4 and -4.3 ($SiMe_2$), -1.1 ($SiMe_3$), 18.1 (CMe_3), 21.2 ($OCOCH_3$), 23.3 (7-Me), 25.9 (*t*-Bu), 32.5 (C-7), 29.4 (weak, C-6), 38.0 (C-3), 107.2 (weak, C-5), 125.5 (C-1), 144.0 (C-2 and C-4), 169.8 (CO). HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, found 368.2200.

2-acetoxy-5-(t-butyldimethylsiloxy)-7-methyl-3-(trimethylsilyl)cyclohepta-1,4-diene: a colorless oil, R_f = 0.45 (hexane : Et_2O = 10 : 1). IR (film) 1760 cm^{-1}. ^{1}H NMR δ 0.00 (9H, s, $SiMe_3$), 0.12 and 0.12 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 1.11 (3H, d, *J* = 6.4 Hz, 7-Me), 1.88 (1H, dddd, *J* = 16.7, 11.8, 2.8, 2.1 Hz, H-6), 2.07 (1H, dd, *J* = 16.7, 5.8 Hz, H-6), 2.11 (3H, s, $OCOCH_3$), 2.42 (1H, dddd, *J* = 11.8, 6.4, 5.8, 1.9 Hz, H-7), 2.92 (1H, dd, *J* = 4.3, 2.8 Hz, H-3), 4.77 (1H, dd, *J* = 4.3, 2.1 Hz, H-4), 6.95 (1H, d, *J* = 1.9 Hz, H-1). ^{13}C NMR δ -4.2 and -4.1 ($SiMe_2$), -2.1 ($SiMe_3$), 17.4 (7-Me), 18.2 (CMe_3), 21.1 ($OCOCH_3$), 25.9 (*t*-Bu), 28.7 (C-3), 30.9 (C-7), 39.6 (C-6), 102.9 (C-4), 126.2 (C-1), 127.2 (C-2), 147.6 (C-5), 168.3 (CO). HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, found 368.2193.

i: a colorless plates, mp 65 °C (petroleum), R_f = 0.56 (hexane : Et_2O = 5 : 1). IR (KBr) 1745 cm^{-1}. ^1H NMR δ -0.02 (9H, s, $SiMe_3$), 0.11 and 0.11 (each 3H, s, $SiMe_2$), 0.81 (1H, dd, *J* = 6.4, 4.3 Hz, H-6), 0.91 (9H, s, *t*-Bu), 1.08 (3H, d, *J* = 6.8 Hz, 5-Me), 1.80 (1H, ddd, *J* = 15.8, 8.6, 1.9 Hz, H-4), 1.86 (1H, dd, *J* = 15.8, 5.6 Hz, H-4), 1.99 (1H, dddd, *J* = 8.6, 6.8, 5.6, 4.3 Hz, H-5), 2.02 (3H, s, $OCOCH_3$), 3.88 (1H, d, *J* = 6.4 Hz, H-7), 4.57 (1H, d, *J* = 1.9 Hz, H-2). ^{13}C NMR δ -4.2 and -4.2 ($SiMe_2$), -3.4 ($SiMe_3$), 18.2 (CMe_3), 21.1 ($OCOCH_3$), 23.0 (5-Me), 23.4 (C-6), 25.7 (C-5), 25.9 (*t*-Bu), 37.3 (C-4), 60.5 (C-7), 98.3 (C-2), 153.5 (C-3), 171.9 (CO). Anal. Calcd for $C_{19}H_{36}O_3Si_2$: C, 61.92; H, 9.85. Found: C, 62.07; H, 9.93. X ray; triclinic $P\bar{1}$ (#2), a = 10.641(8), b = 12.789(2), c = 8.547(1) Å, α = 95.24(1)°, β = 90.49(3)°, γ = 82.83(2)°, V = 1149.2(8) $Å^3$, Z = 2, D_{calc} = 1.065 g/cm^3, R = 4.4 for 3743 reflections. Diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Ka radiation and 12 kW rotating generator. The structure was solved by the direct methods and expanded using Fourier techniques.

Reaction of enol silyl ether (*Z*)-39 with Fischer carbene complex (50). To a cooled (-40 °C) solution of the above carbene complex (160 mg, 477 μmol) in CH_2Cl_2 (1.2 mL) was added dropwise acetyl bromide (39 μL, 525 μmol), and then the reaction mixture was stirred at the same temperature for 1 h. To this mixture was added dropwise a solution of (*Z*)-**39** (245 mg, 954 μmol) in CH_2Cl_2 (7.6 mL) over 6 min. The reaction mixture was allowed to warm to -20 °C over 2 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution (10 mL), and extracted with hexane (10 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 15 g; elution with 20 : 1 hexane-Et_2O) followed by MPLC (elution with 50:1 hexane-Et_2O) to give **53** (21 mg, 12%), **54** (16 mg, 8%), and **i** (36 mg, 21%).

53: a colorless oil, R_f = 0.57 (hexane : Et_2O = 5 : 1). IR (film) 1760 cm^{-1}. ^1H NMR δ 0.14 (9H, s, $SiMe_3$), 0.07 and 0.09 (each 3H, s, $SiMe_2$), 0.84 (9H, s, *t*-Bu), 1.36 (1H, d, *J* = 7.7 Hz, H-3), 1.41 (1H, d, *J* = 7.7 Hz, H-3), 1.73 (3H, dd, *J* = 6.4, 1.5 Hz, 2'-Me), 2.00 (3H, s, $OCOCH_3$), 5.48 (1H, dq, *J* = 15.6, 6.4 Hz, H-2'), 5.58 (1H, dq, *J* = 15.6, 1.5 Hz, H-1'), 5.80 (1H, d, *J* = 14.7 Hz, H-1"), 6.52 (1H, d, *J* = 14.7 Hz, H-2"). ^{13}C NMR δ -3.0 and -2.9 ($SiMe_2$), -1.1 ($SiMe_3$), 18.1 (CMe_3), 18.2 (2'-Me), 21.4 ($OCOCH_3$), 25.9 (C-3), 25.9 (*t*-Bu), 63.4 (weak) and 64.9 (C-1 and C-2), 125.3 (C-2'), 126.8 (C-1'), 136.7 (weak, C-1"), 143.8 (C-2"), 170.3 (CO). HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2234.

54: a colorless oil, R_f = 0.58 (hexane : Et_2O = 5 : 1). IR (film) 1755 cm^{-1}. ^1H NMR δ 0.04 (9H, s, $SiMe_3$), 0.13 and 0.15 (each 3H, s, $SiMe_2$), 0.91 (9H, s, *t*-Bu), 1.21 (3H, d, *J* = 7.1 Hz, 7-Me), 1.42 (1H, dd, *J* = 8.9, 3.5 Hz, H-6), 2.08 (3H, s, $OCOCH_3$), 2.41-2.49 (1H, m, H-7), 2.88 (1H, d, *J* = 21.6 Hz, H-3), 3.16 (1H, d, *J* = 21.6 Hz, H-3), 5.02 (1H, dd, *J* = 8.9, 0.5 Hz, H-5), 5.53 (1H, dd, *J* = 8.6, 1.9 Hz, H-1). ^{13}C NMR δ -4.3 and -4.2 ($SiMe_2$), -1.6 ($SiMe_3$), 18.1 (CMe_3), 21.3 ($OCOCH_3$), 22.9 (7-Me), 25.9 (*t*-Bu), 30.2 (C-7), 32.9 (C-6), 39.0 (C-3), 108.0 (C-5), 123.0 (C-1), 143.4 and 144.7 (C-2 and C-4), 169.7 (CO). HRMS calcd for $C_{19}H_{36}O_3Si_2$ 368.2203, Found 368.2175.

Reaction of 51 with MeLi. This procedure is representative of reactions of **51** and **53** with MeLi: To a cooled (-80 °C) solution of **24** (21 mg, 55.6 μmol) in THF (2.8 mL) was added dropwise MeLi (1.07 M in Et_2O, 115 μL, 123 μmol). After stirring at -80 °C for 5 min, the reaction was quenched by addition of AcOH (7.4 mg, 123 μmol) in THF (0.5 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (5 mL), and then extracted with Et_2O (5 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residue was subjected to MPLC (5 μ silica gel, elution with 50:1 hexane-Et_2O) to give **55** (7.0 mg, 39%) and **56** (6.5 mg, 35%).

55: a colorless oil, R_f = 0.48 (hexane : Et_2O = 5 : 1). IR (film) 1710 cm^{-1}. ^1H NMR δ 0.02 (9H, s, $SiMe_3$), 0.14 and 0.17 (each 3H, s, $SiMe_2$), 0.92 (9H, s, *t*-Bu), 0.95 (3H, d, *J* = 6.6 Hz, 6-Me), 1.60 (1H, dd, *J* = 7.9, 3.2 Hz, H-5), 2.37 (1H, dd, *J* = 11.1, 6.2 Hz, H-7), 2.44-2.50 (1H, m, H-6), 2.62 (1H, dd, *J* = 11.1, 9.8 Hz, H-7), 2.82

(1H, d, *J* = 18.6 Hz, H-2), 3.43 (1H, dm, *J* = 18.6 Hz, H-2), 4.92 (1H, dd, *J* = 7.9, 2.4 Hz, H-4). ^{13}C NMR δ -4.4 and -4.1 ($SiMe_2$), -1.6 ($SiMe_3$), 18.2 (CMe_3), 19.3 (6-Me), 25.8 (*t*-Bu), 28.7 (C-5), 36.1 (C-6), 50.4 (C-7), 51.0 (C-2), 105.5 (C-4), 149.6 (C-3), 208.9 (C-1). HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2069.

56: a pale yellow oil, R_f = 0.53 (hexane : Et_2O = 5 : 1). IR (film) 1700 cm^{-1}. ^{1}H NMR δ 0.00 (9H, s, $SiMe_3$), 0.12 (6H, s, $SiMe_2$), 0.88 (9H, s, *t*-Bu), 1.31 (2H, d, *J* = 8.5 Hz, H-8), 1.88 (3H, dd, *J* = 6.8, 1.7 Hz, H-1), 3.21 (2H, s, H-5), 4.79 (1H, t, *J* = 8.5 Hz, H-7), 6.25 (1H, dq, *J* = 15.6, 1.7 Hz, H-3), 6.90 (1H, dq, *J* = 15.6, 6.8 Hz, H-2). ^{13}C NMR δ -4.3 ($SiMe_2$), -1.6 ($SiMe_3$), 16.7 (C-8), 18.2 (CMe_3), 18.4 (C-1), 25.9 (*t*-Bu), 44.7 (C-5), 106.4 (C-7), 130.7 (C-3), 143.0 (C-2), 143.8 (C-6), 197.0 (C-4). HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2076.

57: a colorless oil, R_f = 0.47 (hexane : Et_2O = 5 : 1). IR (film) 1710 cm^{-1}. ^{1}H NMR δ 0.07 (9H, s, $SiMe_3$), 0.12 (6H, s, $SiMe_2$), 0.90 (9H, s, *t*-Bu), 1.05 (3H, d, *J* = 6.8 Hz, Me), 1.35 (1H, ddd, *J* = 9.2, 7.5, 1.0 Hz, H-5), 2.52 (1H, dd, *J* = 14.1, 8.1 Hz, H-7), 2.16-2.24 (1H, m, H-6), 2.62 (1H, dd, *J* = 14.1, 4.1 Hz, H-7), 2.95 (1H, d, *J* = 17.5 Hz, H-2), 3.35 (1H, ddd, *J* = 17.5, 1.3, 1.1 Hz, H-2), 4.99 (1H, dd, *J* = 7.5, 1.3 Hz, H-4). ^{13}C NMR δ -4.2 and -4.2 ($SiMe_2$), -1.4 ($SiMe_3$), 18.1 (CMe_3), 23.9 (Me), 25.8 (*t*-Bu), 33.3 (C-5), 31.5 (C-6), 50.4 (C-7), 49.9 (C-2), 109.3 (C-4), 144.2 (C-3), 209.2 (C-1). HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2118.

58: a colorless oil, R_f = 0.27 (hexane : Et_2O = 5 : 1). IR (film) 1720 cm^{-1}. ^{1}H NMR δ -0.03 (9H, s, $SiMe_3$), 0.16 and 0.17 (each 3H, s, $SiMe_2$), 0.93 (9H, s, *t*-Bu), 1.72 (3H, dd, *J* = 6.0, 1.3 Hz, Me), 1.89 (2H, dd, *J* = 2.8, 0.9 Hz, H-2), 2.15 (1H, d, *J* = 16.2 Hz, H-5), 2.23 (1H, s, OH), 2.67 (1H, ddd, *J* = 16.2, 2.4, 1.5 Hz, H-5), 4.64 (1H, ddd, *J* = 2.8, 2.4, 0.9 Hz, H-3), 5.65 (1H, dd, *J* = 15.4, 1.3 Hz, H-1'), 5.72 (1H, dq, *J* =15.4, 6.0 Hz, H-2'). HRMS calcd for $C_{17}H_{34}O_2Si_2$ 326.2097, Found 326.2100.

Low-Temperature Quenching of Reactions of (*E*)- and (*Z*)-11 with 13c. : To a stirred and cooled (-80°C) solution of lithium diisopropylamide prepared from diisopropylamine (572 μL, 413 mg, 4.08 mmol) and *n*-BuLi (1.28 M in hexane, 3.19 mL, 4.08 mmol) in THF (2 mL) was added dropwise a solution of 3-nonen-2-one (614 μL, 521 mg, 3.71 mmol) in THF (2 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **(*E*)-11** (900 mg, 3.71 mmol) in THF (170 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (234 μL, 245 mg, 4.08 mmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (40 mL), and then extracted with Et_2O (40 mL x 3). The combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g; elution with 30:1 hexane-AcOEt) to give **(*E*)-63** (613 mg, 43%), **(*E*)-11** (155 mg, 17%), 3-none-2-one (182 mg, 35%), and **15c** (172 mg, 12%). **(*E*)-63**: a colorless oil, R_f = 0.29 (hexane : Et_2O = 15 : 1). IR (film) 3645, 1665 (weak) cm^{-1}. ^{1}H NMR δ -0.01 (9H, s, $SiMe_3$), 0.01 (6H, s, $SiMe_2$), 0.89 (3H, t, *J* = 6.8 Hz, H-12), 0.95 (9H, s, *t*-Bu), 1.26-1.35 (4H, m, H-10 and H-11), 1.46 (2H, br tt, *J* = 6.8, 6.8 Hz, H-9), 2.20 (2H, dt, *J* = 6.8, 6.8 Hz, H-8), 2.72 (1H, d, *J* = 15.4 Hz, H-4), 3.04 (1H, d, *J* = 15.4 Hz, H-4), 3.79 (1H, s, OH), 5.67 (1H, d, *J* = 19.0 Hz, H-2), 6.02 (1H, dt, *J* = 15.0, 1.5 Hz, H-6), 6.12 (1H, d, *J* = 19.0 Hz, H-1), 6.77 (1H, dt, *J* = 15.8, 6.8 Hz, H-7). ^{13}C NMR δ -7.7 and -7.4 ($SiMe_2$), -1.0 ($SiMe_3$), 14.1 (C-12), 18.5 (CMe_3), 28.0 (*t*-Bu), 22.6, 29.9, 31.6 (C-9, C-10, and C-11), 32.6 (C-8), 44.9 (C-4), 73.9 (C-3), 124.9 (C-2), 131.6 (C-6), 148.9 (C-7), 150.1 (C-1), 202.1 (C-5). HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, Found 382.2710.

To a stirred and cooled (-80°C) solution of lithium diisopropylamide prepared from diisopropylamine (191 μL, 138 mg, 1.36 mmol) and *n*-BuLi (1.28 M in hexane, 1.06 mL, 1.36 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (205 μL, 174 mg, 1.24 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **(*Z*)-11** (300 mg, 1.24 mmol) in THF (58 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (78 μL, 82 mg, 1.36 mmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl

solution (10 mL), and then extracted with Et_2O (20 mL x 3). The combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g; elution with 20:1 hexane-AcOEt) to give **(*Z*)-63** (20 mg, 4%), **(*Z*)-11** (231 mg, 77%), 3-nonen-2-one (127 mg, 73%). **(*Z*)-63**: a colorless oil, R_f = 0.59 (hexane : AcOEt = 10 : 1). IR (film) 3435, 1655 (weak) cm^{-1}. ^1H NMR δ -0.07 and 0.02 (each 3H, s, $SiMe_2$), 0.11 (9H, s, $SiMe_3$), 0.89 (3H, t, *J* = 6.2 Hz, H-12), 0.99 (9H, s, *t*-Bu), 1.25-1.40 (4H, m, H-10 and H-11), 1.46 (2H, br tt, *J* = 7.5, 7.5 Hz, H-9), 2.21 (2H, dt, *J* = 7.1, 7.1 Hz, H-8), 2.72 (1H, d, *J* = 15.0 Hz, H-4), 2.99 (1H, d, *J* = 15.0 Hz, H-4), 3.91 (1H, s, OH), 5.36 (1H, d, *J* = 14.3 Hz, H-1), 6.02 (1H, dd, *J* = 15.8, 0.9 Hz, H-6), 6.25 (1H, dd, *J* = 14.3, 0.6 Hz, H-2), 6.78 (1H, dt, *J* = 15.8, 7.1 Hz, H-7). ^{13}C NMR δ -6.9 and -6.8 ($SiMe_2$), 2.2 ($SiMe_3$), 14.1 (C-12), 18.6 (CMe_3), 28.1 (*t*-Bu), 22.6, 31.5 (C-10 and C-11), 27.9 (C-9), 32.7 (C-8), 45.0 (C-4), 75.9 (C-3), 125.8 (C-2), 131.5 (C-6), 149.5 (C-7), 150.6 (C-1), 202.2 (C-5). HRMS calcd for $C_{21}H_{42}O_2Si_2$ 382.2723, Found 382.2730.

Reactions of (*E*)- and (*Z*)-63 with LDA. To a cooled (-80°C) solution of **(*E*)-63** (186 mg, 486 μmol) in THF (21 mL) was added dropwise a solution of lithium diisopropylamide prepared from diisopropylamine (68 μL, 49 mg, 486 μmol) and *n*-BuLi (1.28 M in hexane, 380 μL, 486 μmol) in THF (3 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (28 μL, 29 mg, 483 μmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (8 mL), and then extracted with Et_2O (20 mL x 3). The combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 18 g; elution with 15:1 hexane-Et_2O) to give **15c** (69 mg, 37%), **(*E*)-64** (19 mg, 16%), and 3-nonen-2-one (25 mg, 36%). **(*E*)-64:** a colorless oil, R_f = 0.34 (hexane : AcOEt = 15 : 1). IR (film) 3435 cm^{-1}. ^1H NMR δ -0.05 and -0.02 (each 3H, s, $SiMe_2$), 0.06 (9H, s, $SiMe_3$), 0.95 (9H, s, *t*-Bu), 4.21 (1H, dd, *J* = 4.7, 2.1 Hz, H-1), 5.67 (1H, dd, *J* = 18.8, 2.1 Hz, H-3), 6.28 (1H, dd, *J* = 18.8, 4.7 Hz, H-2). ^{13}C NMR δ -8.7 and -7.4 ($SiMe_2$), -0.9 ($SiMe_3$), 17.3 (CMe_3), 27.1 (*t*-Bu), 69.6 (C-1), 122.9 (C-3), 148.6 (C-2). HRMS calcd for $C_{12}H_{28}OSi_2$ 244.1679, Found 244.1654.

To a cooled (-80°C) solution of **(*Z*)-63** (57 mg, 149 μmol) in THF (6.5 mL) was added dropwise a solution of lithium diisopropylamide prepared from diisopropylamine (21 μL, 15 mg, 149 μmol) and *n*-BuLi (1.28 M in hexane, 116 μL, 149 μmol) in THF (1 mL). After stirring at the same temperature for 30 min, the reaction was quenched by acetic acid (9 μL, 9 mg, 149 μmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH_4Cl solution (3 mL), and then extracted with Et_2O (7 mL x 3). The combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 6.5 g; elution with 30:1 hexane-AcOEt) to give **22c** (1.7 mg, 3%), **(*Z*)-11** (27 mg, 75%), and 3-nonen-2-one (9.8 mg, 47%).

General Procedure for the Reaction of 70 with Lithium Enolate of 3-Nonen-2-one (13c). This procedure is representative of reactions of **70** with lithium enolate of 3-nonen-2-one. To a stirred and cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (122 μL, 88 mg, 0.870 mmol) and *n*-BuLi (1.44 M in hexane, 605 μL, 0.871 mmol) in THF (1 mL) was added dropwise a solution of 3-nonen-2-one (131 μL, 111 mg, 0.792 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **70a** (168 mg, 0.791 mmol) in THF (36 mL). The reaction mixture was allowed to warm to 0 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (30 mL). The mixture was extracted with Et_2O (20 mL x 2), and the combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 28 g; elution with 10:1 hexane-AcOEt) to give **71a** (207 mg, 75% as a colorless oil). **71a:** a colorless oil, R_f = 0.48 (hexane:AcOEt = 10:1). IR (film) 1715, 1655, 1250 cm^{-1}. ^1H NMR δ 0.13 and 0.17 (each 3H, s, $SiMe_2$), 0.84, 0.86 (each 3H, d, *J* = 6.4 Hz, Me_2), 0.87 (3H, t, *J* = 6.4 Hz, H-5"), 0.91 (9H, s, *t*-Bu), 1.08-1.42 (8H, m, H-1", H-2", H-3", and H-4"), 1.52-1.60 (1H, m, C*H*Me_2), 1.75 (1H, ddd, *J* = 10.4, 7.3,

4.1 Hz, H-5), 2.24-2.32 (1H, m, H-6), 2.42 (1H, dd, *J* = 10.5, 7.3 Hz, H-7), 2.51 (1H, dd, *J* = 10.5, 10.5 Hz, H-7), 2.77 (1H, d, *J* = 19.2 Hz, H-2), 3.35 (1H, dm, *J* = 19.2 Hz, H-2), 4.72 (1H, dd, *J* = 7.3, 2.1 Hz, H-4). ^{13}C NMR δ -4.4 and -4.1 ($SiMe_2$), 14.2 (C-5'), 18.1 (*C*Me_3), 20.3, 22.5 (Me_2), 25.8 (*t*-Bu), 22.8, 26.5, 29.1 and 32.0 (C-1', 2', 3' and 4'), 29.6 (*C*HMe_2) 41.5 (C-6), 45.9 (C-5), 46.5 (C-7), 51.2 (C-2), 110.8 (C-4), 147.3 (C-3), 212.0 (C-1). HRMS calcd for $C_{21}H_{40}O_2Si$: 352.2798, Found: 352.2777.

71b: a colorless oil, R_f = 0.42 (hexane:AcOEt = 15:1). IR (film) 1720, 1655, 1255 cm^{-1}. ^{1}H NMR δ0.13 and 0.16 (each 3H, s, $SiMe_2$), 0.86-0.90 (6H, m, H-5", H-3'), 0.91 (9H, s, *t*-Bu), 1.20-1.42 (12H, m, H-1", H-2", H-3", H-4", H-1' and H-2'), 2.08-2.16 (1H, m, H-6), 2.22-2.28 (1H, m, H-5), 2.44 (1H, dd, *J* = 11.8, 6.6 Hz, H-7), 2.50 (1H, dd, *J* = 11.8, 9.4 Hz, H-7), 2.81 (1H, d, *J* = 17.9, Hz, H-2), 3.45 (1H, dm, *J* = 17.9 Hz, H-2), 4.74 (1H, dd, *J* = 7.0, 2.2 Hz, H-4). ^{13}C NMR δ-4.4 and -4.2 ($SiMe_2$), 14.3, 14.4 (C-5', C-3"), 18.1 (*C*Me_3), 21.3, 22.8, 26.8, 30.2, 32.1, 35.1 (C1', C-2', C-3', C-4', C-1" and C-2"), 25.8 (*t*-Bu), 38.5 (C-5), 42.8 (C-6) 47.0 (C-7), 51.1 (C-2), 111.5 (C-4), 146.8 (C-3), 210.5 (C-1). HRMS: calcd for $C_{21}H_{40}O_2Si$: 352.2798, Found: 352.2771.

71c: a colorless oil, R_f = 0.38 (hexane:AcOEt = 15:1). IR (film) 1710, 1655, 1250 cm^{-1}. ^{1}H NMR δ 0.14 and 0.17 (each 3H, s, $SiMe_2$), 0.86 (3H, t, *J* = 7.1 Hz, H-5"), 0.92 and 0.93 (each 9H, s, *t*-Bu), 1.10-1.48 (8H, m, H-1", H-2", H-3", and H-4"), 2.14 (1H, dd, *J* = 7.7, 2.8 Hz, H-5), 2.31-2.38 (1H, m, H-6), 2.44 (1H, dd, *J* = 11.3, 6.4 Hz, H-7), 2.58 (1H, dd, *J* = 11.3,7.1 Hz, H-7), 2.77 (1H, d, *J* = 16.9 Hz, H-2), 3.52 (1H, dd, *J* = 16.9, 2.1 Hz, H-2), 4.96 (1H, dd, *J* = 7.7, 2.1 Hz, H-4). ^{13}C NMR δ-4.3 and -4.0 ($SiMe_2$), 14.3 (C-5'), 18.1 (*C*Me_3-TBS), 22.9, 27.2, 30.8, 32.2 (C1', C-2', C-3' and C-4'), 25.8 (*t*-Bu-TBS), 29.2 (*t*-Bu), 33.5 (*C*Me_3), 42.2 (C-6), 49.1 (C-7) 49.8 (C-5), 51.3 (C-2), 108.2 (C-4), 147.2 (C-3), 209.4 (C-1). HRMS calcd for $C_{22}H_{42}O_2Si$: 366.2954, Found: 366.2964.

71d: a colorless oil, R_f = 0.55 (hexane:AcOEt = 10:1). IR (film) 1715, 1655, 1250 cm^{-1}. ^{1}H NMR δ0.13 and 0.17 (each 3H, s, $SiMe_2$), 0.71-0.81 (2H, m), 0.87 (3H, t, *J* = 7.1 Hz, H-5"), 0.92 (9H, s, *t*-Bu), 1.10-1.40 (12H, m), 1.60-1.80 (5H, m), 1.84 (1H, ddd, *J* = 7.5, 7.1, 4.1 Hz, H-5), 2.24-2.32 (1H, br m, H-6), 2.42 (1H, dd, *J* = 10.5, 7.3 Hz, H-7), 2.52 (1H, dd, *J* = 10.5, 10.5 Hz, H-7), 2.76 (1H, d, *J* = 19.2 Hz, H-2), 3.34 (1H, dm, *J* = 19.2 Hz, H-2) 4.72 (1H, dd, *J* = 7.5, 2.1 Hz, H-4). ^{13}C NMR δ-4.4 and -4.0 ($SiMe_2$), 14.3 (C-5"), 18.1 (*C*Me_3), 25.8 (*t*-Bu), 22.9, 26.3, 26.5, 26.5, 26.7, 29.3, 30.3, 32.1, 32.6, and 38.7 (C1", C-2", C-3", C-4", C1', C-2', C-3', C-4', C-5' and C-6'), 40.7 (C-6), 44.1 (C-5) 46.4 (C-7), 51.2 (C-2), 110.7 (C-4), 147.3 (C-3), 212.1 (C-1). HRMS calcd for $C_{24}H_{44}O_2Si$: 392.3111 Found: 392.3104.

General procedure for the reaction of 70 with lithium enolate of 4-methoxy-3-buten-2-one (72). This procedure is representative of reactions of **70** with lithium enolate of 4-methoxy-3-buten-2-one (**72**): To a stirred and cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (202 μL, 146 mg, 1.44 mmol) and *n*-BuLi (1.44 M in hexane, 1.00 mL, 1.44 mmol) in THF (1 mL) was added dropwise a solution of 4-methoxy-3-buten-2-one (122 μL, 120 mg, 1.20 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **70a** (255 mg, 1.20 mmol) in THF (58 mL). The reaction mixture was allowed to warm to 0 °C over 1 h, and then quenched by saturated aqueous NH_4Cl solution (50 mL). The mixture was extracted with Et_2O (50 mL x 2), and the combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 15:1 hexane-AcOEt) to give **73a** (261 mg, 70% as a colorless oil).

73a: a colorless oil, R_f = 0.28 (hexane:AcOEt = 15:1). IR (film) 1715, 1655, 1260 cm^{-1}. ^{1}H NMR δ 0.13 and 0.16 (each 3H, s, $SiMe_2$), 0.88-0.91 (9H, m, CH*Me*$_2$ and H-5"), 0.91 (9H, s, *t*-Bu), 1.69 (1H, ddd, *J* = 13.0, 6.6, 3.2 Hz, H-5), 1.75-1.82 (1H, m, C*H*Me_2), 2.81 (1H, dd, *J* = 10.5, 7.1 Hz, H-7), 2.94 (1H, ddd, *J* = 10.5, 7.1, 0.9 Hz, H-7), 2.93 (1H, d, *J* = 19.3 Hz, H-2), 3.29 (3H, s, OMe), 3.33 (1H, dm, *J* = 19.3 Hz, H-2), 3.80 (1H, ddd, *J* = 7.1, 7.1, 3.2 Hz, H-6), 4.84 (1H, dd, *J* = 6.6, 1.9 Hz, H-4). ^{13}C NMR δ -4.1 and -4.5 ($SiMe_2$), 18.1 (*C*Me_3),

20.5 and 21.8 (CH*Me*$_2$), 25.8 (*t*-Bu), 29.4 (*C*HMe$_2$), 46.4 (C-7), 47.2 (C-5), 51.0 (C-2), 56.7 (OMe), 80.4 (C-6), 110.2 (C-4), 147.3 (C-3), 207.8 (C-1). HRMS calcd for $C_{17}H_{32}O_3Si$: 312.2121, Found: 312.2120.

73b: a colorless oil, R_f = 0.35 (hexane:AcOEt = 10:1). IR (film) 1715, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.13 and 0.15 (each 3H, s, SiMe$_2$), 0.89 (3H, t, *J* = 7.0 Hz, H-3'), 0.90 (9H, s, *t*-Bu), 1.24-1.39 (2H, m, H-2'), 1.45 (2H, dt, *J* = 7.1, 7.1 Hz, H-1'), 2.21 (1H, dtd, *J* = 7.1, 7.1, 3.0 Hz, H-5), 2.78 (1H, dd, *J* = 11.8, 6.0 Hz, H-7), 2.92 (1H, dd, *J* = 11.8, 7.5 Hz, H-7), 3.01 (1H, d, *J* = 18.2 Hz H-2), 3.31 (3H, s, OMe), 3.33 (1H, d, *J* = 18.2 Hz, H-2), 3.65 (1H, ddd, *J* = 7.5, 6.4, 3.0 Hz, H-6), 4.80 (1H, dd, *J* = 7.1, 1.7 Hz, H-4). ^{13}C NMR δ -4.2 and -4.5 (SiMe$_2$), 14.3 (C-3'), 18.1 (*C*Me$_3$) 20.9 (C-2'), 25.8 (*t*-Bu), 34.1 (C-1'), 40.0 (C-7), 46.6 (C-5), 51.0 (C-2), 57.2 (OMe), 81.6 (C-6), 110.3 (C-4), 146.6 (C-3), 206.8 (C-1). HRMS calcd for $C_{17}H_{32}O_3Si$: 312.2121, Found: 312.2097.

73c: a colorless oil, R_f = 0.27 (hexane:AcOEt = 10:1). IR (film) 1715, 1655, 1250 cm^{-1}. ^{1}H NMR δ 0.14 and 0.16 (each 3H, s, SiMe$_2$), 0.90 (9H, s, *t*-Bu-TBS), 0.95 (9H, s, *t*-Bu), 1.90 (1H, dd, *J* = 6.8, 2.8 Hz, H-5), 2.73 (1H, dd, *J* = 11.5, 5.8 Hz, H-7), 2.94 (1H, dd, *J* = 11.5, 6.6 Hz, H-7), 3.0 (1H, d, *J* = 17.9 Hz, H-2), 3.26 (3H, s, OMe), 3.36 (1H, dm, *J* = 17.9 Hz, H-2), 3.90 (1H, ddd, *J* = 6.6, 5.8, 2.8 Hz, H-6), 5.05 (1H, dd, *J* = 6.8, 1.5 Hz, H-4). ^{13}C NMR δ -4.1 and -4.4 (SiMe$_2$), 18.1 (*C*Me$_3$-TBS), 25.8 (*t*-Bu), 28.8 (*t*-Bu), 33.3 (*C*Me3), 47.2 (C-7), 50.3 (C-5), 51.0 (C-2), 56.2 (OMe), 81.0 (C-6), 107.7 (C-4), 147.1 (C-3), 206.9 (C-1). HRMS calcd for $C_{18}H_{34}O_3Si$: 326.2277, Found: 326.2283.

73d: a colorless oil, R_f = 0.29 (hexane:AcOEt = 15:1). IR (film) 1715, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.13 and 0.16 (each 3H, s, SiMe$_2$), 0.75-0.90 (2H, m), 0.90 (9H, s, *t*-Bu), 1.08-1.15 (1H, m), 1.18-1.28 (2H, m), 1.42-1.51 (1H, m, H-1'), 1.60-1.82 (6H, m), 2.80 (1H, dd, *J* = 10.3, 6.8 Hz, H-7), 2.90 (1H, d, *J* = 19.2 Hz, H-2), 2.94 (1H, ddd, *J* = 10.3, 7.3, 0.9 Hz, H-7), 3.27 (3H, s, OMe), 3.33 (1H, dm, *J* = 19.2, H-2), 3.82 (1H, ddd, *J* = 7.3, 6.8, 3.2 Hz, H-6), 4.82 (1H, dd, *J* = 7.1, 2.1, H-4). ^{13}C NMR δ -4.2 and -4.1 (SiMe$_2$), 18.1 (*C*Me$_3$), 25.8 (*t*-Bu), 26.3, 26.5, 26.7, 30.5, 32.2, 38.4, 45.8, 46.3, 50.9 (C1', C-2', C-3', C-4', C-5' and C-6'), 56.6 (OMe), 79.7 (C-6), 110.1 (C-4), 147.4 (C-3), 207.8 (C-1). HRMS calcd for $C_{20}H_{36}O_3Si$: 352.2434, Found: 352.2411.

Cyclopentenecarbonyl(dimethyl)phenylsilane (74) To a cooled (-80 °C) solution of PhMe$_2$SiLi (0.28 M in Et$_2$O, 133 mL, 37.4 mmol) in Et$_2$O (100 mL) was added dropwise cyclopentenecarboxaldehyde[1] (3.00 g, 31.2 mmol). The solution was allowed to warm to 0 °C over 1.5 h, and then quenched by saturated aqueous NH$_4$Cl solution (100 mL). The mixture was diluted with water (100 mL), and then extracted with Et$_2$O (100 mL x 2), and the combined organic phases were washed with saturated brine (200 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g; elution with 25:1 hexane-AcOEt) to give cyclopetenyl(dimethyl(phenyl)-silyl)methanol (4.99 g, 69% as an yellow oil).

A solution of this material (4.99 g, 21.5 mmol) in CH$_2$Cl$_2$ (3 mL) was added at -60 °C and over 5 min to a solution of chloro(dimethyl)sulfonium chloride, which was prepared by dropwise addition of oxalyl chloride (2.10 mL, 3.06 g, 24.1 mmol) to a cooled (-80 °C) solution of DMSO (2.83 mL, 3.12 g, 39.9 mmol) in CH$_2$Cl$_2$ (60 mL). After stirring at ca. -60 °C for 15 min, triethylamine (13.9 mL, 10.1 g, 99.8 mmol) was added. The solution was allowed to warm to room temperature over 15 min. The mixture was diluted with water (100 mL), and then extracted with CH$_2$Cl$_2$ (50 mL x 2). The combined organic phases were washed with saturated brine (100 mL), dried, and concentrated. The residual oil was subjected to column chromatography twice (silica gel; elution with 10:1 hexane-AcOEt) to give **74** (3.30 g, 67% as an yellow oil), which solidified on keeping in a refrigerator. yellow prisms, mp 69-70 °C (Et$_2$O-hexane), R_f = 0.55 (hexane:AcOEt = 5:1). IR (film) 1605 cm^{-1}. ^{1}H NMR δ 0.52 (6H, s, SiMe$_2$), 1.82 (2H, tt, *J* = 7.7, 7.7 Hz, H-4'), 2.44-2.50 (4H, m, H-3' and H-5'), 6.59 (1H, br s, H-2') , 7.35-7.42 (3H, m, Ar), 7.54-7.57 (2H, m, Ar). ^{13}C NMR δ -2.9 (SiMe$_2$), 22.2, 29.7, 34.5 (C-3,

(1) Brown, J. B.; Hembest, H. B.; Jones, E. R. H. *J. Chem. Soc.* **1950**, 3634-3641.

C-4, and C-5), 128.3, 129.8, 134.1, and 136.3 (Ar) 148.0 (C-2), 151.6 (C-1), 232.0 (C=O). Anal. calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.87, Found: C, 73.00; H, 7.77.

Cyclohexenecarbonyl(dimethyl)phenylsilane (75) To a cooled (-80 °C) solution of $PhMe_2SiLi$ (0.32 M in Et_2O, 140 mL, 44.8 mmol) in Et_2O (100 mL) was added dropwise cyclohexenecarboxaldehyde[2] (4.10 g, 37.2 mmol) in THF (5 mL). The solution was allowed to warm to 0 °C over 2 h, and then quenched by saturated aqueous NH_4Cl solution (100 mL). The mixture was extracted with Et_2O (50 mL x 2), and the combined organic phases were washed with saturated brine (100 mL), dried, and concentrated. The residual oil was subjected to column chromatography three times (silica gel; elution with 10:1, 20:1, and 25:1 hexane-AcOEt) to give cyclohexenyl(dimethyl(phenyl)silyl)methanol (3.70 g, 41% as an yellow oil).

A solution of this material (3.70 g, 15.0 mmol) in CH_2Cl_2 (1 mL) was added at -60 °C and over 5 min to a solution of chloro(dimethyl)sulfonium chloride, which was prepared by dropwise addition of oxalyl chloride (1.4 mL, 2.04 g, 16.1 mmol) to a cooled (-80 °C) solution of DMSO (2.10 mL, 2.31 g, 29.6 mmol) in CH_2Cl_2 (47 mL). After stirring at ca. -60 °C for 15 min, triethylamine (10.5 mL, 7.62 g, 75.3 mmol) was added. The solution was allowed to warm to room temperature over 15 min. The mixture was diluted with water (100 mL), and then extracted with CH_2Cl_2 (50 mL x 2). The combined organic phases were washed with saturated brine (100 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 80 g; elution with 15:1 hexane-AcOEt) to give **75** (3.00 g, 82% as an yellow oil), which solidified on keeping in a refrigerator. yellow prisms, mp 73-74 °C, (Et_2O-hexane), R_f = 0.58 (hexane:AcOEt = 5:1). IR (film) 1635, 1260, 1240 cm^{-1}. ^1H NMR δ 0.52 (6H, s, Me_2), 1.56-1.58 (4H, m, H-4 and H-5), 2.10-2.18 (4H, m, H-3 and H-6), 6.77-6.79 (1H, m, H-2) , 7.35-7.79 (3H, m, Ar), 7.51-7.54 (2H, m, Ar). ^{13}C NMR δ -2.2 ($SiMe_2$), 21.8, 22.1, 26.4 (C-3, C-4, C-5, and C-6), 128.2, 129.6, 134.0 and 136.9 (Ar) 145.8 (C-1), 147.0 (C-2), 233.8 (C=O). Anal. calcd for $C_{15}H_{20}OSi$: C, 73.7; H, 8.25, Found: C, 73.50; H, 8.06.

General procedure for the [3 + 4] annulation using acylsilanes 74. This procedure is representative of reactions of **74** with lithium enolate of 3-none-2-one (**13c**): To a stirred and cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (84 μL, 61 mg, 0.603 mmol) and *n*-BuLi (1.41 M in hexane, 426 μL, 0.600 mmol) in THF (0.5 mL) was added dropwise a solution of 3-nonen-2-one (99 μL, 84 mg, 0.600 mmol) in THF (1 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (0 °C) solution of **74** (125 mg, 0.542 mmol) in THF (24 mL). The reaction mixture was stirred at 0 °C for 30 min, and then quenched by acetic acid (36 mg, 0.600 mmol). The mixture was concentrated, and then the residue was subjected to column chromatography (silica gel, 10 g; elution with 10:1 hexane-AcOEt) to give **76a** (164 mg, 82%).

76a: a colorless oil, R_f = 0.26 (hexane:AcOEt = 20:1). IR (film) 1705, 1685, 1250 cm^{-1}. ^1H NMR δ0.47 and 0.46 (each 3H, s, $SiMe_2$), 0.89 (3H, t, *J* = 7.1 Hz, H-5'), 0.08-1.42 (9H, m), 1.42-1.52 (1H, m, H-8), 1.62-1.65 (1H, m, H-9), 1.80-1.87 (1H, m, H-8), 1.94-2.00 (1H, m, H-6), 1.99-2.08 (1H, br m, H-10), 2.35-2.42 (1H, m, H-10), 2.47 (2H, d, *J* = 5.8 Hz, H-5), 2.81-2.86 (1H, br m, H-7), 2.82 (1H, d, *J* = 15.0 Hz, H-3), 3.53 (1H, dm, *J* = 15.0 Hz, H-3), 7.35-7.42 (3H, m, Ar), 7.52-7.62 (2H, m, Ar). ^{13}C NMR δ-0.6 ($SiMe_2$), 14.3 (C-5'), 22.8, 25.3 (C-9), 27.4, 29.0, 31.2 (C-8), 31.3 (C-10), 32.2, 41.1 (C-6), 44.5 (C-7), 48.4 (C-5), 51.5 (C-3), 125.7 (C-2), 128.0, 130.0, 133.6 and 136.0 (Ar), 137.4 (C-2), 207.4 (C-4). HRMS calcd for $C_{23}H_{34}O_2Si$: 370.2328, Found: 370.2330.

76b: a colorless oil, R_f = 0.23 (hexane:AcOEt = 20:1). IR (film) 1705, 1655, 1250 cm^{-1}. ^1H NMR δ 0.45 and 0.45 (each 3H, s, $SiMe_2$), 0.85 (3H, d, *J* = 6.6 Hz, CH*Me*$_2$), 0.91 (3H, d, *J* = 6.8 Hz, CH*Me*$_2$), 1.44-1.52 (2H, m, H-8 and H-9), 1.66-1.71 (2H, m, H-9 and C*H*Me_2), 1.99 (1H, dddd, *J* = 10.5, 4.5, 4.5, 4.5 Hz, H-6), 2.26 (1H, dd, *J* = 13.7, 4.5 Hz, H-5), 2.26-2.32 (2H, br m, H-10), 2.51 (1H, dd, *J* = 13.7, 10.5 Hz, H-5), 2.72-2.79 (1H, br

(2) Heilbron, I.; Jones, E. R. H.; Richardson, R. W.; Sondheimer, F. *J. Chem. Soc.* **1949**, 737-741.

m, H-7), 2.77 (1H, d, *J* = 16.9 Hz, H-3), 3.54 (1H, dddd, *J* = 16.9, 2.6, 2.6, 2.6 Hz, H-3), 7.36-7.43 (3H, m, Ar), 7.58-7.61 (2H, m, Ar). ^{13}C NMR δ -0.6 and -0.58 ($SiMe_2$), 19.4 and 22.2 ($CHMe_2$), 24.0 and 28.3 (C-8 and C-9), 29.0 ($CHMe_2$), 30.0 (C-10), 40.6 (C-5), 42.9 (C-7), 44.8 (C-6), 50.2 (C-3), 125.8 (C-1), 128.1, 130.1, 133.5 and 135.3 (Ar), 137.4 (C-2), 210.5 (C-4). HRMS calcd for $C_{21}H_{30}O_2Si$: 342.2015, Found: 342.2010.

76c: a colorless oil, R_f = 0.19 (hexane:AcOEt = 20:1). IR (film) 1705, 1685, 1255 cm^{-1}. ^{1}H NMR δ 0.46 and 0.48 (each 3H, s, $SiMe_2$), 0.78 (3H, s, Me), 0.97 (3H, s, Me), 1.30-1.39 (1H, m, H-8), 1.46-1.54 (1H, br m, H-9), 1.63-1.71 (1H, m, H-8), 1.75-1.83 (1H, m, H-9), 1.92-2.01 (1H, m, H-10), 2.21 (1H, d, *J* = 10.9 Hz, H-5), 2.39 (1h, d, *J* = 10.9 Hz, H-5), 2.44-2.51 (2H, br m, H-5 and H-10), 2.79 (1H, d, *J* = 16.2 Hz H-3), 3.40 (1H, m, *J* = 16.2 Hz, H-3), 7.36-7.43 (3H, m, Ar), 7.59-7.62 (2H, m, Ar). ^{13}C NMR δ -0.65 ($SiMe_2$), 22.4 (Me), 25.4 (C-8'), 29.0 (Me), 29.1 (C-9), 31.2 (C-10), 41.1 (C-6), 49.0 (C-7), 51.3 (C-3), 58.3 (C-5), 126.5 (C-1), 128.1, 130.1, 133.6 and 137.0 (Ar), 137.3 (C-2), 207.5 (C-4). HRMS calcd for $C_{20}H_{28}O_2Si$: 328.1859, Found: 328.1884.

76d: a colorless oil, R_f = 0.11 (hexane:AcOEt = 15:1). IR (film) 1710, 1685, 1250 cm^{-1}. ^{1}H NMR δ 0.41 (3H, s, $SiMe_2$), 0.45 and 0.46 (each 3H, s, $SiMe_2$), 1.34-1.44, 1.70-1.80 and 1.80-1.86 (4H, m, H-8 and H-9), 2.30-2.37 (1H, m) and 2.14-2.24 (each 1H, m, H-10), 2.60 (1H, ddd, *J* = 12.4, 4.9, 0.9 Hz, H-5), 2.69 (1H, br dd, *J* = 5.1, 5.1 Hz, H-7), 2.85 (1H, dd, *J* = 12.4, 5.1 Hz, H-5), 2.99 (1H, d, *J* = 15.5 Hz, H-3), 3.32 (3H, s, OMe), 3.38 (1H, dm, *J* = 15.5 Hz, H-3), 3.61 (1H, ddd, *J* = 5.1, 4.9, 2.4 Hz, H-6), 7.26-7.43 (3H, m, Ar), 7.58-7.63 (2H, m, Ar). ^{13}C NMR δ -0.69 and -0.58 ($SiMe_2$), 25.4 (C-9), 31.2 (C-10), 31.2 (C-8), 44.8 (C-7), 47.8 (C-5), 51.6 (C-3), 57.3 (OMe), 81.5 (C-6), 124.5 (C-1), 128.0, 133.2, 133.5 and 136.1 (Ar), 137.7 (C-2), 205.3 (C-4). HRMS calcd for $C_{19}H_{26}O_3Si$: 330.1650, Found: 330.1639.

76e: a colorless oil, R_f = 0.51 (hexane:AcOEt = 5:1). IR (film) 1700, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.46 and 0.47 (each 3H, s, $SiMe_2$), 1.16-1.26 (1H, m), 1.27-1.44 (3H, m), 1.60-1.77 (5H, m), 1.83-1.90 (1H, m), 1.97-2.04 (1H, m, H-13), 2.42-2.51 (2H, m, H-9 and 13), 2.78-2.85 (1H, m, H-5), 2.87 (1H, app t, *J* ≅ 8 Hz, H-10), 3.09 (1H, dm, *J* = 15.6 Hz, H-3), 3.24 (1H, dm, *J* = 15.6 Hz, H-3), 7.36-7.42 (3H, m, Ar), 7.60-7.63 (2H, m, Ar). ^{13}C NMR δ -0.68 and -0.58 ($SiMe_2$), 25.4, 25.6, 26.9, 29.5, 33.7, 32.1 (C-13), 40.6 (C-10), 48.1 (C-9), 49.1 (C-3), 57.2 (C-5), 125.1 (C-1), 128.0, 130.1, 133.6 and 136.4 (Ar), 137.4 (C-2), 210.1 (C-1). HRMS calcd for $C_{21}H_{28}O_2Si$: 340.1857, Found: 340.1841.

76f: a colorless oil, R_f = 0.22 (hexane:AcOEt = 20:1). IR (film) 1700, 1655, 1250 cm^{-1}. ^{1}H NMR δ 0.47 and 0.49 (each 3H, s, $SiMe_2$), 0.67 (1H, ddd, *J* = 13.0, 13.0, 3.3 Hz, H-9), 1.08-1.17 (2H, m), 1.32-1.42 (2H, m), 1.42-1.50 (2H, m), 1.62-1.74 (3H, m), 1.76-1.86 (1H, m, H-14), 1.86-1.93 (1H, m, H-10), 1.88-1.97 (1H, m, H-12), 2.05 (1H, dm, *J* = 13.2 Hz, H-6), 2.41 (1H, dm, *J* = 15.3 Hz, H-14), 2.72-2.76 (1H, app br t, H-5), 2.76 (1H, d, *J* = 12.8 Hz, H-3), 2.93 (1H, br dd, *J* = 8.3, 8.3 Hz, H-10a), 3.66 (1H, dm, *J* = 12.8 Hz, H-3), 7.34-7.41 (3H, m, Ar), 7.61-7.63 (2H, m, Ar). ^{13}C NMR δ -0.63 and -0.59 ($SiMe_2$), 22.3, 26.1, 26.6, 31.2, 23.4, 28.4 (C-6), 31.2 (C-14), 31.8 (C-12), 45.6 (C-11), 47.3 (C-10), 51.5 (C-3), 55.4 (C-5), 126.1 (C-1), 127.9, 130.0, 133.8 and 135.8 (Ar), 137.3 (C-2), 205.7 (C-4). HRMS calcd for $C_{22}H_{30}O_2Si$: 354.2013, Found: 354.2037.

76g: a colorless oil, R_f = 0.21 (hexane:AcOEt = 20:1). IR (film) 1775, 1560, 1260 cm^{-1}. ^{1}H NMR δ 0.46 and 0.46 (each 3H, s, $SiMe_2$), 1.50-1.59 (1H, m, H-10), 1.62-1.69 (1H, m, H-8), 1.72-1.79 (1H, m, H-10), 1.87-1.93 (1H, m, H-9), 2.05-2.13 (1H, m, H-8), 2.23-2.29 (1H, m, H-9), 3.20 (1H, d, *J* = 18.2 Hz, H-3), 3.46 (1H, d, *J* = 18.2 Hz, H-3), 3.70 (1H, dd, *J* = 9.2, 4.3 Hz, H-7), 7.18-7.31 (4H, m, Ar), 7.37-7.44 (3H, m, Ar), 7.58-7.62 (2H, m, Ar). ^{13}C NMR δ 0.93 and 1.29 ($SiMe_2$), 27.2 (C-10), 28.0 (C-9), 35.1 (C-8), 54.2 (C-7), 60.2 (C-3), 124.1 (C-1), 125.0, 127.8, 128.1, 128.9, 129.9, 133.4, 128.9 and 145.6 (Ar), 146.3 (C-2), 213.7 (C-4). HRMS calcd for $C_{22}H_{24}O_2Si$: 348.1544, Found: 348.1545.

77a: a colorless oil, R_f = 0.45 (hexane:AcOEt = 10:1). IR (film) 1710, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.45 and 0.47 (each 3H, s, $SiMe_2$), 0.89 (3H, t, *J* = 7.0 Hz, H-5'), 1.00-1.13 (2H, m), 1.27-1.36 (9H, m), 1.54 (1H, br dd,

J = 12.8, 12.8 Hz, H-11), 1.59-1.65 (2H, m), 1.75 (1H, dm, *J* = 13.0 Hz), 2.12 (1H, dm, *J* = 11.5 Hz, H-7), 2.22 (1H, dd, *J* = 14.1, 3.6 Hz, H-5), 2.24-2.30 (1H, m, H-6), 2.31 (1H, dd, *J* = 14.1, 2.8 Hz, H-5), 2.72 (1H, d, *J* = 14.3 Hz, H-3), 2.70-2.76 (1H, br m, H-11), 3.76 (1H, dm, *J* = 14.3 Hz, H-3), 7.36-7.42 (3H, m, Ar), 7.59-7.61 (2H, m, Ar). ^{13}C NMR δ -0.92 and -0.87 ($SiMe_2$), 14.3 (C-5"), 22.8, 26.7, 27.1, 27.5, 27.6, 32.1, 33.7, 30.2 (C-11), 35.9 (C-6), 44.8 (C-7), 45.5 (C-5), 48.8 (C-3), 124.8 (C-1), 128.0, 130.0 and 133.6 (Ar), 137.4 (C-2), 207.7 (C-4). HRMS calcd for $C_{24}H_{36}O_2Si$: 384.2482, Found: 384.2458.

77b: a colorless oil, R_f = 0.37 (hexane:AcOEt = 10:1). IR (film) 1710, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.45 and 0.47 (each 3H, s, $SiMe_2$), 0.94 (3H, d, *J* = 6.6 Hz, CH*Me*$_2$), 0.95 (3
H, d, *J* = 6.4 Hz, CH*Me*$_2$), 0.99-1.10 (2H, m), 1.26-1.37 (1H, m, H-9), 1.45 (1H, dddd, *J* = 13.0, 13.0, 3.4, 3.4 Hz, H-11), 1.50-1.56 (1H, m, C*H*Me$_2$), 1.57-1.67 (2H, m), 1.76 (1H, br d, *J* = 12.6 Hz, H-9), 1.82-1.90 (1H, m, H-6), 2.22 (1H, dd, *J* = 17.4, 12.7 Hz, H-5), 2.32 (1H, br d, *J* = 12.0 Hz, H-7), 2.47 (1H, ddm, *J* = 17.4, 3.8 Hz, H-5), 2.71 (1H, d, *J* = 14.1 Hz, H-3), 2.82 (1H, br dm, *J* = 13.0 Hz, H-11), 3.78 (1H, ddd, *J* = 14.1, 2.6, 2.6 Hz, H-3), 7.36-7.42 (3H, m, Ar), 7.59-7.62 (2H, m, Ar). ^{13}C NMR δ -0.9 and -0.9 ($SiMe_2$), 21.5 and 21.8 ($CHMe_2$), 26.8 (C-8), 27.4 (C-9), 28.0 (C-10), 29.4 (*C*HMe$_2$), 30.8 (C-11), 42.0 (C-6), 42.8 (C-7), 44.3 (C-5), 48.4 (C-3), 125.2 (C-1), 128.0, 130.0, 133.3 and 133.6 (Ar), 137.4 (C-2), 207.5 (C-4). HRMS calcd for $C_{22}H_{32}O_2Si$: 356.2170, Found: 356.2197.

77c: a colorless oil, R_f = 0.4 (hexane:AcOEt = 10:1). IR (film) 1705, 1655, 1255 cm-1. ^{1}H NMR δ 0.47 and 0.47 (each 3H, s, $SiMe_2$), 0.91 (3H, s, Me), 0.98 (3H, s, Me), 1.20-1.31 (2H, m), 1.43-1.57 (3H, m), 1.58-1.66 (1H, m), 1.80-1.88 (1H, m, H-11), 1.85 (1H, d, *J* = 10.5 Hz, H-5), 2.00 (1H, dd, *J* = 6.6, 6.6 Hz, H-7), 2.64 (1H, d, *J* = 10.5 Hz, H-5), 2.72-2.78 (1H, m, H-11), 2.73 (1H, dd, *J* = 19.9, 1.1 Hz, H-3), 3.26 (1H, dd, *J* = 19.9, 3.2 Hz, H-3), 7.36-7.43 (3H, m, Ar), 7.57-7.59 (2H, m, Ar). ^{13}C NMR δ -0.96, -0.79 ($SiMe_2$), 22.5, 23.3 and 23.5, 23.7 (C-11), 25.2 and 27.2 (Me), 42.4 (C-6), 44.2 (C-7), 50.2 (C-3), 55.6 (C-5), 120.7 (C-1), 128.2, 130.2, 133.5 and 136.9 (Ar), 140.2 (C-2), 210.0 (C-4). HRMS calcd for $C_{21}H_{30}O_2Si$: 342.2013, Found: 342.2026.

77d: a pale yellow oil, R_f = 0.34 (hexane:AcOEt = 5:1). IR (film) 1705, 1655, 1255 cm^{-1}. ^{1}H NMR δ 0.45 and 0.46 (each 3H, s, $SiMe_2$), 1.12-1.22 (1H, m), 1.32-1.43 (2H, m) and 1.53-1.60 (1H, m), 1.63-1.81 (4H, m), 2.26-2.31 (1H, br m, H-7), 2.56 (1H, dd, *J* = 16.5, 3.6 Hz, H-5), 2.70 (1H, dd, *J* = 16.5, 8.8 Hz, H-5), 2.67-2.73 (1H, m, H-11), 3.29 (2H, s, H-3), 3.31 (3H, s, OMe), 3.72 (1H, ddd, *J* = 8.8, 3.6, 3.6 Hz, H-6), 7.36-7.43 (3H, m, Ar), 7.57-7.61 (2H, m, Ar). ^{13}C NMR δ -0.86 ($SiMe_2$), 26.4, 26.8, 28.7 (C-8, C-9 and C-10), 29.2 (C-11), 44.4 (C-5), 44.7 (C-7), 50.2 (C-3), 57.3 (OMe), 78.9 (C-6), 121.5 (C-1), 128.1, 130.1, 133.6 and 134.2 (Ar), 137.2 (C-2), 205.8 (C-4). HRMS calcd for $C_{20}H_{28}O_3Si$: 344.1806, Found: 344.1816.

77e: a colorless oil, R_f = 0.45 (hexane:AcOEt = 10:1). IR (film) 1700, 1660, 1250 cm^{-1}. ^{1}H NMR δ 0.45 and 0.47 (each 3H, s, $SiMe_2$), 1.20-1.64 (9H, m), 1.69-1.78 (2H, m), 1.88-2.17 (2H, m), 2.34 (1H, ddd, *J* = 14.1, 6.0, 4.9 Hz, H-6), 2.45 (1H, dddd, *J* = 9.2, 9.2, 9.2, 2.6 Hz, H-11), 2.60-2.65 (1H, br m, H-10), 2.81 (1H, dddm, *J* = 9.2, 9.2, 9.2 Hz, H-1), 2.86 (1H, d, *J* = 14.7 Hz, H-3), 3.57 (1H, dm, *J* = 14.7 Hz, H-3), 7.36-7.42 (3H, m, Ar), 7.60-7.62 (2H, m, Ar). ^{13}C NMR δ -0.91, -0.68 ($SiMe_2$), 22.6, 23.0, 24.7, 24.9, 26.8, 27.4 and 29.1 (C-6, C-7, C-8, C-9, C-12, C-13 and C-14), 40.0 (C-10), 49.0 (C-3), 50.0 (C-11), 58.3 (C-1), 121.6 (C-5), 128.0, 130.0, 133.7 and 137.4 (Ar), 137.8 (C-4), 207.7 (C-2). HRMS calcd for $C_{22}H_{30}O_2Si$: 354.2013, Found: 354.2038.

77e' (C-1 epimer of 77e): a colorless oil, R_f = 0.45 (hexane:AcOEt = 10:1). IR (film) 1705, 1650, 1250 cm^{-1}. ^{1}H NMR δ 0.44 and 0.45 (each 3H, s, $SiMe_2$), 1.04-1.15 (2H, m), 1.33-1.73 (7H, m), 1.74-1.85 (4H, m), 2.30 (1H, br dm, *J* = 12.2 Hz, H-11), 2.33-2.40 (1H, m, H-10), 2.57 (1H, ddd, *J* = 10.9, 8.5, 8.5 Hz, H-1), 2.88 (1H, d, *J* = 18.2 Hz, H-3), 2.92 (1H, br dm, *J* = 13.2 Hz, H-6), 3.69 (1H, ddd, *J* = 18.2, 2.8, 2.8 Hz, H-3), 7.36-7.42 (3H, m, Ar), 7.53-7.59 (2H, m, Ar). ^{13}C NMR δ -0.82 and -0.72 ($SiMe_2$), 25.1, 26.9, 27.1, 27.7, 28.4, 29.3 (C-7, C-8, C-9, C-11, C-12, C-13 and C-14), 30.3 (C-6), 42.8 (C-11), 43.1 (C-10), 48.8 (C-3), 52.0 (C-1), 124.5 (C-

5), 128.1, 130.0, 133.6 and 134.1 (Ar), 137.3 (C-4), 209.7 (C-2). HRMS calcd for $C_{22}H_{30}O_2Si$: 354.2013, Found: 354.2024.

77f: colorless prisms, $R_f = 0.47$ (hexane:AcOEt = 10:1). mp 75 °C (hexane). IR (KBr) 1700, 1670, 1250 cm^{-1}. ^1H NMR δ 0.47 and 0.49 (each 3H, s, $SiMe_2$), 0.76 (1H, dddd, *J* = 12.2, 12.2, 12.2, 3.2 Hz, H-9), 1.08-1.68 (13H, H-6, H-7, H-8, H-9, H-12, H-13 and H-14), 1.90 (1H, br dm, *J* = 12.2 Hz, H-10), 2.05 (1H, br dm, *J* = 13.0 Hz, H-6), 2.54 (1H, ddd, *J* = 14.5, 7.4, 2.0 Hz, H-15), 2.67-2.73 (2H, m, H-5 and 11), 2.73 (1H, *J* = 12.4 Hz, H-3), 7.34-7.41 (3H, m, Ar), 7.61-7.64 (2H, m, Ar). ^{13}C NMR δ -0.8 and -0.6 ($SiMe_2$), 21.2, 22.0, 22.4, 23.0,24.7, 26.4, 27.8 (C-7, C-8, C-9, C-12, C-13, C-14 and C-15), 27.9 (C-6), 43.0 (C-11), 49.7 (C-10), 50.2 (C-3), 55.9 (C-5), 121.6 (C-2), 127.9, 129.9, 133.9 and 137.2 (Ar), 137.8 (C-2), 205.0 (C-4). HRMS calcd for $C_{23}H_{32}O_2Si$: 368.2170, Found: 368.2170. Anal. calcd for $C_{23}H_{32}O_2Si$: C, 74.90; H, 8.75. Found: C, 74.86; H, 8.64.

77g: a colorless oil, $R_f = 0.42$ (hexane:AcOEt = 10:1). IR (film) 1780 cm^{-1}. ^1H NMR δ 0.45 and 0.49 (each 3H, s, $SiMe_2$), 1.09 (1H, dddd, *J* = 13.2, 11.8, 3.6, 1.5 Hz, H-8), 1.26-1.34 (1H, m, H-9), 1.40-1.50 (1H, m, H-10), 1.58-1.75 (3H, m, H-9, H-10 and H-11), 2.05-2.10 (1H, br m, H-8), 2.26 (1H, br dm, *J* = 13.7 Hz, H-11), 3.03 (1H, d, *J* = 16.5 Hz, H-3), 3.04 (1H, dd, *J* = 13.2, 6.4 Hz, H-7), 3.67 (1H, d, *J* = 16.5 Hz, H-3), 7.13-7.26 (4H, m, Ar), 7.30-7.47 (3H, m, Ar), 7.52-7.72 (2H, m, Ar). ^{13}C NMR δ 1.1 and 0.7 ($SiMe_2$), 22.5 (C-10), 24.0 (C-9), 24.9 (C-11), 33.0 (C-8), 43.6 (C-7), 59.6 (C-3), 124.5 (C-1), 125.4, 127.8, 128.1, 128.9, 129.9, 133.6, 138.9 and 144.2 (Ar), 148.1 (C-2), 213.7 (C-4). HRMS calcd for $C_{23}H_{26}O_2Si$: 362.1700, Found: 362.1716.

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Table 1. Crystallographic Data for Compounds 15f and 77f

	15f	**77f**
Diffractometer	Rigaku AFC7R	Rigaku RAXIS-II
Radiation	Mo-Kα (λ = 0.71069Å)	Mo-Kα (λ = 0.71070Å)
Molecular formula	$C_{20}H_{38}O_2Si_2$	$C_{23}H_{32}O_2Si$
Formula weight	366.69	368.59
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$ (#4)	Fdd2 (#43)
a, Å	13.358(5)	18.7152(7)
b, Å	6.663(5)	54.445 (2)
c, Å	14.382(4)	8.2853(3)
β, deg	117.31(2)	
V, Å^3	1137.4(9)	8442.3604 (8)
Z	2	16
D_{calc}, g/cm^{-3}	1.071	1.160
μ(Mo*K*α), cm^{-1}	1.65	1.25
F_{000}	404.00	3200.00
Goodness of fit indicator	1.59	1.33
No. of observations (I>3.00σ(I))	1790	1499
No. of variable parameters	216	234
Residual: R	0.047	0.048
Residual: R_w	0.049	0.069

ケイ素の特性を利用する [3 + 2] アニュレーション法の開発とその天然物合成への応用

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Development of a Silicon-Mediated [3 + 2] Annulation and Its Application to the Synthesis of Natural Products

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This review describes highly efficient [3 + 2] annulation based on Brook rearrangement for functionalized cyclopetenols, which we have recently developed, and its application to the synthesis of natural products.

本総合論文では，最近われわれが開発した Brook 転位を利用する [3 + 2] アニュレーションによる五員炭素環形成反応とその天然物合成への応用について概説する．

Key words:

[3 + 2] annulation; cyclopentane; Brook rearrangement; synthesis; prostanoid

はじめに

五員炭素環は，多くの医薬品や生物活性天然物そして理論的に興味が持たれる化合物の構成成分となっていることから近年注目を集めており，ジカルボニル化合物のアルドール反応に代表されるような従来法に加えて，種々の新しい環形成法が報告されてきている．[1)]中でも，複数の炭素-炭素結合形成反応により一挙に環化を行うアニュレーション法，特に三炭素単位と二炭素単位との組み合わせを用いる [3 + 2] アニュレーションはほぼ同数の炭素原子を用いるため，位置および立体選択的な置換基の導入といった観点からも，最も効率的なものと考えられる．[2)] この [3 + 2] アニュレーションにおいて鍵となるのは，いかにして反応性の高い三炭素単位を構築するかという点であり，これまでに開発されている代表的な三炭素単位としては，野依らによるオキシアリルカチオン，[2f)] Boger らの非局在化ビニルカルベン[2c)]などが挙げられる．しかし，Diels-Alder 反応に代表される六員環形成反応と比較した場合，選択性，基質の入手の容易さなどの点でまだ同じレベルに達しているとはいい難く，新しい方法論の開発が望まれている．

１９９０年，われわれはケイ素の特性，特にケイ素の炭素原子から酸素原子への 1,2-転位，いわゆる Brook 転位の合成反応への展開を目的として研究を開始した．以来，五および七員炭素環の新しい形成反応の開発に成功したが，[3),4)]本総合論文では主として五員環形成反応に対象を限定し，合成反応としての展開を中心に述べる．

1. Brook 転位を利用する **[3 + 2]** アニュレーションの開発

Acylsilane **1**と求核剤との反応で生成する α-silylalkoxide **2** におけるケイ素の炭素原子から酸素原子への 1,2-転位 (**2**→**3**) は Brook 転位と呼ばれており，カルボニル基が求電子・求核剤として機能する点で極めてユニークなものである．[5),6)] しかしこの転位は平衡反応で，その平衡は生成するカルバニオンの安定性に依存するが，一般には α-silylalkoxide **2** の側に偏っているため，合成反応として用いるためには工夫が必要である．

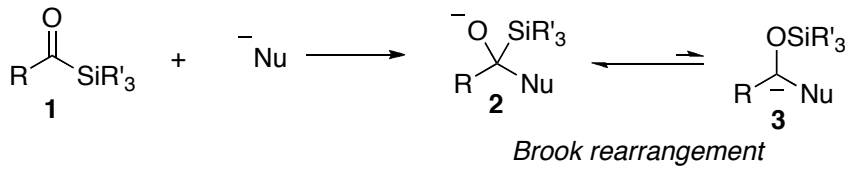


Chart 1

Brook, Reich らは acylsilane や求核剤に脱離基を導入することにより強制的に平衡をカルバニオンの側に移動させることを見い出し，位置選択的な enol silyl ether の生成などへ応用している．[6),7)]

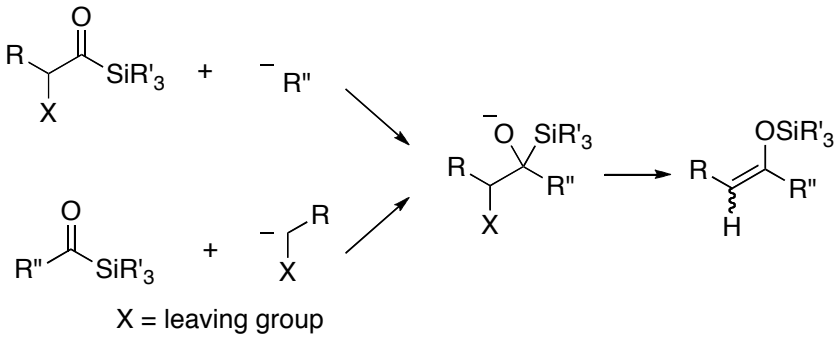


Chart 2

われわれが，この Brook 転位の合成反応への応用の研究を開始するに際して最初に考えたのは，アシルシランのカルボニル基にカルバニオンを安定化するようなヘテロ原子を導入すれば，転位が促進されるのではないかということであった．まず，**4** のようなアシルシランの合成を検討することにした．X が $SiMe_3$ 基のものは文献既知[8] であったので，まずその合成から行ったが極めて不安定であり合成試薬としては適さないことが明らかとなった．また，他のヘテロ原子を有するアシルシラン **4** の合成も dithiane 法を含む種々の方法で試みたが，不成功に終わった．

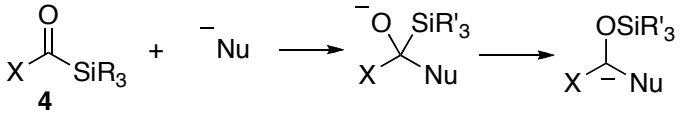


Chart 3

そこで次に，ケトンエノレートのような分子内求核・求電子剤を用いれば，生成したカルバニオンがβカルボニル基により cyclopropanolate **5** として捕捉され，転位が加速されるのではないかと考えた．

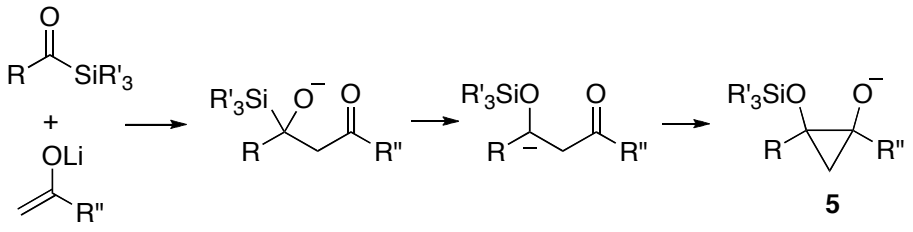


Chart 4

それまでアシルシランとケトンエノレートとの反応はほとんど知られておらず，桑島らによるα-クロロアシルシランとの反応で脱クロル化を伴うケイ素の 1,2-転位がおこることが報告されているのが唯一の例であった．[9] 最初に heptanoylsilane **6** と alkyl methyl ketone の lithium enolate **7** との反応を行った．しかし，生成したのは 1,2-付加体 **8** のみで，Brook 転位体は得られなかった．

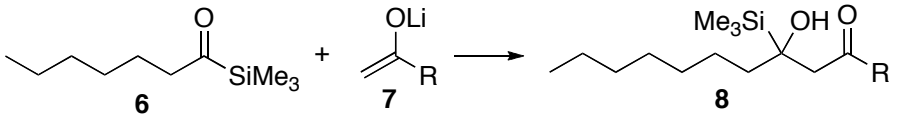
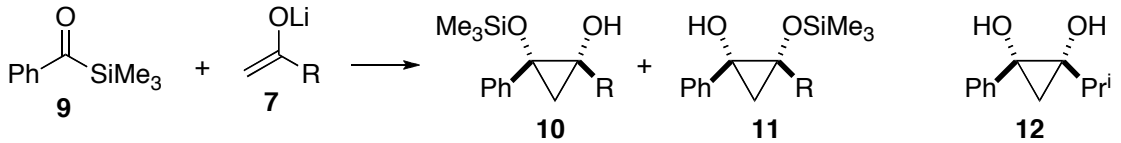


Chart 5

一方，benzoyltrimethylsilane **9** との反応では -80 ° ~ -30 ℃ という条件で，Brook 転位により生じたカルバニオンがβカルボニル基によって捕捉された，*cis*-1,2-cyclopropanediol 誘導体 **10** およびその Me_3Si 基が転位したもの **11** が生成した．いずれの場合もシス体のみが得られたが，その立体化学は MeOH で処理することにより得られる，空気酸化に対して極めて不安定な diol 体 **12** の X 線結晶解析により決定した．立体的に不利なシスジオール誘導体の選択的な生成は，ケイ素原子とアルコキサイドの分子内キレーションにより説明が可能である．



R = Et	64%	21%
R = *n*-Pr	59%	21%
R = *i*-Pr	90%	7%

Chart 6

同形式の反応は crotonoylsilane **13** でも進行し，1,4-付加体 **15** が副生するものの，対応する vinylcyclopropanol **14** が生成した．しかしカルボニル基を持たない *n*-BuLi との反応では付加体 **16** (50%) と Brook 転位体 **17** (28%) が生成し，付加体が主成績体であった．

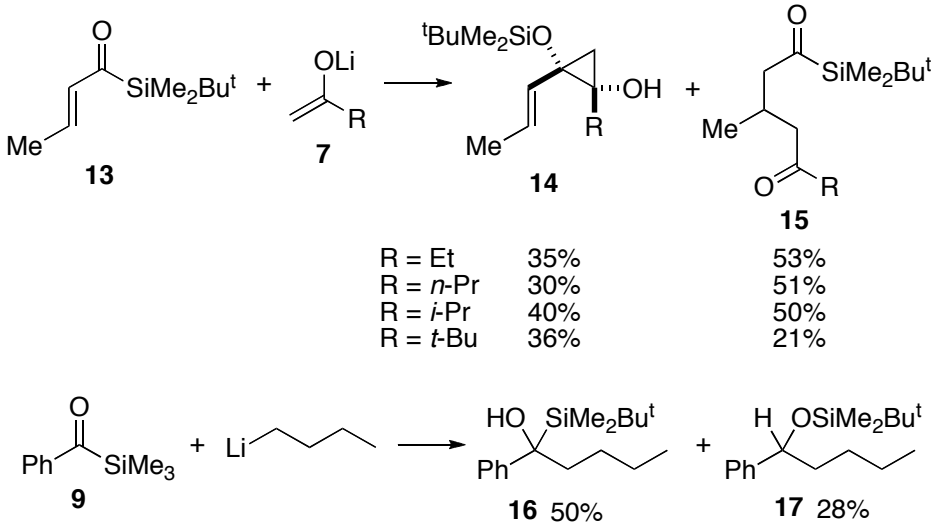


Chart 7

以上の結果から，Brook 転位を効率よく進行させるためにはβカルボニル基単独では不十分であり隣接する不飽和基の存在が不可欠だが，βカルボニル基が Brook 転位を加速していることは明らかである．[10)]

4 のような，カルボニル基にヘテロ原子が直接結合した acylsilane の合成は困難であることがわかったので，次にβ位にヘテロ原子をもつα,β-不飽和アシルシラン **18** に着目した．**18** は **4** の vinylogous 誘導体で，求核剤との反応により Brook 転位／アリル転位を経て 1,3-dipole 等価体 **21** として機能することが期待される．

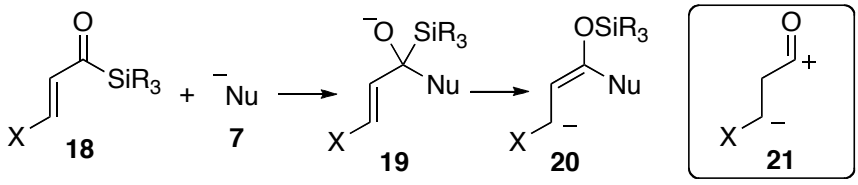


Chart 8

ここで，求核剤としてケトンエノレートのような求核・求電子剤を用いれば Brook 転位／アリル転位／分子内アルドール反応 (**22**→**23**→**24**) により五員環が生成し，新しい [3 + 2] 型の五員環形成反応の開発に

つながるのではないかと考えた．

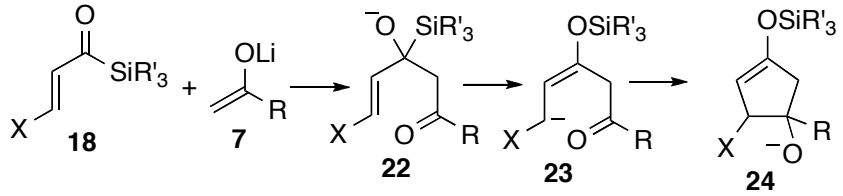


Chart 9

アシルシランとしては，Reich らの方法[11] により propargyl alcohol から allenylsilane **25** を経て容易に合成可能な β-phenylthio 体 **26** および β-trimethylsilyl 体 **27** を用いることにした．これらのアシルシランは大量合成および冷蔵庫中での長期間の保存が可能で，*E*/*Z* の分離もクロマトグラフィーで行うことができる．

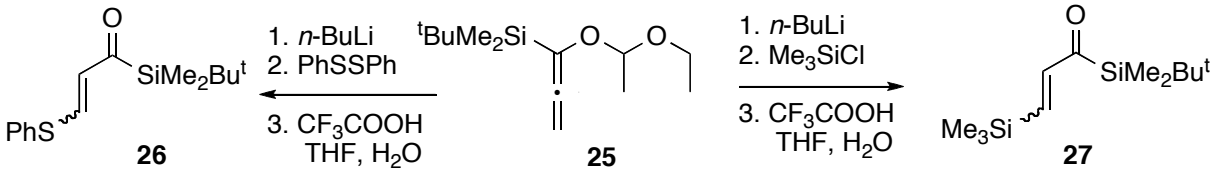
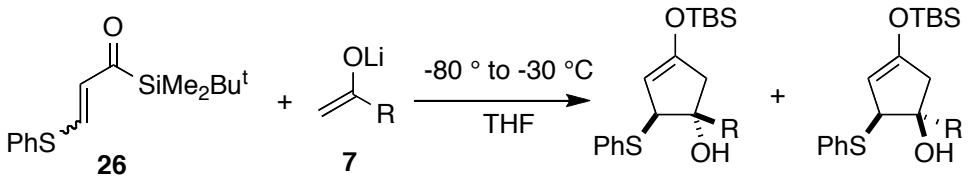


Chart 10

β-phenylthio 体 **26** (*E*/*Z* 混合物）の THF 溶液に -80 °C で，lithium diisopropylamide (LDA) により調製したエノレート **7** を加え -30 °C まで昇温したところ，二種の cyclopentenol **28**, **29** が高収率で生成した．[3] 二種の異性体の生成比は純粋な *E* および *Z* 体を用いてもほとんど変化がなく，いずれの場合も **28** が主成績体であった．これらの構造は，**28** (R = *i*-Pr) の X 線結晶解析の結果に基づいて決定した．

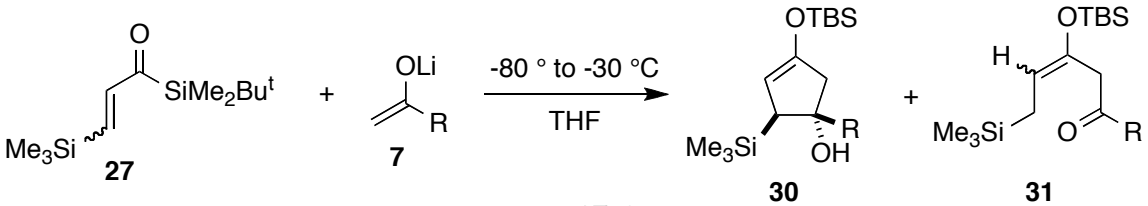


TBS = $SiMe_2Bu^t$

R = Et	70%	5%
R = *n*-Pr	74%	7%
R = *i*-Pr	55%	19%
R = *n*-octyl	71%	8%

Chart 11

次に，β-trimethylsilyl 体 **27** と **7** との反応を同様の条件で行ったところ，*E*, *Z* いずれの場合も一種類の環化体 **30** と非環化体 **31** を与えたが，それらの生成比は *E* 体と *Z* 体とで完全に逆転し，(*E*)-**27** の場合 **31** が主成績体であったが，(*Z*)-**27** では **30** が主に生成した．β-phenylthio 体と β-trimethylsilyl 体で生成物分布が大きく異なるという結果は，β置換基がアルキル基の場合には五員環が生成せず cyclopropanediol 誘導体 **14** が得られるという上述の結果とともに，本反応の反応機構を考える上で非常に興味深い．

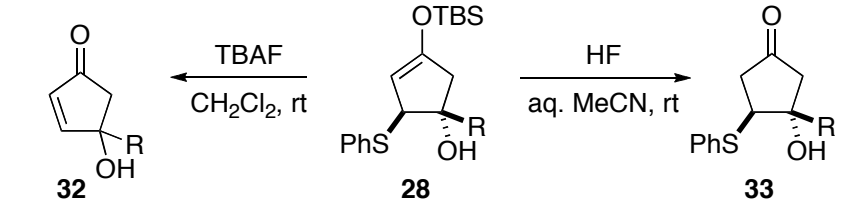


(*E*)-**27**		
R = Et	17%	43%
R = *n*-Pr	11%	57%
R = *i*-Pr	14%	63%
(*Z*)-**27**		
R = Et	48%	16%
R = *n*-Pr	55%	22%
R = *i*-Pr	51%	21%

Chart 12

26 の反応で得られる cyclopentenol 誘導体 **28**, **29** は，enol silyl ether 構造，phenylthio 基，そして水

酸基を含むため，種々の官能基変換が容易であり，例えば tetra-*n*-butylammonium fluoride (TBAF) と反応させると 4-hydroxy-2-cyclopentenone **32** が得られ，また，aq. MeCN 中 HF で処理した場合 phenylthio 基が残った cyclopentanone **33** が生成する．



R = Et	70%	R = Et	83%
R = *n*-Pr	77%	R = *n*-Pr	87%
R = *i*-Pr	77%	R = *i*-Pr	79%
R = *n*-octyl	66%	R = *n*-octyl	73%

Chart 13

以上のように， Brook 転位を基盤とするβヘテロ原子置換アクリロイルシランとアルキルメチルケトンのエノレートとの反応を用いて，非常に緩和な条件下，多官能性の五員炭素環を一挙に合成し得る [3 + 2] アニュレーションの開発に成功した．本アニュレーションの環化様式は従来のものとは全く異なるもので，Brook 転位の新しい可能性を開いたものと考えている．

2. [3 + 2] アニュレーションの天然物合成への応用

上記の [3 + 2] アニュレーションから導かれる，4-hydroxy-2-cyclopentenone 骨格は clavulone をはじめとするプロスタノイドなどの天然物に含まれることから，本アニュレーションの有用性を検証すべく，いくつかの天然物の合成への応用を検討した．

2.1 Chromomoric acid DII methyl ester (37) の合成[3)]

Chromomoric acid[12)] は *chromolaceana morii* から単離された一群の cyclopentenone で，Liu らにより DI methyl ester の合成が報告されている．[13)] 構造が比較的単純であるので，[3 + 2] アニュレーションを用いる最初の標的化合物として選んだ．合成計画は，ω 側鎖を備えた methyl ketone 体 **34** と acryloylsilane **26** との反応により一挙に chromomoric acid のω鎖を有する cyclopentenone 骨格を構築しようとするものである．methyl ketone 体 **34** は，8-bromo-1-octanol を出発原料として以下に示すよう

な経路により合成した．**34** を lithium 2,2,6,6-tetramethylpiperi- dide (LTMP) により lithium enolate とした後，-80 °C で acylsilane **26** (*E/Z* 混合物）に加え -30 °C まで昇温し，生成する cyclopentenol を単離することなく TBAF で処理したところ，52% の通算収率で **35** を得ることができた．ついで，**35** に2当量のLDA を作用させ enolate とした後，(*E*)-2-pentenal との反応を行い trienone 体 **36** を *E* : *Z* = 1.1 : 1 の混合物として得た (58%)．*E/Z* の分離後，末端酸素官能基をエステルに変換することにより chromomoric acid DII methyl ester (**37**) を合成することができた (32%)．

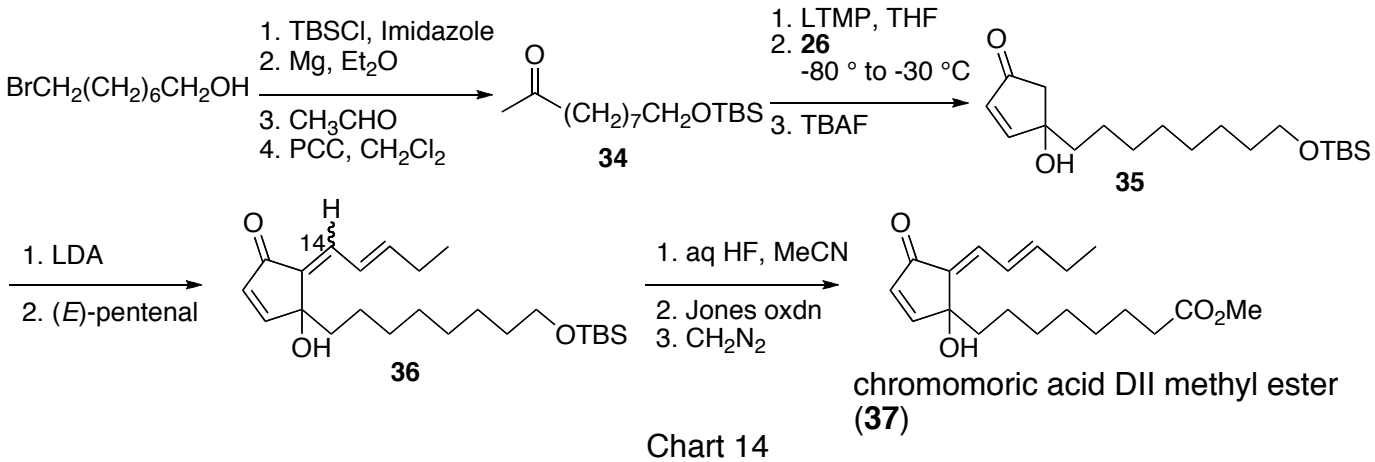


Chart 14

2.2 海産 **cyclopentenone Untenone A (38)** の合成[14),15)]

Untenone A (**38**)[16)] は沖縄産海綿 *Plakortis* sp. から単離された cyclopentenone で，同海域から単離されている海産天然物 manzamenone A (**39**)[17)] の生合成前駆体と考えられている．Untenone A の 4-hydroxy-2-cyclopentenone 骨格は上述の [3 + 2] アニュレーションにより容易に構築できるものと予想されたが，５位のメトキシカルボニル基の立体選択的な導入は生成物の安定性とも関連して問題が生ずる可能性があったため，当初β-ketoester の lithium enolate **40** を用いた [3 + 2] アニュレーションにより一挙に untenone A を得ようと考えた．しかし，エノレートの求核性が低いため環化体を得ることができなかった．

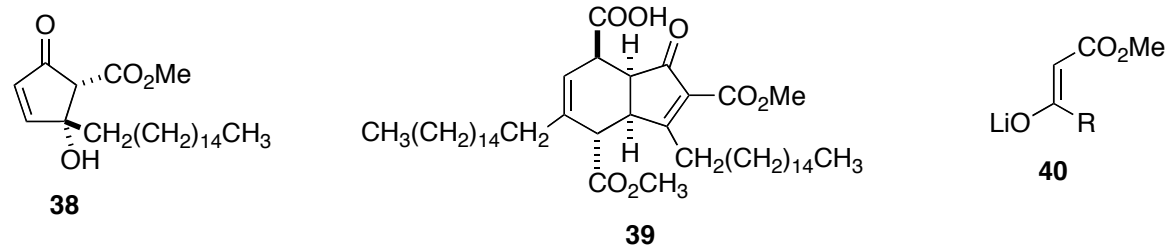


Chart 15

そこで，メトキシカルボニル基は最後に導入することとし，2-octadecanone[18] の lithium enolate **41** を用いて [3 + 2] アニュレーションを行ったところ，二種の cyclopentenol **42**, **43** が得られた．それぞれを TBAF で処理後，三級アルコールを methoxymethyl (MOM) 基で保護して cyclopentenone **45** に導いた．次に，Mander 法[19] を用いて**45** の α-methoxycarbonyl 化を行ったところ，2:1 の生成比で分離不可能なエピマーの混合物が得られた．最後に，混合物のままMOM 基を除去して untenone A (**38**) に変換した．**38** のエピマーは得られなかった．

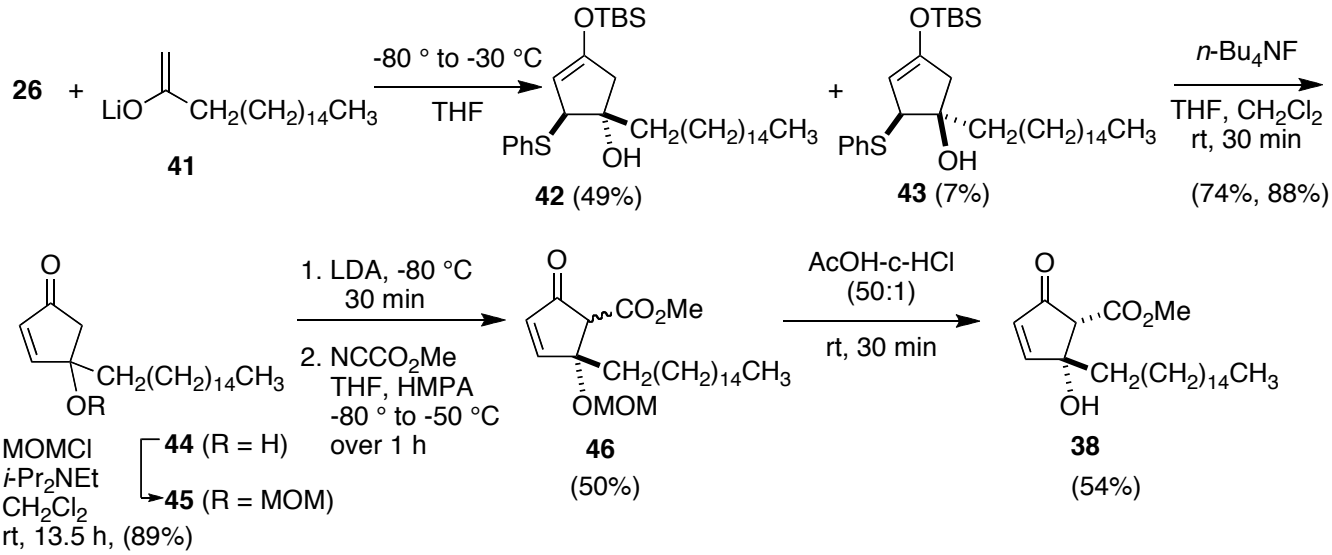


Chart 16

2.3 海産抗腫瘍性プロスタノイド **clavulone (claviridenone)** 類の合成[20)]

Clavulone (claviridenone) 類は沖縄産海洋動物 *Clavularia viridis* から単離されたプロスタノイドで，交差共役系をもつ 4-hydroxy-2-cyclopentenone 骨格を含む特異な構造に加えて，強力な抗腫瘍活性を示す点で従来のプロスタノイドとは大きく異なっている．[21),22)]これまでに数例の全合成の報告があるが，それらの多くは五員環化合物を出発原料としており，五員環の合成に主眼を置いたものは少ない．[23),24)] これらの化合物の合成に [3 + 2] アニュレーションを利用するに際し，以下に示すような二つのルートを考えた．一つは，ω 側鎖のシス二重結合の導入を五員環構築後に行うもので，アルデヒド体 **48** の合成が鍵となる．もう一つは ω 側鎖を備えたエノレート **50** を用いて cyclopentenone **47** を一挙に構築しようとするものである．二番目のルートは，エノレート **50** の生成の段階での二重結合の異性化の問題などが予想されたので，まず **48** を経由するルートから検討を開始した．

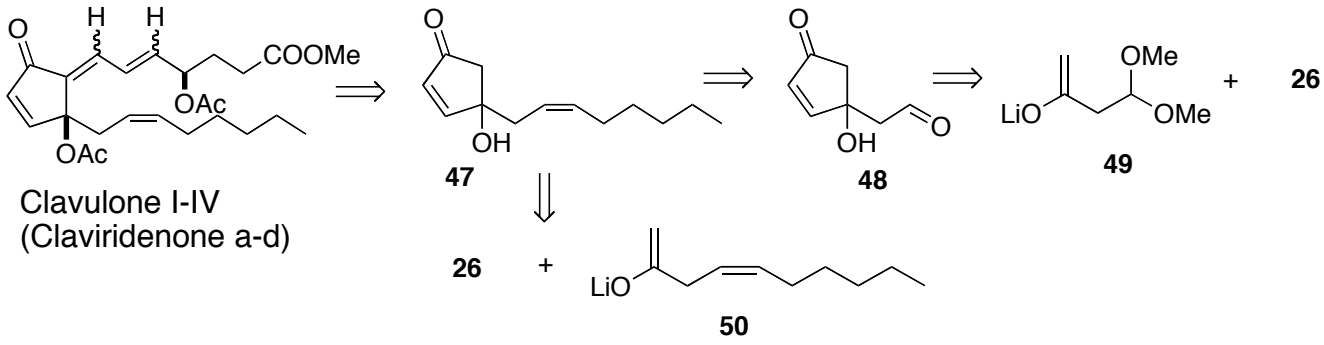


Chart 17

26 とエノレート **49** との反応から導いた cyclopentenone **51** のアセタールの加水分解は，生成するアルデヒド体 **48** が不安定なためかなり難航したが，acetone 中１当量の *p*-TsOH と処理するという条件で低収率ながら行うことができた．しかし，**48** の Wittig 反応は 10% 程度の収率でしか進行せず，また水酸基を保護しても収率が向上しなかったので，このルートは断念した．

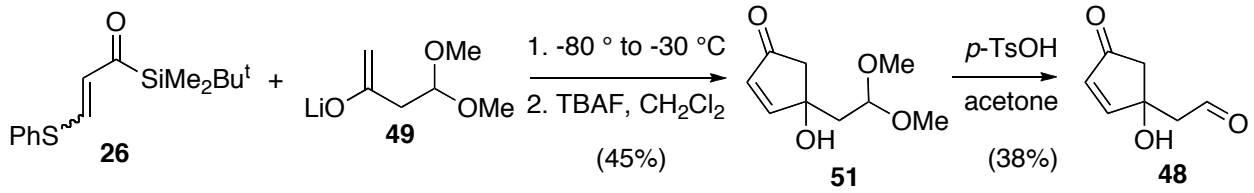


Chart 18

次に，2番目のルートを試みた．山口らの方法[25]により 1-heptyne から導いたケトン体 **52** に対し，-98 °C で LTMP を用いてエノレート **50** とし，同温で **26** と反応させた後 TBAF で処理したところ，22% (59% based on consumed **26**) の収率 で **47** を与えた．本反応における主な副生成物は，**52** が3位で **26** に 1,4-付加した後環化したと考えられる **53** のような化合物であった．収率的には満足の行くものではないが，clavulone のω鎖を含む cyclopentenone が一挙に構築できる点で効率的なものと考えている．

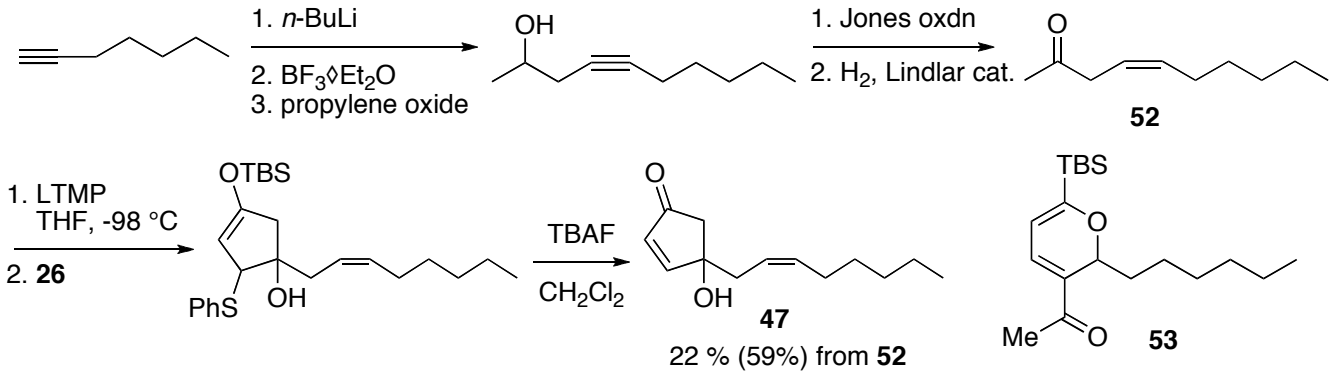


Chart 19

α鎖となるアルデヒド体 **59** は D-glutamic acid (**54**) から光学活性体として合成した．**54** をジアゾ化ついでジボラン還元[24b),24c),26)] に付し hydroxylactone 体 **55** とした後，アルコールをベンジル基で保護し **56** とした．**56** の acetoxy ester 体 **57** への変換は，水酸化ナトリウムと加熱することにより生ずるカルボン酸の Na 塩を tetra-*n*-butylammonium 塩とした後，ヨウ化メチルついで無水酢酸と反応させることにより行った．[27] **57** は脱ベンジル化後 Swern 酸化により **58** とした後，Wittig 反応を行い **59** に導いた．

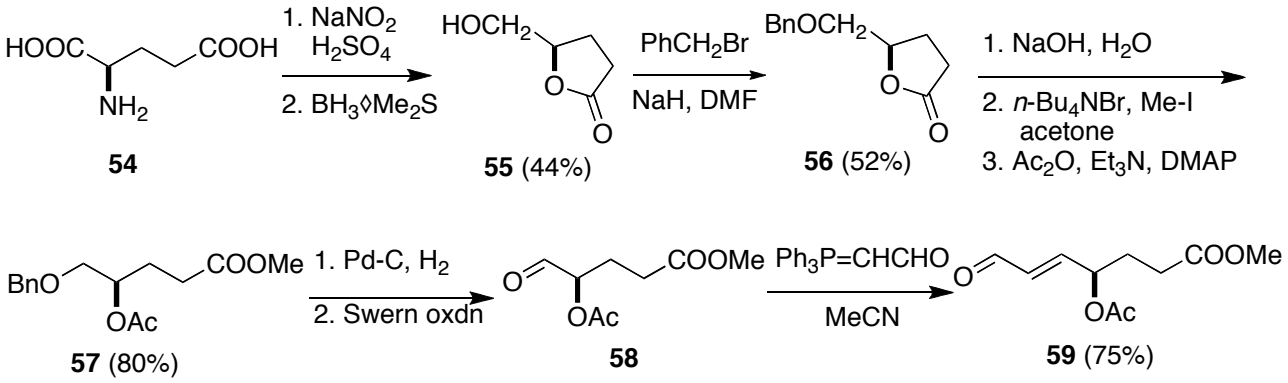


Chart 20

α鎖の導入は，cyclopentenone **47** を２当量の LDA によりエノレートとした後，アルデヒド体 **59** を反応させ，生成したアルコールの混合物を pyridine 中 4-(*N*,*N*-dimethylamino)pyridine (DMAP) の存在下過剰の無水酢酸と処理するという方法[24b] で行った．その結果，clavulone II (claviridenone c) (10%) および clavulone III (claviridenone b) (25%) を得ることができた．

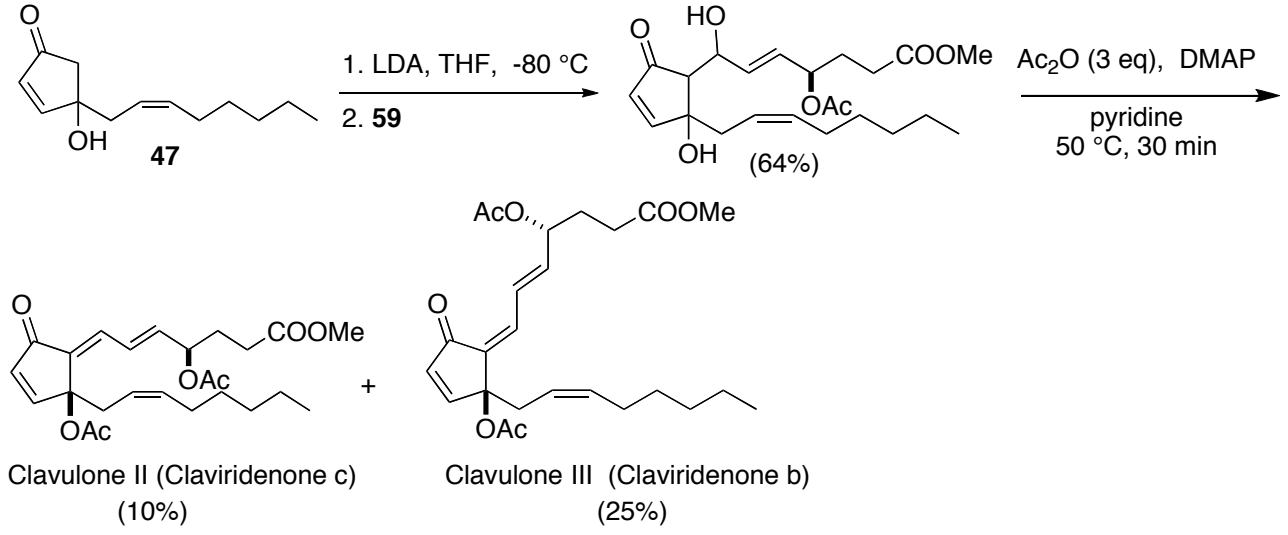


Chart 21

おわりに

以上，Brook 転位を利用した[3 + 2] アニュレーションの開発とその天然物合成への応用について述べた．[3 + 2] アニュレーションの反応機構に関する研究は現在進行中であるが，アクリロイルシランのβ位置換基のα-カルバニオン安定化能が重要な役割を果たしていることが明らかになっている．また，本反応を [3 + 4] アニュレーションに拡張し，新しい七員炭素環の形成反応の開発にも成功している．これらについては，別の機会に述べることにしたい．

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1) (a) Ramaiah M. *Synthesis,* **1984**, 529; (b) Hudlicky T., Rulin F., Lovelace T. C., Reed J. W., "Studies in Natural Products Chemistry", Attaur-Rahman T., Ed., Elsevier Science, Essex, U.K. 1989, pp. 3-72; (c) Ho T.-L., "Carbocycle Construction in Terpene Synthesis", VCH: New York, 1988.

2) (a) Little R. D., "Comprehensive Organic Synthesis", Trost B. M., Fleming I., Eds., Pergamon, Oxford, 1991, Vol. 5, pp. 239-270; (b) Mulzer J., Altenbach H-J., Braun M., Krohn K., Reissig H.-U., "Organic Synthesis Highlight", VCH, Weinheim, 1991, pp. 96-104; (c) Boger D. L., Brotherton-Pleiss C. E., "Advances in Cycloaddition", Curran D. P. Ed., JAI Press, Greenwich, 1990, Vol. 2, pp. 147-219; (d) Binger P., Büch H. M., *Top. Curr. Chem.*, **135**, 77 (1987); (e) Trost B. M., *Angew. Chem. Int. Ed. Engl.*, **25**, 1 (1986); (f) Noyori R., Hayakawa Y., *Org. React.*, **29**, 163 (1983).

3) Takeda K., Fujisawa M., Makino T., Yoshii E., Yamaguchi K., *J. Am. Chem. Soc.*, **115**, 9351 (1993).

4) (a) Takeda K., Takeda M., Nakajima A., Yoshii E., *J. Am. Chem. Soc.*, **117**, 6400 (1995); (b) Takeda K., Nakajima A., Yoshii E., *Synlett,* **1996**, 753.

5) アシルシランの総説: (a) Cirillo P. F., Panek J. S., *Org. Prep. Proc. Int.*, **24**, 553 (1992); (b) Bulman Page P. C., Klair S. S., Rosenthal S., *Chem. Soc. Rev.*, **19**, 147 (1990); (c) Ricci A., Degl'Innocenti A.,

Synthesis, **1989**, 647.

6) Brook 転位の総説: Brook A. G., Bassindale A. R., "Rearrangements in Ground and Excited States", de Mayo P., Ed., Academic Press, New York, 1980, pp. 149-221.

7) (a) Reich H. J., Holtan R. C., Bolm C., *J. Am. Chem. Soc*., **112**, 5609 (1990); (b) Nakajima T., Segi M., Sugimoto F., Hioki R., Yokota S., Miyashita K., *Tetrahedron,* **37**, 8343 (1993).

8) Ricci A., Degl'Innocenti A., Ancillotti M., Seconi G., Dembech P., *Tetrahedron Lett.,* **27**, 5985 (1986).

9) Kuwajima I., Matsumoto K., *Tetrahedron Lett*., **42**, 4095 (1979).

10) Takeda K., Nakatani J., Nakamura H., Sako K., Yoshii E., Yamaguchi K., *Synlett*, **1993**, 841.

11) Reich H. J., Kelly M. J., Olson R. E., Holtan R. C., *Tetrahedron,* **39**, 949 (1983).

12) Bohlmann F., Borthakur N., King R. M., Robinson H., *Phytochemistry*, **21**, 125 (1982).

13) Liu Z.-Y., Chu X.-J., *Tetrahedron Lett*., **34**, 349 (1993).

134) Takeda K., Nakayama I., Yoshii E., *Synlett,* **1994**, 178.

15) a) Asami M., Ishizaki T., Inoue S., *Tetrahedron Lett*., **36**, 1893 (1995); b) Miyaoka H., Watanuki T., Saka, Y, Yamada Y., *Tetrahedron*, **51**, 8749 (1995).

16) Ishibashi M., Takeuchi S., Kobayashi J., *Tetrahedron Lett*., **34**, 3749 (1993).

17) Tsukamoto S., Takeuchi S., Ishibashi M., Kobayashi J., *J. Org. Chem*., **57**, 5255 (1992).

18) Bergbreiter D. E., Killough J. M., *J. Org. Chem*., **41**, 2750 (1976).

19) a) Mander L. N., Sethi S. P., *Tetrahedron Lett*., **24**, 5425 (1983); b) Crabtree S. R., Mander L. N., Sethi E. P., *Org. Synth*., **70**, 256 (1991).

20) Takeda K., Kitagawa K., Nakayama I., Yoshii E., *Synlett,* 印刷中.

21) (a) Kikuchi H., Tsukitani Y., Iguchi, K., Yamada Y., *Tetrahedron Lett*., **23**, 5171 (1982); (b) Kikuchi H., Tsukitani Y., Iguchi K., Yamada Y., *Tetrahedron Lett*., **24**, 1549 (1983).

22) (a) Kobayashi M., Yasuzawa T., Yoshihara M., Akutsu Y., Kyogoku Y., Kitagawa I., *Tetrahedron Lett*., **23**, 5331 (1982); (b) Kobayashi M., Yasuzawa T., Yoshihara M., Son B. W., Kyogoku Y., Kitagawa I., *Chem. Pharm. Bull*., **31**, 1440 (1983).

23) 長岡博人，山田泰司， *有合化*, **44**, 1145 (1986).

24) (a) Corey E. J., Mehrotra M. M., *J. Am. Chem. Soc*., **106**, 3384 (1984); (b) Nagaoka H., Miyakoshi T., Yamada Y., *Tetrahedron Lett*., **25**, 3621 (1984); (c) Hashimoto S., Arai Y., Hamanaka N., *Tetrahedron Lett*., **26**, 2679 (1985); (d) Shibasaki M., Ogawa Y., *Tetrahedron Lett*., **26**, 3841 (1985); (e) Klunder A. J. H., Zwanenburg B., Liu Z. Y., *Tetrahedron Lett*., **32**, 3131 (1991).

25) Yamaguchi M., Hirao I., *Tetrahedron Lett.,* **24**, 391 (1983).

26) Larcheveque M., Lalande J., *Tetrahedron,* **40**, 1061 (1984).

27) Weber A. E., Halgren T. A., Doyle J. J., Lynch R. J., Siegl P. K. S., Parsons W. H., Greenlee W. J., Patchett A. A., *J. Med. Chem*., **34**, 2692 (1991).