Reaction of Silyl Thioketones with Lithium Diethylphosphite:  
First Observation of Thia-Brook Rearrangement  

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Abstract  
Reaction of silyl thioketone 7 with lithium diethylphosphite at –98 °C afforded an S-attack product 8 and a formal C-attack products 10 and 11, which were formed by S-to-C migration of the phosphoryl group in 8 followed by C-to-S migration of the silyl group (thia-Brook rearrangement), in a ratio depending on the conditions. The relative facility of the thia-Brook rearrangement was compared with that of the Brook rearrangement using the (t-butyldimethylsilyl)diphenylmethyl derivatives 22 and 23.  

Key words:  
Inter-element linkage; Silyl thioketone; Thia-Brook rearrangement; Sulfur-phosphorus bond; sulfur-silicon bond  

1. Introduction  
The reactions of thioketones with nucleophiles have attracted considerable interest because the attack of the nucleophiles can either occur in a thiophilic or carbophilic fashion, depending on the structures of both the thioketones and the nucleophiles [1-3]. Closely related silyl thioketones have only recently emerged as promising synthetic intermediates that allow the synthesis of a variety of compounds containing the Si-C-S unit [4]. Bonini and co-workers reported that the carbon nucleophiles, such as alkyllithium, attack at the sulfur atom in the reaction with silyl thioketone to afford sulfide, a thiophilic attack product [5]. We became interested in exploiting the reaction of silyl thioketones 1 with heteroatom nucleophiles X, from the point of view of the direction of attack of the nucleophiles, thiophilic or carbophilic to give 2 and 3, respectively. And, we were also interested in which the inter-element linkage, S-Si or S-X, is formed in the C-adduct 3 (path a or path b).  

We chose t-butyldimethylsilyl phenyl thioketone 7 as a silyl thioketone and lithium diethyl phosphite as a nucleophile. The former choice was based on Bonini’s finding that the corresponding trimethylsilyl derivative was relatively unstable [5].
2. Results and discussion

2.1. Synthesis of silyl thioketone

This compound was prepared by a procedure of Bonini [5] as described for the corresponding trimethylsilyl derivative. Treatment of acylsilane 6 with HCl/H₂S afforded relatively stable silyl thioketone 7 in 90% yield. Blue-colored 7 could be stored in a freezer for a few days without significant decomposition.

2.2. Reaction of silyl thioketone with lithium diethylphosphite

When a solution of lithium diethylphosphite in THF, generated from the reaction of diethyl phosphite with n-butyllithium, was added to a solution of silyl thioketone 7 in THF at −98 °C (MeOH-liq. N₂) and then stirred at the same temperature for 1 min, a thiophilic attack product 8 was obtained in 61% yield (Table 1, entry 1). The structure of 8 was verified by NMR comparison of its desilylation product by n-Bu₄NF with the compound derived from phosphorylation of phenylmethanethiol. Prolonged reaction times and/or elevated reaction temperatures (-30 °C) resulted in lower yields of 8 due to the formation of unidentified decomposition products. The effect of changing the solvent polarity was briefly examined. Although the reaction was not sensitive to changing from THF to toluene (entry 5), the use of THF-HMPA (9:1) resulted in a lower yield of 8 (Table 1, entry 6).
When the order of the addition was reversed (silylthioketone added to phosphite), however, it resulted in the formation of compound 10, a product formally arising from C-attack followed by C-to-O 1,2-anionic rearrangement of the silyl group, and/or its hydrolysis product 11, in addition to 8 (Table 2).

The structure of 11 was determined on the basis of its $^{13}$C NMR and $^1$H NMR spectra to be a carbon-phosphorus geminal coupling with $J = 148.2$ Hz at 38.4 ppm, and a doublet of doublets peak of the SH proton at 2.64 ppm (dd, $J = 18.8$, 8.1 Hz). Also, 11 was silylated by TBSCI to give 10. In order to examine whether 10 arises directly from a carbophilic attack of the phosphite or from an S-attack of the nucleophile followed by an S-to-C rearrangement of the phosphoryl group and then C-to-S migration of the silyl group, we carried out the reaction of 7 with a catalytic amount of lithium diethylphosphite in the presence of diethyl phosphite, anticipating that the carbanion or thioxide anion resulting from the initial attack of the nucleophile would be immediately protonated by the phosphorous acid. When 7 was treated with 0.1 equiv. of lithium diethylphosphite and 0.9 equiv. of

Table 1

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Table 2

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When the order of the addition was reversed (silylthioketone added to phosphite), however, it resulted in the formation of compound 10, a product formally arising from C-attack followed by C-to-O 1,2-anionic rearrangement of the silyl group, and/or its hydrolysis product 11, in addition to 8 (Table 2).
diethyl phosphite, irrespective of the order of addition, 8 was the only isolated product and neither 10 nor 11 was detected. These results suggest that the initial attack of the nucleophile occurs at the sulfur atom and then the phosphoryl group migrates from S to O depending on the reaction conditions. To verify the feasibility of the rearrangement of the phosphoryl group, we examined the deprotonation of 8 by a variety of bases. Although the use of most bases including LDA, n-butyllithium, and t-butyllithium, resulted in recovery of the starting material or in attack at the phosphoryl group followed by cleavage of the P-S bond, reaction of 8 with MeLi afforded 11, formed via S-to-C migration followed by thia-Brook rearrangement, in 16% yield in addition to 12 and 13.

\[
\begin{align*}
\text{MeLi, THF, -98 °C} & \quad \text{S-H} \quad \text{S-H} \\
8 & \quad \text{Ph-SiMe}_2\text{Bu}^t & \quad \text{Ph-SiMe}_2\text{Bu}^t \\
& \quad \text{Ph-C=O} & \quad \text{Ph-C=O} \\
& \quad \text{Li-P(OEt)}_2 & \quad \text{Li-P(OEt)}_2 \\
& \quad + & \quad + \\
& \quad \text{Me-P(OEt)}_2 & \quad \text{Me-P(OEt)}_2 \\
& \quad \text{14} & \quad \text{15} \\
& \quad \text{16} & \quad \text{10}
\end{align*}
\]

Scheme 3

Although the origin of the difference in product distribution depending on the order of addition and the precise mechanism are not clear at the present time, it is reasonable to assume that the reaction path involves the initial attack of the phosphoryl group at the sulfur atom followed by an S-to-O migration of the phosphoryl group and a C-to-S migration of the silyl group (thia-Brook rearrangement).

In order to test the feasibility of the unprecedented thia-Brook rearrangement [6], we attempted to trap 14 and to prepare 16 by silylation (base/TBSCl) of 10 followed by desilylation, but we had no success.
Next, we decided to examine the possibility of the thia-Brook rearrangement occurring at a reasonable rate at –98 °C using a simpler model system.

### 2.3. Thia-Brook rearrangement of (tert-butyldimethylsilyl)diphenylmethanethiol to tert-butyldimethylsilyl diphenylmethyl sulfide

West reported that treatment of benzyl trimethylsilyl sulfide (17) with t-BuLi at –78 °C afforded α-(trimethylsilyl)phenylmethanethiol (18) in 90% yield and that its reverse rearrangement occurred only under radical conditions [7].

We envisaged that replacement of the hydrogen atom by a phenyl group in 18 would produce an increase in the rate of occurrence of the thia-Brook rearrangement, because Brook reported that the change from a hydrogen atom to a phenyl group resulted in rate enhancement by factors of 1000 in the oxygen counterpart [8]. When (tert-butyldimethylsilyl)diphenylmethanethiol (21), prepared from diphenylmethanethiol 19 [9] via the silylation-desilylation sequence, was treated with MeLi at –98 °C for 10 min, the rearranged product 20 was obtained in 81% yield.
Next, we compared the relative rates of occurrence of the thia-Brook and Brook rearrangements. Effective reaction conditions for the rearrangement were examined on 21 and 23 using several amine bases in solvents by monitoring using $^1$H NMR [8, 10]. The reactions proceeded at a reasonable rate when using 1.0 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CDCl$_3$ (50 mM) at 23 °C. Under these conditions, the half-lives of the reactions were measured as 11.0 min and 2.4 min for 21 and 23, respectively.

These results indicate that the thia-Brook rearrangement can occur at a reasonable rate when the generated carbanion can be stabilized by two phenyl groups, and they suggest the possibility of the thia-Brook rearrangement from 14 to 15 in which the carbanion is stabilized by a phenyl group and a phosphoryl group. The difference between the rates of occurrence of the thia-Brook and Brook rearrangements can be interpreted as the result of a balance between the strengths of S-Si and O-Si and the relative stabilities of the anions involved.

In conclusion, we have demonstrated that the reaction of silyl thio ketone with lithium diethylphosphite can proceed via a thiophilic attack followed by S-to-C migration of the phosphoryl group and the thia-Brook rearrangement, C-to-S migration, of the silyl group. Moreover, we have
shown that the unprecedented thia-Brook rearrangement is slower by a factor of about 5 relative to the oxygen counterpart.

3. Experimental

IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer. $^1$H NMR spectra were taken on Varian UnityPlus 500 (500 MHz) and Varian Gemini 300 (300 MHz) in CDCl$_3$ with reference to CHCl$_3$ ($\delta$ 7.26). $^{13}$C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) in CDCl$_3$ with reference to the CDCl$_3$ triplet ($\delta$ 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-D-300 spectrometer combined with a JEOL JMA-2000 data-processing system. For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; and 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.

3.1. tert-Butyldimethylsilyl Phenyl thioketone (7)

Hydrogen chloride and hydrogen sulfide were bubbled into a solution of tert-butylidemethylsilyl phenyl ketone 6 (600 mg, 2.72 mmol) in Et$_2$O (22 mL) at $-10 \, ^{\circ}\text{C}$ for 5 min. The solution was poured into a mixture of aqueous saturated NaHCO$_3$ (50 mL) and Et$_2$O (30 mL). The phases were separated and the aqueous phase was extracted with Et$_2$O (30 mL x 2). Combined organic phases were washed with water (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g; elution with hexane) to give 7 (578 mg, 90%). a blue oil, $R_f = 0.36$ (hexane). IR (film) 1250 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.39 (6H, s, SiMe$_2$), 0.91 (9H, s, t-Bu), 7.37 (2H, tm, Ar-H), 7.48 (1H, tm, Ar-H), 7.62 (2H, dm, Ar-H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ -2.4 (SiMe$_2$), 17.6 (CMe$_3$), 27.2 (t-Bu), 125.5, 128.3, 131.2, and 153.7 (Ar), 294.0 (C=S). HRMS calced for C$_{19}$H$_{36}$O$_3$Si$_2$ 236.1055, found 236.1087.

3.2.1. General procedure for the reaction of 7 with lithium diethylphosphate

Method A: The following procedure for reaction of 7 at $-98 \, ^{\circ}\text{C}$ is representative: To a cooled (-98 $^{\circ}\text{C}$) solution of 7 (500 mg, 2.12 mmol) in THF (20 mL) was added a cooled (-98 $^{\circ}\text{C}$) solution of lithium diethylphosphate, which was prepared from diethyl phosphate (273 µL, 2.12 mmol) in
THF (1 mL) and n-BuLi (1.44 M in hexane, 1.47 mL, 2.12 mmol), by the use of cannula over a period of 1 min. The solution was stirred for 60 min at the same temperature and then quenched by the addition of a solution of AcOH (120 µL, 2.12 mmol) in THF (1 mL). The mixture was passed through a short pad of silica gel and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g; elution with 2:1 hexane-AcOEt) to give \( \mathbf{8} \) (452 mg, 57%) and \( \mathbf{9} \) (29 mg, 10%). \( \mathbf{8} \): a colorless oil, \( R_f = 0.46 \) (hexane: AcOEt = 3 : 1). IR (film) 1250, 1020 cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) -0.11, 0.19 (each 3H, s, SiMe\(_3\)), 0.85 (9H, s, \( t \)-Bu), 1.02, 1.12 (each 3H, t, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 3.52-3.60 (1H, m, OCH\(_2\)), 3.73 (1H, d, \( J = 16.7 \) Hz, CH), 3.74-3.99 (3H, m, OCH\(_2\)), 7.10-7.13 (1H, m, Ar-H), 7.21-7.26 (4H, m, Ar-H). \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) -6.7, -6.4 (SiMe\(_2\)), 15.8, 16.0 (OCH\(_2\)CH\(_3\)), 18.0 (CMe\(_3\)), 27.0 (\( t \)-Bu), 35.4 (CH), 63.2 (OCH\(_2\)), 126.1, 128.3, 128.4, and 142.7 (Ar). HRMS calcd for C\(_{17}\)H\(_{35}\)O\(_3\)PSSi 374.1501, found 374.1463.

Method B: The following procedure is representative: To a cooled (\(-98 \) °C) solution of lithium diethyl phosphite, which was prepared from diethyl phosphite (274 µL, 2.12 mmol) in THF (20 mL) and n-BuLi (1.44 M in hexane, 1.47 mL, 2.12 mmol), was added \( \mathbf{7} \) (500 mg, 2.12 mmol) in THF (1 mL) by the use of cannula over a period of 1 min. The solution was stirred for 30 min at the same temperature and then quenched by the addition of a solution of AcOH (121 µL, 2.12 mmol) in THF (1 mL). The mixture was passed through a short pad of silica gel and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g; elution with 2:1 hexane-AcOEt) to give \( \mathbf{8} \) (152 mg, 19%), \( \mathbf{10} \) (2%, calculated from \( ^1\)H NMR integration), \( \mathbf{11} \) (100 mg, 18%), (72 mg, 25%), and \( \mathbf{9} \) (47 mg, 16%). \( \mathbf{10} \): a colorless oil, \( R_f = 0.39 \) (hexane: AcOEt = 1 : 1). IR (film) 1250, 1025 cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 0.01, 0.25 (each 3H, s, SiMe\(_3\)), 0.91 (9H, s, \( t \)-Bu), 1.12, 1.29 (each 3H, t, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 3.74-3.79 (1H, m, OCH\(_2\)), 3.96-4.01 (1H, m, OCH\(_2\)), 4.01 (1H, d, \( J = 21.6 \) Hz, CH), 4.11-4.19 (2H, m, OCH\(_2\)), 7.22-7.31 (3H, m, Ar-H), 7.46-7.48 (2H, m, Ar-H). \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) -3.6, -3.3 (SiMe\(_2\)), 16.4, 16.6 (OCH\(_2\)CH\(_3\)), 19.1 (CMe\(_3\)), 26.4 (\( t \)-Bu), 40.9 (d, \( J = 148.2 \) Hz, CH), 63.6, 63.7 (OCH\(_2\)), 127.7, 128.4, 129.6, and 138.1 (Ar). HRMS calcd for C\(_{17}\)H\(_{35}\)O\(_3\)PSSi 374.1501, found 374.1512. \( \mathbf{11} \): a colorless oil, \( R_f = 0.32 \) (hexane: AcOEt = 1 : 2). IR (film) 1250, 1025 cm\(^{-1}\). \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 1.12, 1.32 (each 3H, t, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 2.64 (1H, dd, \( J = 10.9, 8.1 \) Hz, SH) 3.77-3.87 (1H, m, OCH\(_2\)), 3.95-4.03 (1H, m, OCH\(_2\)), 4.08 (1H, dd, \( J = 18.8, 8.1 \) Hz, CH), 4.12-4.21 (2H, m, OCH\(_2\)), 7.28 (1H, tm, \( J = 7.5 \) Hz, Ar-H), 7.33 (2H, tm, \( J = 7.5 \) Hz, Ar-H), 7.45 (2H, dm, \( J = 7.5 \) Hz, Ar-H). \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 16.4, 16.6 (OCH\(_2\)CH\(_3\)), 38.4 (d, \( J = 148.2 \) Hz, CH), 63.7, 63.8 (OCH\(_2\)), 128.2, 128.8, 129.0, and 136.6 (Ar). HRMS calcd for C\(_{11}\)H\(_{17}\)O\(_3\)PS 260.0636, found 260.0654.

3.2.2. Reaction of \( \mathbf{8} \) with methyllithium
To a cooled (-98 °C) solution of 8 (185 mg, 494 μmol) in THF (5 mL) was added MeLi (0.37 M, 1.34 mL, 496 μmol). After being stirred at the same temperature for 15 min, the reaction was quenched by the addition of AcOH (29 μL, 507 μmol). The mixture was passed through a short pad of silica gel and concentrated. The residual oil was subjected to column chromatography (silica gel, 18 g; elution with 1:1 hexane-AcOEt) to give 11 (21 mg, 16%), 12 (48 mg, 41%), and 13 (48%, calculated from 1H NMR integration)

3.3.1. tert-Butyldimethylsilyl diphenyl sulfide (20)

To a solution of diphenylmethanethiol (19) (1.63 g, 8.14 mmol) in CH₂Cl₂ (20 mL) was added tert-butyldimethylsilylchloride (1.48 g, 9.77 mmol), Et₃N (1.48 mL, 10.6 mmol), and DMAP (399 mg, 3.26 mmol). After being stirred at room temperature for 3 h, the solution was diluted with CH₂Cl₂ (5 mL) and washed with water (20 mL). The aqueous phase was extracted with CH₂Cl₂ (20 mL x 3), and combined organic phases were washed with saturated aqueous NH₄Cl (40 mL), and then concentrated. The residual oil was subjected to column chromatography (silica gel, 250 g; elution with hexane: Et₂O = 50 : 1) to give 20 (2.15 g, 84%). a colorless oil, Rf = 0.64 (hexane: Et₂O = 10 : 1). 1H NMR (500 MHz, CDCl₃) δ 0.14 (6H, s, SiMe₂), 0.95 (9H, s, t-Bu), 5.26 (1H, s, CH), 7.22 (2H, t, J = 7.7 Hz, Ar-H), 7.32 (4H, t, J = 7.7 Hz, Ar-H), 7.49 (4H, t, J = 7.7 Hz, Ar-H). 13C NMR (125 MHz, CDCl₃) δ -3.4 (SiMe₂), 19.0 (CMe₃), 26.5 (t-Bu), 49.9 (CH), 126.9, 128.2, 128.5, and 144.6 (Ar). HRMS calcld for C₁₉H₂ₙ₂ₙSSi 314.1525, found 314.1544.

3.3.2. (tert-Butyldimethylsilyl)diphenylmethanethiol (22)

To a cooled (-80 °C) solution of 20 (2.98 g, 9.48 mmol) in THF (12 mL) was added n-BuLi (1.40 M in hexane, 6.80 mL, 9.48 mmol), and the solution was stirred at the same temperture for 15 min before the addition of tert-butyldimethylsilylchloride (1.43 g, 9.48 mmol) in THF. The solution was allowed to warm to 0 °C, diluted with saturated aqueous NH₄Cl (20 mL), and then extracted with Et₂O (20 mL x 3). Combined organic phases were washed with saturated brine (40 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 400 g; elution with hexane: Et₂O = 50 : 1) to give 21 (2.20 g, 55%) and 20 (1.16 g, 39%).

To a solution of 21 (2.20 g, 5.13 mmol) in CH₂Cl₂ (51 mL) was added an excess of 5% HF in MeCN, and the solution was stirred at room temperature for 90 min. The mixture was poured into saturated aqueous NaHCO₃ solution and then extracted with Et₂O (50 mL x 3). Combined organic phases were successively washed with H₂O (50 mL) and saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 170 g; elution with hexane: Et₂O = 50 : 1) to give 22 (1.44 g, 90%). a colorless oil, Rf = 0.32 (hexane). IR (film)
1595, 1490, 1255 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.44 (6H, s, SiMe\(_2\)), 0.69 (9H, s, t-Bu), 2.19 (1H, s, SH), 7.19 (2H, t, \(J = 7.3\) Hz, Ar-H), 7.27 (4H, t, \(J = 7.3\) Hz, Ar-H), 7.43 (4H, t, \(J = 7.3\) Hz, Ar-H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) -2.9 (SiMe\(_2\)), 20.1 (CMe\(_3\)), 28.2 (t-Bu), 47.7 (C-S), 126.1, 128.0, 129.3, and 148.3 (Ar). HRMS calcd for C\(_{19}\)H\(_{26}\)SSi 314.1525, found 314.1553.

3.3.3. Reaction of 22 with MeLi

To a cooled (-98 °C) solution of 22 (133 mg, 424 µmol) in THF (3.9 mL) was added MeLi (1.14 M in Et\(_2\)O, 372 µL, 424 µmol). After being stirred at the same temperture for 10 min, the reaction was quenched by the addition of AcOH (24.3 µL, 424 µmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH\(_4\)Cl (20 mL), and extracted with Et\(_2\)O (20 mL x 3). Combined organic phases were washed with saturated brine (40 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g; elution with 60:1 hexane-Et\(_2\)O) to give 20 (107 mg, 81%).

3.3.4. Thia-Brook Rearrangement of 22 into 20 with DBU

22 (14.9 mg, 47.4 µmol) was dissolved in CDCl\(_3\) (877 µL) in an NMR tube, and 10% DBU solution in CDCl\(_3\) (70.9 µL, 47.4 µmol) was added. The \(^1\)H NMR (300 MHz) was recorded at intervals of ca. 30 s at 23 °C. Half-live values were determined by following the disapperance of a peak at 2.19 ppm assigned as SH in 22 and the appearance of a peak at 5.26 ppm assinged as CH in 20.

3.3.5 (tert-Butyldimethylsilyldiphenylmethanol (23)

To a cooled (-80 °C) solution of 6 (960 mg, 4.36 mmol) in toluene (2 mL) was added dropwise PhLi (1.04 M in cyclohexane-diethylether, 4.20 mL, 4.36 mmol). The reaction was immediately quenched by addition of AcOH (250 µL, 4.36 mmol) in THF (1 mL). The mixture was diluted with saturated aqueous NH\(_4\)Cl (20 mL), and extracted with Et\(_2\)O (20 mL x 3). Combined organic phases were washed with saturated brine (40 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g; elution with 25:1 hexane-AcOEt) to give 23 (262 mg, 20%), a colorless oil, \(R_f\) = 0.48 (hexane:AcOEt = 10 : 1). IR (film) 3520 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.20 (6H, s, SiMe\(_2\)), 0.80 (9H, s, t-Bu), 2.08 (1H, s, OH), 7.21 (2H, t, \(J = 7.3\) Hz, Ar-H), 7.33 (4H, t, \(J = 7.3\) Hz, Ar-H), 7.51 (4H, t, \(J = 7.3\) Hz, Ar-H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) -5.0 (SiMe\(_2\)), 19.0 (CMe\(_3\)), 28.3 (t-Bu), 77.0 (C-OH), 126.2, 126.2, 128.1, and 147.0 (Ar). HRMS calcd for C\(_{19}\)H\(_{26}\)OSi 298.1775, found 298.1775.
3.3.6. Brook Rearrangement of 23 into 24 with DBU

23 (13 mg, 44.6 µmol) was dissolved in CDCl₃ (825 µL) in an NMR tube, and 10% DBU solution in CDCl₃ (66.7 µL, 44.6 µmol) was added. The ¹H NMR (300 MHz) was recorded at an interval of ca. 30 s at 23 °C. Half-live values were determined by following the disappearance of a peak at 0.80 ppm assigned as t-Bu in 23 and the appearance of a peak at 0.97 ppm assigned as t-Bu in 24. 24: a colorless oil, Rₛ = 0.67 (hexane: AcOEt = 20 : 1). ¹H NMR (500 MHz, CDCl₃) δ 0.03 (6H, s, SiMe₂), 0.97 (9H, s, t-Bu), 5.80 (1H, s, CH), 7.24 (2H, t, J = 7.3 Hz, Ar-H), 7.32 (4H, t, J = 7.3 Hz, Ar-H), 7.40 (4H, t, J = 7.3 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ -4.6 (SiMe₂), 18.5 (CMe₃), 26.0 (t-Bu), 76.8 (C-O), 126.5, 127.1, 128.3, and 145.4 (Ar). HRMS calcd for C₁₉H₂₆OSi 298.1753, found 298.1737.

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References


