Demethylation of an Allene Bearing Two Dimethoxythioxanthene Groups by Oxidation

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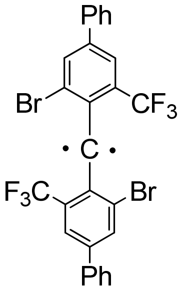
With the objective of preparing an isolable triplet carbene, we have carried out the oxidation of an allenic compound bearing two thioxanthene moieties (**5**). Relatively weak oxidants such as $Ph_3C^+BF_4^-$ gave **8**, which is the conjugate acid of **5**, as a result of a one-electron oxidation followed by hydrogen abstraction, whereas relatively strong oxidants such as $SbCl_5$ furnished a dicationic ketal (**9**) as a consequence of oxidation and demethylation. Computations on the supposed dicationic intermediate suggest that the singlet state is more stable than the triplet state by 6.7 kcal/mol and that the reason for this peculiarity is because the singlet state is essentially a vinyl cation stabilized by a coordinating methoxy group.

Introduction

Carbenes in a primary sense are neutral divalent carbon compounds which assume either a singlet or triplet state ground state.[1] Although carbenes of both states are generally too reactive to be isolated, stabilization by the introduction of adjacent heteroatoms has enabled the isolation of storable singlet carbenes, some of which have enjoyed successful application in organic synthesis.[2-5]

On the other hand, isolable triplet carbenes are much more difficult to obtain than their singlet counterparts.[1,6,7] Therefore**,** the use of diazo compounds as precursors is usually required and the triplet carbenes are generated from them by photolysis in low temperature matrices with electron spin resonance (ESR), ultraviolet (UV) or infrared (IR) measurements used for detection.



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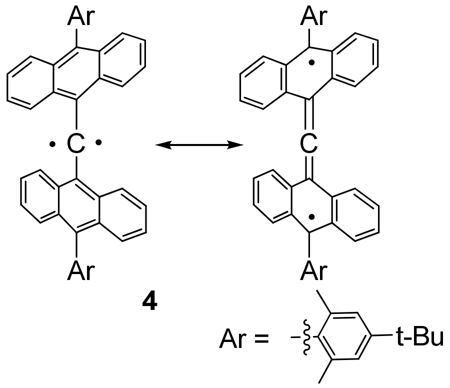

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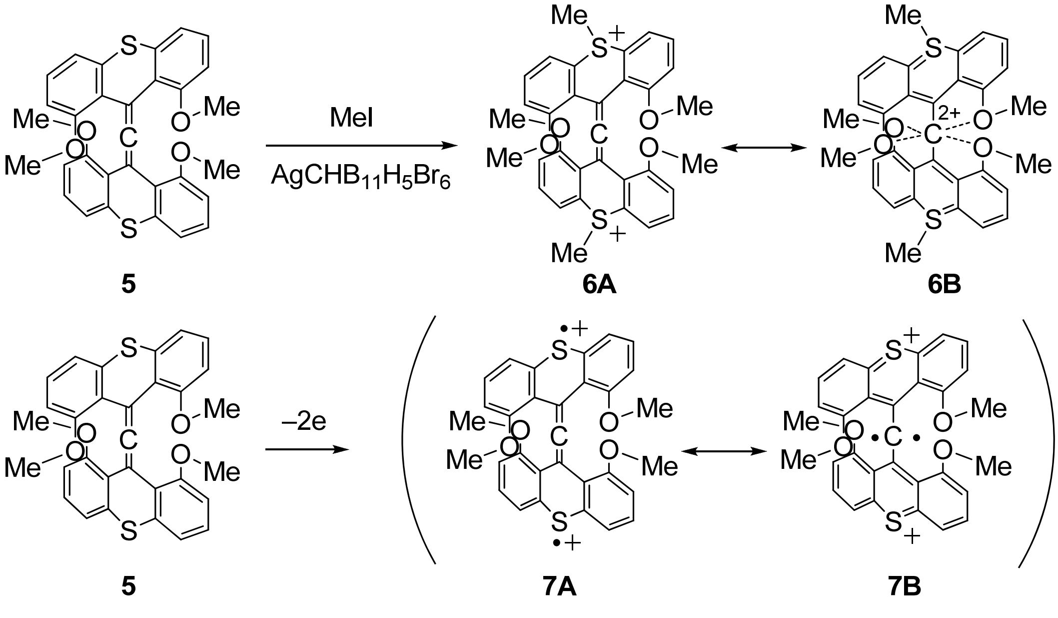
A major breakthrough was brought forth by Tomioka et al., who delivered two long-living carbenes **3**[8] and **4**.[9] Diaryl carbene **3**, in which the central carbene is protected by bulky bromine atoms and trifluoromethyl groups was found to survive nearly 1 day in benzene at room temperature. Dianthryl carbene **4**, which is further stabilized by strong resonance effects, survived nearly two weeks under the same conditions. However, this stability was still not enough to enable the "direct" observation of **4** by X-ray structural analysis, and only by in situ X-ray analysis of the triplet carbene partially generated by irradiation of a single crystal of the precursor diazo compound was it possible to gain solid phase parameters, although this in itself was a remarkable achievement.[10]

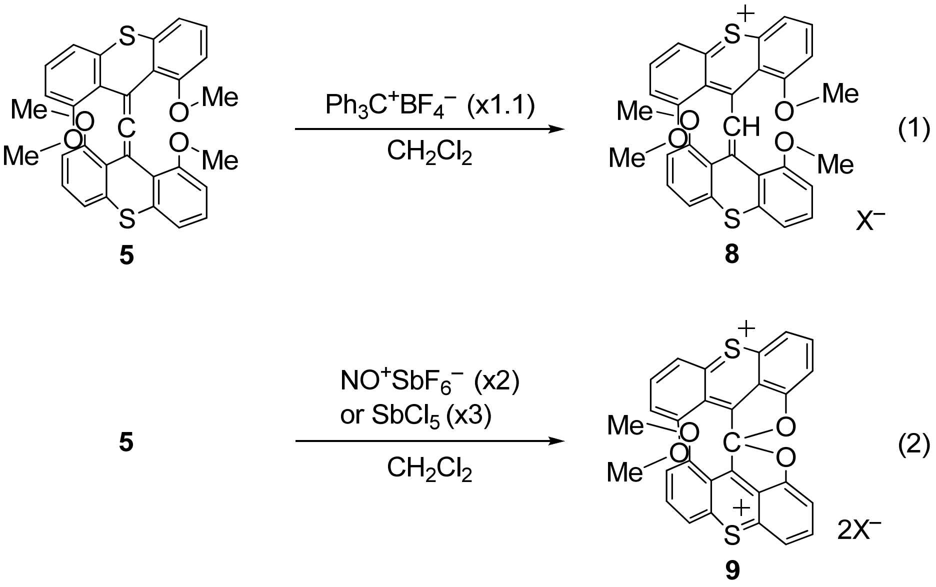
We have recently found thioxanthene to be a versatile framework for the preparation of some novel compounds and for the demonstration of unique chemistry.[11] In particular, allenic 9,9'-methanetetraylbis(1,8-dimethoxy-9*H*-thioxanthene) **5** which bears two such moieties in an orthogonal arrangement was found to be a suitable precursor for 9,9'-methanetetraylbis(1,8-dimethoxy-10-methyl-9*H*-thioxanthenium) dication **6**, which could be regarded as a hexacoordinate carbon species.[11c] During the course of these studies, we hit upon the idea that **5** might also be appropriate as a precursor for a stable triplet carbene, which could be obtained by oxidation. We envisaged that the presence of the sulfur atoms would facilitate oxidation of the allenic moiety, enabling us to directly carry out oxidation with commercially available oxidizing reagents, and avoid the preparation and use of azo compounds. The presence of the four methoxy groups was anticipated to add kinetic stability to the carbene.



Scheme 1. Two-electron oxidation of **5**.

Contrary to expectation, however, the oxidation of **5** did not furnish a stable triplet carbene but instead gave a ketal as a result of two demethylations. Interestingly, theoretical calculations suggested that the intermediate that gave rise to the product was an unexpected onium ion and not a triplet carbene. Herein, we provide details of our findings.

Results and Discussion



Scheme 2. Attempted two-electron oxidation of **5**.

The oxidation reaction of **5** was carried out with several oxidizing reagents.[12] The reaction of **5** with 2 equivalents of (p-$BrC_6H_4)_3N^{\bullet+}SbCl_6^-$ or $Ph_3C^+X^-$ ($X^- = BF_4^-$, $B(C_6F_5)_4^-$, $CHB_{11}H_5Br_6^-$) in CH_2Cl_2 afforded cation **8**~~, which has a hydrogen atom at the~~

~~central carbon~~ which is the conjugate acid of **5** (Scheme 2, eq. 1). The product of the reaction with Ph_3C^+ was cleaner than that with aminium, which yielded another unidentified compound as a by-product. Furthermore, the reaction of **5** with only 1.1 equivalents of $Ph_3C^+BF_4^-$ also afforded **8** in high yield (94%), thus indicating that only a single oxidation is actually required for the formation of **8**. The structure of **8** was identified by the X-ray analysis of its $CHB_{11}H_5Br_6^-$ salt as illustrated in Figure 1.

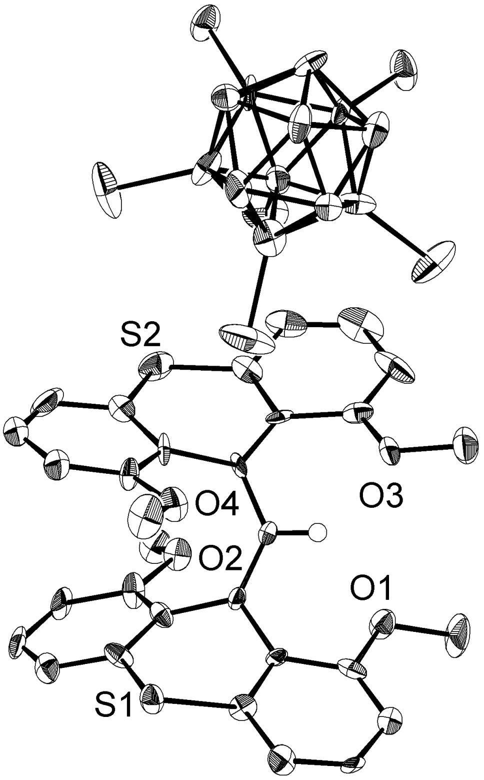
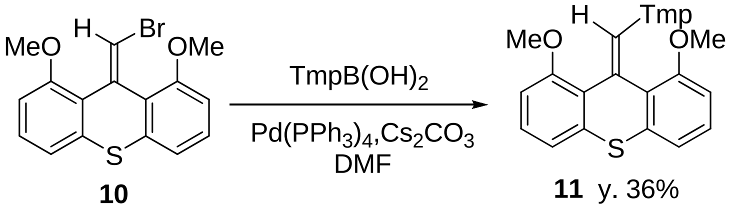


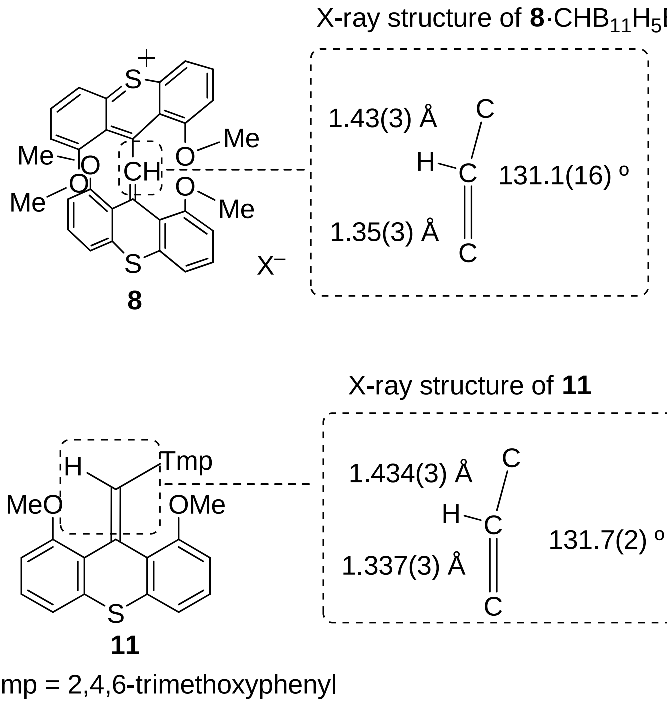
Figure 1. ORTEP drawing of the X-ray structure of **8**·$CHB_{11}H_5Br_6^-$. All hydrogen atoms except that bonded to the central carbon are omitted for clarity.

Since the hydrogen atom anticipated to be attached to the central carbon atom could not be located with certainty, a comparison with supposedly structurally similar and electronically neutral **11**, which could be prepared from **10** by Suzuki coupling, was carried out. The bond lengths and angles around the central carbon of **8** were very similar to those of **11** as shown in Figure 2, thereby ascertaining its vinylic structure. An alternative synthesis of cation **8** by treatment of **5** with a strong acid, such as TfOH, added support for the structural identity of **8**.[13] The ^{1}H NMR spectrum of **8** showed a characteristic singlet at 9.4 ppm ($CDCl_3$), which was assigned to the hydrogen bound to the central carbon atom.



Tmp = 2,4,6-trimethoxyphenyl

Scheme 3. Synthesis of **11**



R = 0.1182 (I>2σ(I))
R_w = 0.4192 (all data)
GOF = 1.038

R = 0.0430 (I>2σ(I))
R_w = 0.1339 (all data)
GOF = 1.071

Figure 2. The geometries of **8** and **11**.

When a stronger oxidizing reagent like $NO^+SbF_6^-$ or $SbCl_5$ was used, the demethylated dication **9** was obtained as the major product (Scheme 2, eq. 2). The structure of **9**·$(SbCl_6^-)_2$ was determined by X-ray analysis as depicted in Figure 3. The structural constitution clearly showed that what had been obtained was indeed a product of multiple oxidations. All attempts to observe intermediate triplet carbene species by ESR failed. This implied that either the ensuing reactions to give non-triplet species were too fast or that triplet species were not involved in the first place.

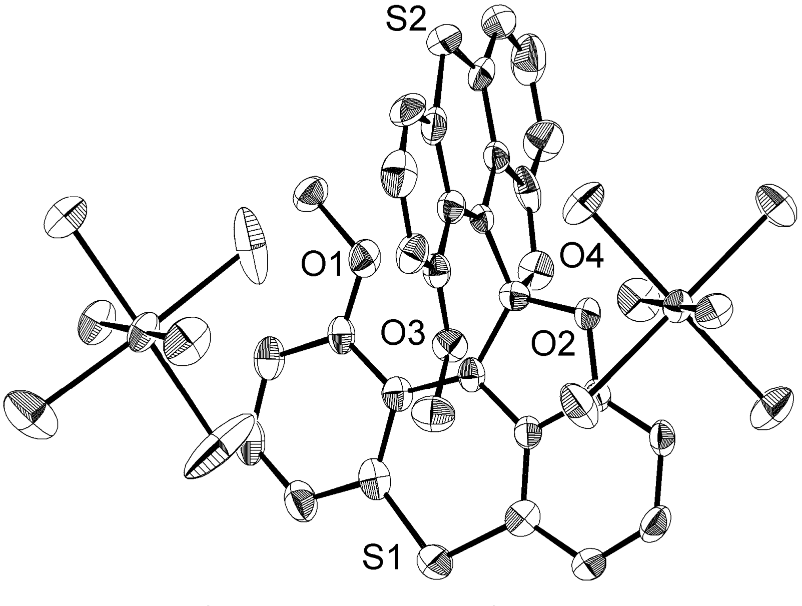


Figure 3. ORTEP drawing of the X-ray structure of **9**·$(SbCl_6^-)_2$. All hydrogen atoms are omitted for clarity.

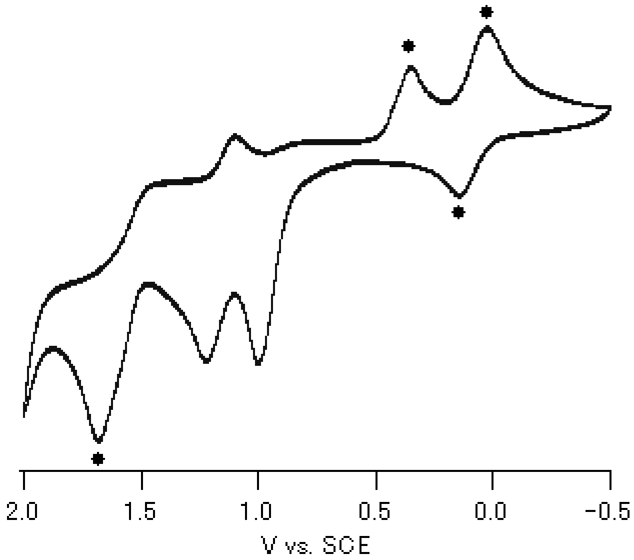


Figure 4. Cyclic voltammogram of **5** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ (vs. SCE). The black dots indicate peaks assigned to **8** (see Figure 5).

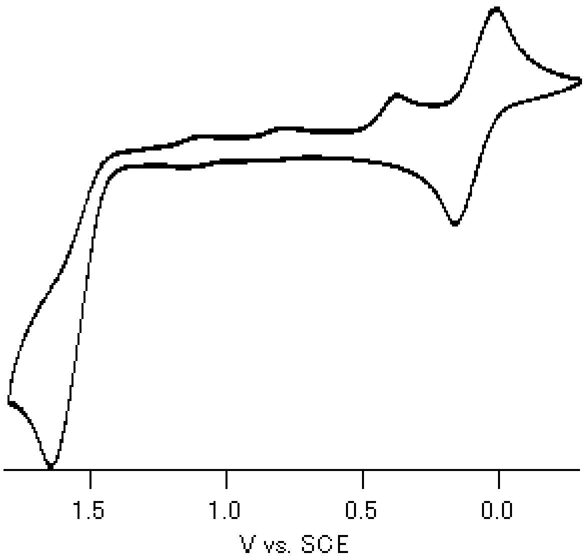
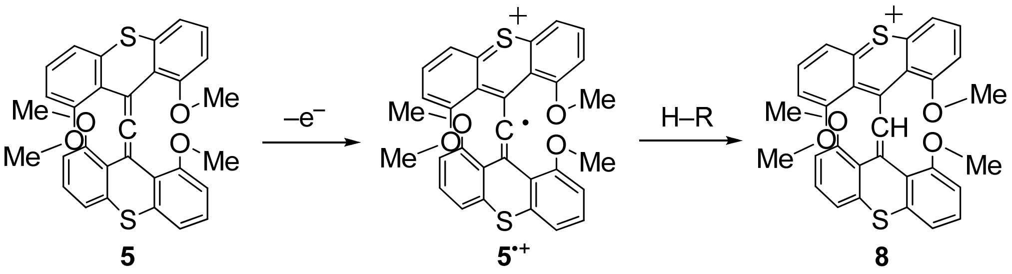


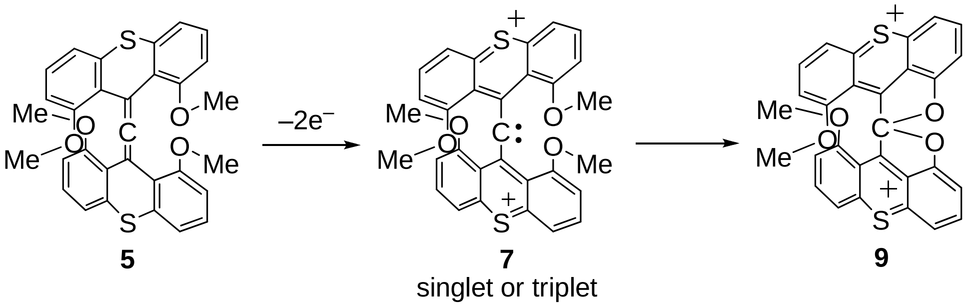
Figure 5. Cyclic voltammogram of **8** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ (vs. SCE).

To assess the redox behavior of **5**, cyclic voltammetry measurements were carried out, as shown in Figure 4. Since **8**~~, formed via partial oxidation of **5**,~~ was anticipated to contribute to the spectrum of **5**, a measurement of **8** was also conducted (Figure 5). A comparison of spectra suggests that the oxidation waves at E_{pa} = 1.00 and 1.23 V, and the reduction wave at E_{pc} = 1.10 correspond to the redox profile of **8**. Since the second oxidation wave (E_{pa} = 1.23 V) has a corresponding reduction wave (E_{pc} = 1.10 V), it could be supposed that the two oxidation peaks each corresponded to one electron oxidation processes, or in other words, the two-electron oxidation was stepwise. This implied that both one- and two-electron oxidations were viable with proper choice of oxidizing agent as we had observed by chemical oxidation.



Scheme 4. Plausible reaction mechanism to afford **8**.

Based upon the experimental results, the reaction of **5** with relatively weak oxidants can be rationalized as follows. One-electron oxidation takes place to give the unstable vinyl radical **5**$^{\bullet+}$ and this is ~~instantly~~ converted to **8** by hydrogen abstraction.



Scheme 5. Plausible reaction mechanism to afford **9**.

On the other hand, as for the reaction of **5** with the relatively strong oxidants, based upon the redox behavior, it is reasonable to assume that a two-electron oxidation had occurred to give a carbene intermediate. Coupled with the fact that the presumed carbene intermediate **7** did not exhibit unpaired electron reactivity as observed for monoradical $\mathbf{5}^{\bullet+}$, it was speculated that the spin state of the intermediate was not the open-shell triplet state but the closed-shell singlet state.

To verify this point, we have carried out theoretical calculations on the dicationic intermediate that arises upon depriving two electrons from **5**. Computations were carried out at the B3PW91/6-31G(d) and UB3PW91/6-31G(d) levels of theory[15], respectively, for the singlet state and the triplet state. The optimized geometries are shown in Figures 6 and 7, respectively.

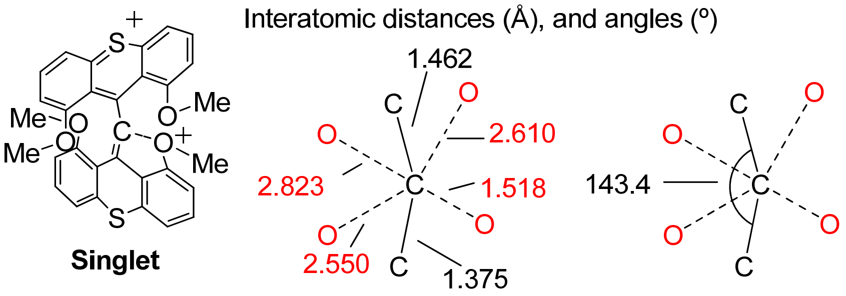


Figure 6. Optimized structure of singlet-**7**.

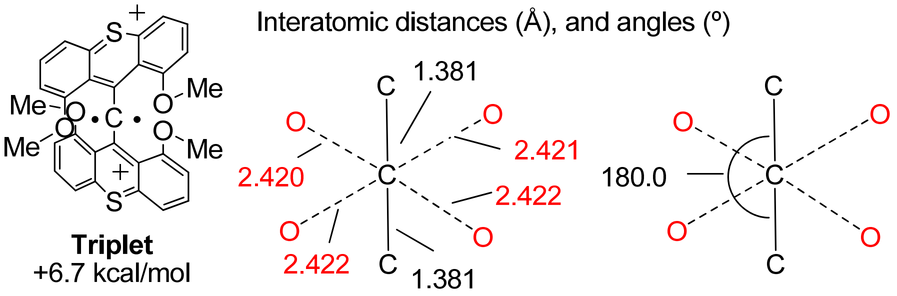


Figure 7. Optimized structure of triplet-**7**.

As expected from the diverse results between the one electron and two electron oxidation reactions, the singlet state was found to be more stable than the triplet state, and that by 6.7 kcal/mol. An interesting point to note on structures is that while the geometry of the triplet state in Figure 7 is essentially a D_{2d} symmetric octahedral with the lengths of the two central C–C bonds being identical, that of singlet-**7** (Figure 6) is completely different. There is a distinct difference in the two bond lengths (1.375 and 1.462 Å) involving the central carbon atom and that the distance between this carbon atom and one flanking methoxy oxygen atom is only 1.518 Å. These unique aspects imply that this carbon does not have the character of a singlet carbene but a vinyl cation, which is stabilized by interaction with the flanking methoxy group. This structural feature as a whole shows likelihood for the central carbon to react with this "coordinating" methoxy group to form an oxonium ion of which the methyl group is prone to nucleophilic attack by even weak nucleophiles for demethylation. A second round of similar events should lead to the second demethylation, thereby accounting for the mechanism of the formation of acetal **9**. There have been theoretical predictions that vinyl cations with a β electron-donating group would favor the triplet state.[15] In this case the δ sulfur atom would have been expected to behave in the same way. However, it turned out that the coordinating property of the methoxy groups on the thioxanthene framework heavily influenced the character of the intermediate ~~carbene~~ to completely prevail over the expected donor effect of sulfur.

Conclusion

We have attempted the preparation of an isolable triplet carbene by the oxidation of an allene compound having two thioxanthene moieties. Although we could not fulfill our objective, we obtained two different products depending upon the strength of the oxidizing agents. Relatively weak oxidants such as $Ph_3C^+BF_4^-$ gave **8** as a result of a one-electron oxidation followed by hydrogen abstraction, whereas relatively strong oxidants such as $SbCl_5$ furnished **9** as a consequence of what we believe to be a two-fold two-electron oxidation process involving two ionic demethylation processes. In order to rationalize the diverse behavior between the supposed intermediates, monoradical cation $5^{\bullet+}$ and ~~carbene~~ dication **7**, theoretical calculations on **7** were carried. Computations indicated that ~~contrary to precedence on similar diaryl carbenes,~~ the singlet state was favored over the triplet state by 6.7 kcal/mol. The optimized structure of the singlet state implied that the reason for this difference was because singlet-**7** is essentially a vinyl cation stabilized by a coordinating methoxy group. Based upon these new findings concerning diaryl carbenes, we have initiated examinations on derivatives that bear other peri-substituents for the unending pursuit of persistent triplet carbenes.

Experimental

General

CH_2Cl_2 was distilled from calcium hydride under argon. Commercially available anhydrous dimethylformamide (DMF) was used as received. Merck silica gel 60 (0.063-0.200 nm) was used for column chromatography and Merck silica gel 60 GF_{254} was used for preparative TLC. Melting points were measured using a Yanagimoto micro-melting point apparatus and are uncorrected. The ^1H NMR (400 MHz) was recorded using a JEOL EX-400 or AL-400 spectrometer. The ^1H NMR chemical shifts (δ) are recorded from internal $CHCl_3$ (δ 7.26), $CHDCl_2$ (δ 5.32) or CHD_2CN for ^1H (δ 1.93). Elemental analysis was performed using a Perkin-Elmer 2400CHN elemental analyzer. All oxidizing agents were used as received. The preparation of **5** and **10** has been described previously.[11c] 2,4,6-Trimethoxyphenylboronic acid was prepared according to a literature procedure.[16]

*Synthesis of **8**·BF_4^-*

A solution of **5** (26 mg, 0.050 mmol) and $Ph_3C^+BF_4^-$ (18 mg, 0.055 mmol) in dry CH_2Cl_2 (2 mL) was stirred for 16 h at room temperature. The solvent was removed in vacuo, and the residue was washed with ether. Compound **8** (29 mg, 0.047 mmol, 94%) was obtained as a purple solid, mp 195-197 ˚C (decomp.). δ_H (400 MHz, CD_2Cl_2) 3.39 (s, 6H, $2CH_3$), 4.16 (s, 6H, $2CH_3$), 6.52 (d, *J* 8.0, 2H, ArH), 7.16-7.37 (m, 6H), 7.52 (d, *J* 8.0, 2H, ArH), 7.71 (t, *J* 8.0, 2H, ArH), 9.36 (s, 1H, CH). δ_C ($CDCl_3$, 100 MHz) 55.9 (CH_3), 57.1 (CH_3), 109.41 (CH), 111.07 (CH), 118.43 (CH), 122.03 (C), 124.96 (C), 127.87 (CH), 127.90 (CH), 133.81 (CH), 134.97 (CH), 139.01 (C), 139.11 (C), 146.81 (C), 156.64 (C), 157.81 (C), 159.04 (C). HRMS (ESI) *m*/*z* calcd for $[C_{31}H_{25}O_4S_2]^+$calcd, 525.1189, found 525.1183. Anal. Calcd for $C_{31}H_{25}BF_4O_4S_2 \cdot H_2O$: C, 59.06; H, 4.32%. Found: C, 58.88; H, 3.97%.

Synthesis of ***9****·*$(SbCl_6^-)_2$

To a stirred solution of **5** (11 mg, 0.021 mmol) in dry CH_2Cl_2 (2 mL) under Ar, $SbCl_5$ (1.0 M in CH_2Cl_2, 0.07 mL, 0.07 mmol) was added at –78 ˚C. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo, and dry CD_3CN (ca. 0.6 mL) was then added to the mixture to give a dark green solution. The solution was transferred to a J. Young NMR tube under Ar for NMR measurements. **9**·$(SbCl_6^-)_2$. mp = >300 ˚C. δ_H (400 MHz, CD_3CN) 2.66 (s, 6H, Me), 7.27 (d, *J* 8.0, 2H, ArH), 7.64 (d, *J* 8.0, 2H, ArH), 8.34 (t, *J* 8.0, 2H, ArH), 8.43 (d, *J* 8.0, 2H, ArH), 8.47 (d, *J* 8.0, 2H, ArH), 8.60 (t, *J* 8.0, 2H, ArH). HRMS (ESI) *m*/*z* calcd for $[C_{29}H_{28}O_4S_2]^{2+}$ 247.0318, found 247.0320. Anal. Calcd for $C_{29}H_{18}Cl_{12}O_4S_2Sb_2 \cdot 2CH_2Cl_2$: C, 27.92; H, 1.66%. Found: C, 27.67; H, 1.52%.

Preparation of a single crystal of ***9****(*$SbCl_6^-)_2$

To a solution of **5** (11 mg, 0.021 mmol) in dry CH_2Cl_2 (0.5 mL) under Ar, $SbCl_5$ (0.51 M in CH_2Cl_2, 0.14 mL, 0.071 mmol) was added at –78 ˚C. The resulting reddish purple solution was settled for 3 h at –78 ˚C to afford single crystals of **9**·$(SbCl_6^-)_2$ as dark plates.

Synthesis of ***11*** *from* ***10***

A suspension of **10** (333 mg, 0.954 mmol), 2,4,6-trimethoxyphenylboronic acid (422 mg, 1.99 mmol), $Pd(PPh_3)_4$ (122 mg, 0.106 mmol) and Cs_2CO_3 (833 mg, 2.56 mmol) in dry DMF (20 mL) was stirred for 24 h at 80 °C under argon. The reaction mixture was filtered through Celite to remove any insoluble material and washed with THF. The filtrate was concentrated and the resulting liquid residue was purified by column chromatography (silica gel, *n*-hexane : CH_2Cl_2 = 1 : 3) to afford **11** (149 mg, 0.341 mmol, 36%) as a brown solid, mp 207-209 ˚C; δ_H ($CDCl_3$, 400 MHz) 3.20 (s, 3H, Me), 3.51 (br, 6H, Me), 3.78 (s, 3H, Me), 3.96 (s, 3H, Me), 6.03 (br, 1H, CH), 6.87 (m, 2H), 6.86-7.12 (m, 6H); δ_C ($CDCl_3$, 100 MHz, 50 ºC) 55.2 (CH_3), 55.3 (CH_3), 55.6 (CH_3), 57.1 (CH_3), 91.3 (CH), 109.55 (CH), 111.49 (C), 112.13 (CH), 118.60 (CH), 119.43 (CH), 125.69 (CH), 126.79 (CH), 126.90 (CH), 127.26 (C), 127.88 (C), 129.12 (C), 135.28 (C), 136.17 (C), 156.31 (C), 156.74 (C), 158.44 (C), 160.36 (C). ; Anal. Calcd for $C_{25}H_{24}O_5S$: C, 68.79; H 5.54%. Found: 68.53; 5.71%.~~Anal. Calcd for $C_{25}H_{24}O_5S$: C, 68.79; H, 5.54%. Found: C, 67.38; H, 5.33%.~~

Theoretical Calculations

DFT calculations were performed using the Gaussian 98 program package.[17] Geometry optimization of the singlet states of **7** and **12** were carried out using the DFT/B3PW91 level of theory with the 6-31G(d) basis set for all atoms. Geometry optimization of the triplet states of **7** and **12** were computed at the DFT/UB3PW91 level of theory with the 6-31G(d) basis set for all atoms. No symmetry constrains were imposed during the optimizations.

Crystallographic data. This material is available on the journal's webpage.

Acknowledgements

This work was supported by two Grants-in-Aid for Scientific Research on Priority Areas (Nos. 14340199, 17350021) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors are grateful to Dr. Shiro Matsukawa of Toho University for assistance in X-ray analysis.

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