

DIRECT OBSERVATION OF A CARBENIUM ION STABILIZED BY NEIGHBORING TWO SULFURS

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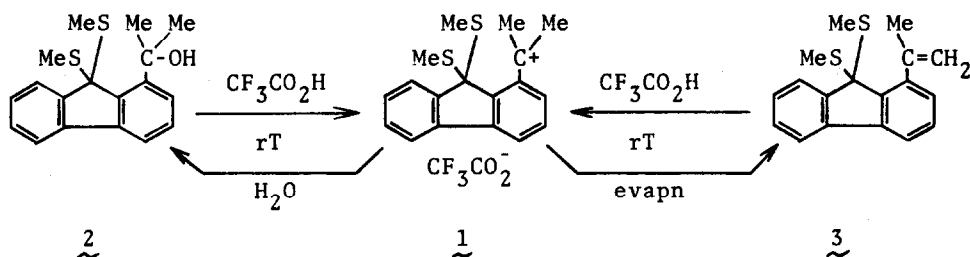
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Attempts¹⁻³ have been made in recent years to observe directly carbenium ions which are stabilized by neighboring two sulfurs situated symmetrically around the cationic center, for instance, with benzyl cation¹, trityl cation², and 9-anthracenylmethyl cation³ systems. Possible observation of a hypervalent carbon species proposed as a metastable intermediate (or transition state) for the S_N2 displacement was another interest of these workers. Although many interesting phenomena were reported with these systems, the species actually and directly observed by nmr were sulfonium ions, and not hypervalent carbon species. We now wish to communicate direct observation of dimethyl-1-fluorenylmethyl cation 1 stabilized by two methylthio groups at the 9-position.

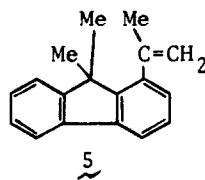
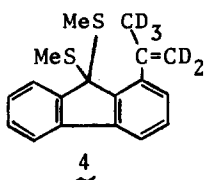
Both alcohol 2 and the corresponding olefin 3 were obtained from dimethyl-dithioacetal of 1-methoxycarbonyl-9-fluorenone by reaction with methylmagnesium iodide⁴. Alcohol 2: mp 145°; nmr^{5a}(CCl₄) δ 7.68-7.20 (m, 7, ar), 4.52 (br, 1, OH), 1.63 (s, 6, C-Me), and 1.56 (s, 6, S-Me). Anal. Calcd for C₁₈H₂₀OS₂: C, 68.31; H, 6.37; S, 20.26. Found: C, 68.10; H, 6.28; S, 19.96. Olefin 3: mp 59-60°; m/e 298; nmr^{5b}(CCl₄) δ 7.62-6.93 (m, 7, ar), 5.22 (m, 1, olefinic), 5.01 (m, 1, olefinic), 2.21 (q, 3, α-Me), and 1.51 (s, 6, S-Me). Anal. Calcd for C₁₈H₁₈S₂: C, 72.44; H, 6.08; S, 21.49. Found: C, 72.59; H, 6.06; S, 21.30.

Alcohol 2 was dissolved in trifluoroacetic acid and its nmr spectrum^{5a} was recorded immediately at 30°; δ 8.05-7.25 (m, 7, ar), 2.70 (s, 3), 2.31 (s, 6), and 1.95 (s, 3). Ultraviolet and visible absorption spectra⁶ of this



solution showed bands at 260nm (ϵ , 31,000), 329 (7,300), 387 (8,300), and 448 (6,400), suggesting formation of a carbenium ion⁷. Thus tentatively, signals at 2.70 and 1.95 were assigned to two C⁺-methyls of the carbenium ion 1 and six protons at 2.31 was ascribed to two S-methyls of ion 1. The same nmr spectrum was also obtained when olefin 3 was dissolved in trifluoroacetic acid, in place of alcohol 2. This solution of carbenium ion 1, which was allowed to stand under hood on an evaporating dish at room temperature, afforded crystals of olefin 3 in an almost quantitative yield. On pouring the solution of carbenium ion 1 onto crashed ice, alcohol 2 was produced in 30% yield, together with 45% yield of olefin 3.

Assignments of the signals for carbenium ion 1 were confirmed as follows. When alcohol 2 was dissolved into CF₃CO₂D, there occurred immediate and complete disappearance of only signals at 2.70 and 1.95. Since in such an acidic condition³ neither SCH₃ nor S⁺CH₃ group undergoes H-D exchange, while this isotopic exchange is possible for C⁺CH₃ group probably via olefins C=CH₂, the signal remaining at 2.31 should be that for six protons of the two equivalent SCH₃ groups. Evaporation of this solution gave white crystals, mp 58-59°, m/e 303, the nmr spectrum of which agreed well to that expected for a deuterated compound 4 containing several per cents of incompletely deuterated olefins. This crystal exhibited again the same nmr spectrum as that of ion 1 on dissolving it into CF₃CO₂H, from which original olefin 3 could be recovered.



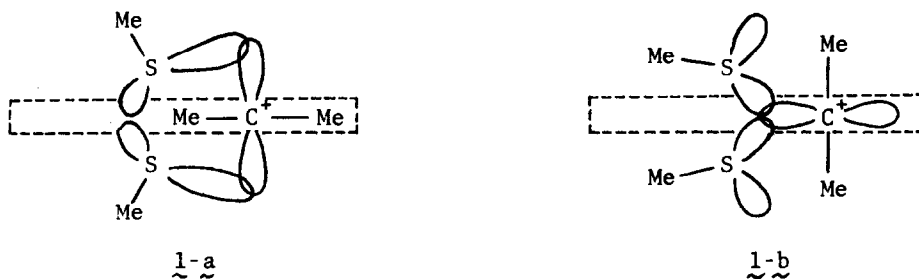


Fig. 1. Two possible conformations for carbenium ion 1. Views from within the plane of the fluorene nucleus.

Two possible conformations for carbenium ion 1 are shown in Figure 1. In one conformation 1-a, participation of non-bonding electrons of the two sulfurs occurs from both sides of the plane of the sp^2 carbon, this central carbon being thus pentacoordinated in some resemblance to the case of transition states for S_N2 displacements. In the other conformation 1-b, overlap of the orbitals occurs only in one side of the sp^2 carbon. The fact that the two C^+ -Me groups are not equivalent in nmr clearly eliminates the possibilities of 1-b, indicating that ion 1 exists in the conformation 1-a.

Regarding extra stability of this carbenium ion 1 due to participation of the two neighboring sulfurs, comparison of the present system with those lacking any participation seems of much importance. 9,9-Dimethyl compound 5⁸ showed essentially the same nmr spectrum even in CF_3CO_2H as in $CDCl_3$ and H-D exchange in CF_3CO_2D is very slow, no exchange being observed at least for several hours at room temperature. Compared with methyl protons (δ 3.60)⁹ of cumyl cation in super acid, C^+ -Me protons in 1 (δ 2.70 and 1.95) are much shielded, probably due to electrons supplied from the two S-Me groups. Consequent deshielding can be seen for the S-Me protons of 1 (δ 2.31), in comparison to those in alcohol 2 (δ 1.56) or those in olefin 3 (δ 1.51).

REFERENCES AND NOTES

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2. R. Breslow, L. Kaplan, and D. LaFollette, J. Am. Chem. Soc., 90, 4056 (1968).
3. J. C. Martin, and R. J. Basalay, J. Am. Chem. Soc., 95, 2572 (1973).
4. Alcohol 2 and olefin 3 were obtained in 40% and 5% yield, respectively. This Grignard reaction often gave considerable amounts of abnormal products with C-S bonds being cleaved. This abnormal Grignard reaction and related data will be published elsewhere.
5. Recorded on a spectrometer, (a) JEOL Model JNM-PS-100; (b) Varian associates Model HA-100; (c) Hitachi Model R-24.
6. Recorded on a Hitachi recorder Model 056-1001 combined with a Hitachi spectrophotometer Model 124.
7. G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, J. Am. Chem. Soc., 88, 1488 (1966).
8. Prepared from ethylenedithioacetal of 1-methoxycarbonyl-9-fluorenone by reaction with methylmagnesium iodide, mp 47-48°; nmr^{5c}(CDCl₃) δ 6.89-7.68 (m, 7, ar), 5.25 (m, 1, olefinic), 4.94 (m, 1, olefinic), 2.08 (q, 3, α-Me), and 1.51 (s, 6, 9-Me). Anal. Calcd for C₁₈H₁₈: C, 92.26; H, 7.74. Found: C, 92.41; H, 7.77.
9. G. A. Olah, J. Am. Chem. Soc., 86, 932 (1964).