Figure 1. Biphenylene. Shaded orbitals have increased p character; hence, unshaded orbital has increased s character.

sults as well as numerous other qualitative observations in the literature obey the following generalization: *aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity toward electrophilic substitution.* Our interpretation follows from Figure 1. The atomic orbitals of the fused aryl carbon used to construct the strained ring have higher p character. Hence, the remaining orbital has higher s character. The o-carbon is thus bound to an orbital of higher electronegativity and the observed properties follow.

(11) National Institutes of Health Predoctoral Fellow, 1964–1966.
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The Crystal and Molecular Structure of the 1:1 Adduct of Antimony(V) Fluoride and Sulfur Dioxide[1]

Sir:

We wish to report on the structure of crystalline $SbF_5 \cdot SO_2$, a compound of increasing interest because of the use of antimony pentafluoride solutions in liquid sulfur dioxide to produce carbonium ions.[2]

The compound was prepared by the method of Aynsley[3] who reported a melting point of 57°. The crude product was purified by sublimation to give a colorless solid, mp 66–72°, which was recrystallized from liquid SO_2, mp 62–67°. *Anal.*[4] Calcd for $SbF_5 \cdot SO_2$: Sb, 43.2; S, 11.4; F, 33.8. Found: Sb, 40.73; S, 10.58; F, 32.19. The infrared spectra of the sublimed and recrystallized materials, obtained on the powdered solid between AgCl plates, were identical, showing bands at 1625 (w), 1323 (s), 1145 (sh w), 1100 (m), 696 (s), and 480 cm^{-1} (w).[5]

The structure was determined by single-crystal X-ray methods. $SbF_5 \cdot SO_2$ crystallizes in the $P2_1/c$ space

(1) Based on the dissertation submitted by J. W. Moore to the Division of Graduate Studies, Wake Forest University, in partial fulfillment of the requirements for the Master of Arts degree.
(2) (a) G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **89**, 2694 (1967), and a number of previous papers of that series; (b) M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966); M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).
(3) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. Ind.* (London), 1117 (1951).
(4) Analysis by Alfred Bernhardt, Mikroanalytisches Laboratorium, im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), West Germany.
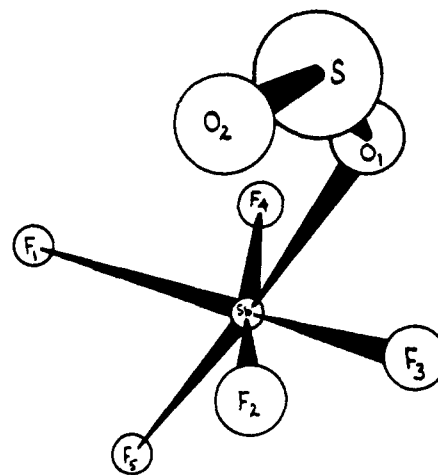(5) The spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer.

Figure 1. Isometric projection of $SbF_5 \cdot SO_2$.

group with unit cell dimensions: $a = 5.84$ Å; $b = 10.50$ Å; $c = 10.54$ Å; $\beta = 109°35'$; $Z = 4$.

The 1003 independent reflections, recorded by the Weissenberg multiple-film technique, were judged visually and gave an R value[6] of 0.09 after the usual Patterson and Fourier syntheses followed by a least-squares refinement with anisotropic temperature factors.[7]

The structure so obtained is shown in Figure 1. The five fluorine atoms and O_1 outline a highly symmetrical octahedron which is elongated in the direction of the F_5–O_1 axis.

The largest standard deviation for the bond lengths, which are uncorrected for thermal rocking motion, is 0.016 Å, and those for the bond angles are commensurate. The bond lengths (Å) are: Sb–O_1, 2.13; Sb–F_1, 1.87; Sb–F_2, 1.84; Sb–F_3, 1.86; Sb–F_4, 1.84; Sb–F_5, 1.85; S–O_1, 1.45; S–O_2, 1.38. The O_1–Sb–F_5 angle is 178.2°, the F_1–Sb–F_3 angle is 170.4°, and the F_2–Sb–F_4 angle is 170.6°. Atoms F_1, F_2, F_3, and F_4 are coplanar within 0.05 Å, and the antimony atom is displaced 0.14 Å from that plane in the direction of F_5. The Sb–O_1–S angle is 138.9°. The oxygen–sulfur–oxygen angle of 119.2°, the S–O_1 bond length of 1.45 Å, and the S–O_2 bond length of 1.38 Å compare with an angle of 119.0° and a bond length of 1.43 Å found in crystalline SO_2.[8] The Sb–O_1 bond length of 2.13 Å is in good agreement with the antimony–oxygen bond length of 2.12 Å found in $SbCl_5 \cdot (CH_3)_2SO_2$.[9] The shortest intermolecular contact distance is 2.86 Å which occurs between S and F_2, and S and F_5.

The ^{19}F nmr spectrum[10] at $-78°$ in liquid SO_2 is consistent with the structure shown. Two peaks are observed, a doublet ($J = 100$ cps) at 105 ppm and a broad resonance at 137 ppm upfield relative to CCl_3F as an external standard. On integration the ratio was 4:1. We were not able to resolve the broad resonance, but its width was consistent with the expected quintet and the J value of 100 cps.

(6) $R = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$.
(7) W. R. Busing, K. O. Martin, and H. A. Levy, OR FLS–A Fortran Crystallographic Least-Squares Program, ORNL-TM-305, Oak Ridge National Laboratory, 1962, modified (H. W. B.) for the IBM 360-30.
(8) B. Post, R. S. Schwartz, and I. Fankuchen, *Acta Cryst.*, **5**, 372 (1952).
(9) C.-I. Brändén, A. Hansson, Y. Hermodsson, and I. Lindqvist, *Z. Krist.*, **117**, 464 (1962).
(10) Obtained on a Varian A 56/60 spectrometer.

A complete structure report will be made.

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The Photochemistry of Silicon Compounds. II.
The Photolysis of Methylsilane as a Source
of Methylsilene

Sir:

The photochemistry of silicon compounds has attracted little attention to date. In part I of this series[1] the mercury-photosensitized decomposition of the methylated silanes had been shown to involve exclusive Si–H bond cleavage and to exhibit, in this and other respects, behavior similar to paraffins. The direct photolysis of alkylsilanes in the vacuum uv, however, would be expected to proceed rather by molecular mode of eliminations if the analogy with paraffins[2] can be further extended, and thus provide a convenient source for the generation of the little investigated family of silenes, the silicon analog of carbenes. As far as can be ascertained from the literature, no previous study has been reported on the vacuum uv photolysis of alkylsilanes.

We photolyzed methylsilane in the gas phase with the 1470-Å radiation of a low-pressure Xe resonance lamp using a conventional vacuum uv photolysis apparatus with LiF windows.

The products of the reaction were hydrogen (1.03), methane (0.23), dimethyldisilane (0.48), methyldisilane (0.26), and a solid polymer along with small amounts of dimethylsilane, ethane, and traces of an oxygenated silane. The figures in parentheses indicate quantum yield values extrapolated to zero exposure time (which was necessitated by the attenuation of the incident light intensity due to polymer deposition on the LiF window) and are based on CO_2 actinometry[3] ($\phi(CO) = 1.0$).

Addition of nitric oxide in concentrations of up to 10% hardly affected the dimeric product yields, indicating that monoradicals are not principal precursors.[4] Addition of ethylene had little effect on the hydrogen yield, but experiments with CH_3SiD_3 revealed that ethylene retarded D_2 formation and increased that of H_2 and HD. These increases are due to the decomposition of ethylene. From these experiments it can be concluded that the disilane products arise from carbene-like precursors, and only a fraction of the hydrogen is scavengeable.

(1) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).
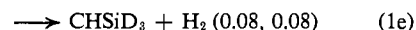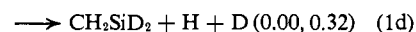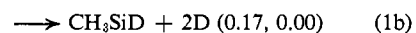(2) J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964); R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, **46**, 4333 (1967); H. Akimoto, K. Obi, and I. Tanaka, *ibid.*, **42**, 3864 (1965).
(3) B. H. Mahan, *ibid.*, **33**, 959 (1960).
(4) In the mercury photosensitization of methylsilane, the methylsilyl radicals could be scavenged with a few torr of NO, as evidenced by the complete suppression of their recombination product, $CH_3SiH_2SiH_2CH_3$, and the appearance of the new product, $CH_3SiH_2OSiH_2CH_3$; *cf.* ref 1.

Further insight into the mechanism comes from deuterium-labeling studies using CH_3SiD_3 and CH_3-SiH_3–CH_3SiD_3 mixtures.

From CH_3SiD_3, the isotopic composition of hydrogen was $\sim 8\%$ H_2, 29% HD, and 63% D_2. The methane contained 90% CH_3D and 10% CH_4, the latter being formed partly from isotopic impurities in CH_3SiD_3. From a comparison of the photolyses of pure CH_3SiH_3 and CH_3SiD_3, no significant H/D isotope effect appeared on the over-all reaction at a pressure of 100 torr. When the isotopic composition of the hydrogen product was determined from the mixtures of CH_3SiD_3 and CH_3SiH_3, corrected for absorption by each component and plotted against mole per cent of CH_3SiH_3, the relative yield of D_2 exhibited a decline from 0.63 to 0.31 and that of HD an increase from 0.29 to 0.67 on going from 100% CH_3SiD_3 to 100% CH_3SiH_3. These scavenging experiments suggest the following hydrogen-producing primary steps

$$CH_3SiD_3 + h\nu \longrightarrow CH_3SiD + D_2 \ (0.32, 0.32) \quad (1a)$$
$$\longrightarrow CH_3SiD + 2D \ (0.17, 0.00) \quad (1b)$$
$$\longrightarrow CH_2SiD_2 + HD \ (0.30, 0.00) \quad (1c)$$
$$\longrightarrow CH_2SiD_2 + H + D \ (0.00, 0.32) \quad (1d)$$
$$\longrightarrow CHSiD_3 + H_2 \ (0.08, 0.08) \quad (1e)$$

where the figures in parentheses indicate limiting quantum yields. The formation of methane, which is also unaffected by NO, requires a fifth primary step

$$CH_3SiD_3 + h\nu \longrightarrow CH_3D + SiD_2 \quad (2)$$
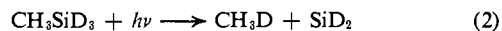
The two silane products can now be rationalized as being formed by the insertion of the silenes into the Si–H bonds of the methylsilane molecule.

$$CH_3SiH + CH_3SiH_3 \longrightarrow CH_3SiH_2SiH_2CH_3 \quad (3)$$
$$SiH_2 + CH_3SiH_3 \longrightarrow CH_3SiH_2SiH_3 \quad (4)$$
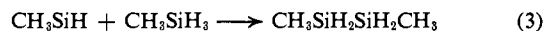
Insertion of the 1,2 diradical, CH_2SiH_2, into an Si–H bond would be a sterically unfavorable process, but its isomerization to the silene structure

$$CH_2—SiH_2 \longrightarrow CH_3SiH \quad (5)$$

should be energetically feasible.[5] The mass spectrometric analysis of the disilane product from the CH_3-SiD_3 reaction indicates a composition of $CH_3SiD_2SiD_2$-CH_3 favoring the insertion of the primary CH_3SiD silene and militating against the importance of the isomerization reaction 5. This is also in agreement with the near coincidence of the quantum yield of primary steps 1a and 1b with that of dimethyldisilane appearance. The main mode of the 1,2-diradical removal is probably by polymerization.

The insertion reactions 3 and 4 are strongly exothermic since their net result is an additional bond formation, and the resulting hot molecules require pressure stabilization. This is clearly evident from the fact that the disilane yields exhibit an increase and the hydrogen yield a decrease with pressure from 10 to 100 torr, but all product yields are invariant with pressure between 100 and 400 torr.

The insertion mechanism indicates that the silenes in reactions 1a and 1b and 2 are formed in a singlet state,

(5) *Cf.* E. W. Dasent, "Nonexistent Compounds," Marcel Dekker Inc., New York, N. Y., 1965, pp 26, 61–65, 71–74.