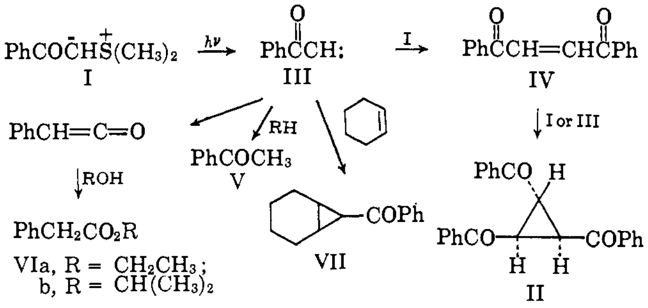
Decomposition of Sulfur Ylides. Evidence for Carbene Intermediates

Sir:

In many over-all chemical transformations, sulfur ylides behave very similarly to diazo compounds. Both classes of intermediates form epoxides from aldehydes and ketones,[1,2] form cyclopropanes from olefinic compounds,[1,3,4] and undergo Wolff rearrangement upon photolysis.[5,6] In some of these reactions of diazo compounds, carbenes have been demonstrated as intermediates.[7] However, no satisfactory demonstration of carbene formation from sulfur ylides has been reported.[8,9] We wish to report compelling evidence to support a carbene as an intermediate in the decomposition of a sulfonium ylide—dimethylsulfoniumphenacylide (I).

Compound I,[10] mp 57–59°, was prepared in 79% yield by treatment of dimethylphenacylsulfonium bromide with 10% aqueous sodium hydroxide at 0–5°. Its photolytic[11] decomposition in chloroform and benzene led to nearly quantitative yields of *trans*-1,2,3-tribenzoylcyclopropane (II). Since I is remarkably stable thermally, its sensitivity to photolysis indicated the formation of a reactive electron-deficient species such as the carbene III (see Scheme I). The cyclopropane arises from reaction of the carbene with a second mole of ylide to produce dibenzoylethylene (IV) which subsequently combined with either I or III to produce II. The likelihood of the Michael reaction of I with IV was demonstrated by preparing a solution of these two reactants in benzene and isolating II after stirring at room temperature for 3 hr.

Scheme I



Photolysis of I in alcohol and cyclohexene confirms the presence of III. Performing the irradiation in ethanol led to approximately 48% yield of three volatile products and 40–45% yield of II. The volatile materials (see Table I) were identified as acetophenone (V), propiophenone, and ethyl phenylacetate (VIa). When 2-propanol was employed as solvent, a drastic reduction in the ratio of phenylacetic ester to acetophenone occurred. If VI arises by a Wolff rearrangement of III, by increasing the abstractability of the hydrogen in the solvent the amount of VI relative to V should decrease, as is observed. Finally, irradiation in cyclohexene produced benzoylnorcarane (VII) in addition to V. These results are summarized in Table I. The photolytic decomposition of dimethylsulfoniumphenacylide produced the same products in very similar ratios as the diazoacetophenone decomposition.[12] This observation indicates the same intermediate, III, is formed in both instances. However, the most efficient trap for the carbene is the ylide I; the formation of tribenzoylcyclopropane as the major product in all the irradiations attests to this fact. The data indicate that I reacts approximately 8000 times faster with III than does cyclohexene. The presence of propiophenone deserves brief comment. A reasonable mechanistic pathway for its formation involves a Stevens rearrangement of the ylide followed by the photolytic decomposition of the resultant α-methylthiopropiophenone.[13]

Table I. Relative Amounts of Volatile Products

Method of decompn[a]	% V	% VI	% VII
1. Irradiation in C_2H_5OH[b]	52	26	
2. Irradiation in $(CH_3)_2CHOH$[c]	97	1.5	
3. Irradiation in cyclohexene[d,e]	83		10
4. Thermolysis in cyclohexene			100

[a] In all cases the major product isolated was II. [b] Propiophenone also formed in 22% relative yield. [c] Propiophenone formed in 1.5% relative yield. [d] Propiophenone formed in 7% relative yield. [e] Bicyclohexenyl isolated in 38% yield.

The thermal degradation of I was also investigated. Although only unreacted starting material was obtained upon heating a solution of I in cyclohexene, benzene, chloroform, or a benzene–cyclohexanone mixture, I rapidly disappeared when anhydrous cupric sulfate was added. For the nonreactive solvents, 90–95% yields of II were obtained. Two paths are conceivable and are outlined in Scheme II. The presence of IX[14] or a species similar in reactivity to it was demonstrated by obtaining benzoylnorcarane (VII; see Table I) in addition to II by using cyclohexene as solvent. A low yield (about 5%) of VII[15] was anticipated since we have shown above that I is a much more effective nucleo-

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(1) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(2) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).

(3) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

(4) F. Weygand and H. J. Bestmann, "Newer Methods of Preparative Organic Chemistry," Vol. III, Academic Press Inc., New York, N. Y., 1964, pp 451–508.

(5) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).

(6) L. Horner and E. Spietschka, *Chem. Ber.*, **85**, 225 (1952).

(7) See W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(8) Three reports[3,9] claim carbene formation from sulfur ylides. Although the results of these reports do not disagree with carbenoid intermediates, they do not necessitate this conclusion. In some of these examples, alternate explanations are more satisfactory.

(9) (a) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961); (b) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

(10) (a) B. M. Trost, to be published. (b) For the preparation and characterization of a similar ylide see H. Nozaki, K. Kondo, and M. Takaku, *Tetrahedron Letters*, No. **4**, 251 (1965).

(11) A Hanovia high-pressure mercury lamp employing a Pyrex filter was employed in all irradiations.

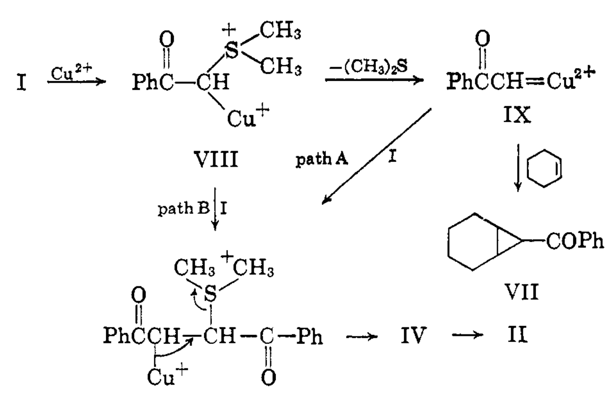
(12) D. D. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

(13) (a) The ylide does not undergo the Stevens rearrangement thermally under these conditions. Thus, to our knowledge, this example represents the first photolytic induced Stevens rearrangement. (b) For a discussion of this type of reaction see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 223–233. (c) For a recent example of the photochemical reaction of an α-thio ketone and a discussion of the photolytic cleavage of electronegative substituents α to a carbonyl group see A. Padwa and D. Crumrine, *Chem. Commun.*, 506 (1965).

(14) (a) p_π–d_π overlap is suggested for the stabilization of carbanions adjacent to heteroatoms. See ref 13b, pp 71–84. (b) Hammond[12] suggested a similar intermediate in the copper-catalyzed decomposition of diazoacetophenone.

(15) A 90% yield of tribenzoylcyclopropane was obtained in this reaction.

Scheme II



phile than cyclohexene. However, we cannot exclude the possibility of both mechanisms in Scheme II being operative in the present case. Although the results of the thermal decomposition are ambiguous, the photolytic decomposition clearly involves benzoylcarbene as an intermediate.

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Lewis Basicity of Metals. III. Boron Halide Adducts of Trichlorostannate(II) and Trichlorogermanate(II)

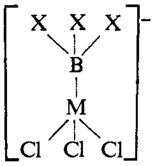
Sir:

Ordinarily, the metal ion in a complex functions as a Lewis acid; however, recent information indicates that transition metals may also serve as Brønsted[1] or Lewis[2] bases. In addition, the basicity of a nontransition metal has been realized through the formation of $SnCl_3^-$ adducts with transition metal acceptors.[3] Nmr data for the $SnCl_3^-$ adducts of platinum(II) indicate that the tin is a weak σ donor and a strong π acceptor.[4] We wish to report several cases in which $SnCl_3^-$ and $GeCl_3^-$ form addition compounds which appear to involve $Sn \rightarrow B$ and $Ge \rightarrow B$ donor-acceptor bonds. For such compounds only σ donation can be involved.

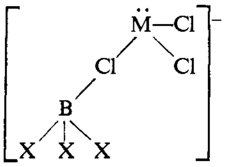
Salts containing $GeCl_3^-$ and $SnCl_3^-$ were prepared by adding $(C_6H_5)_4AsCl$ or $(CH_3)_4NCl$ to HCl solutions of divalent germanium[5] or tin. Good C, H, N, and Cl analyses were obtained on the compounds. Molecular weight information was as follows. Calcd for $(C_6H_5)_4AsGeCl_3$ (one-half formula weight):[6] 281. Found (cryoscopic, sulfolane): 276. Calcd[6] for $(C_6H_5)_4AsSnCl_3$: 304. Found: 283. Infrared spectra of these salts showed MCl_3 stretching vibrations at 285 and 322 cm^{-1} for $GeCl_3^-$ (lit.[7] 253 and 320 cm^{-1}) and 252 and 289 cm^{-1} for $SnCl_3^-$ (lit.[7] 256 and 297 cm^{-1}). Absorptions characteristic of the cations were also present.

In a typical reaction $(C_6H_5)_4AsMCl_3$ (*ca.* 0.075 mmole; M = Sn or Ge) was dissolved in several milliliters of methylene chloride and a twofold excess of Lewis acid was added. A white precipitate generally formed immediately. The mixture was stirred for several hours on the vacuum line after which solvent and excess acid were removed under reduced pressure. Unconsumed BF_3 was determined by PVT measurement, and its purity was checked by an infrared spectrum, which always indicated that no appreciable halide exchange had occurred. With BCl_3, the weight gain of the sample was used to determine stoichiometry of formation. Observed ratios of acid to base and molecular weights in sulfolane follow: $(C_6H_5)_4AsSnCl_3 \cdot BF_3$, 0.99:1; mol wt: calcd[6] 338, obsd 308. $(C_6H_5)_4AsSnCl_3 \cdot BCl_3$, 1.04:1; mol wt: calcd[6] 363, obsd 344. $(C_6H_5)_4AsGeCl_3 \cdot BF_3$, 0.99:1; mol wt: calcd[6] 315, obsd 311. $(C_6H_5)_4AsGeCl_3 \cdot BCl_3$, 1.02:1, mol wt: calcd[6] 340, obsd 343. $(CH_3)_4NSnCl_3 \cdot BF_3$, 0.95:1. Boron(11) nmr spectra of sulfolane solutions showed singlet absorptions at 19.1 ppm for $Cl_3SnBF_3^-$, and 19.0 ppm for $Cl_3GeBF_3^-$, relative to $B(OCH_3)_3$. These absorptions are in the correct region for coordinated BF_3. Infrared spectra of all the compounds show the presence of two bands which could be assigned to MCl_3 stretching vibrations: $Cl_3SnBF_3^-$, 267 and 294 cm^{-1}; $Cl_3SnBCl_3^-$, 255 and 284 cm^{-1}; $Cl_3GeBF_3^-$, 280 and 323 cm^{-1}; and $Cl_3GeBCl_3^-$, 280 and 325 cm^{-1}. Characteristic bands due to coordinated BF_3 and BCl_3 were also present.

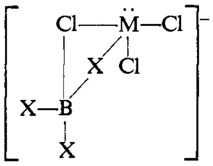
There are four simple structures consistent with the stoichiometry



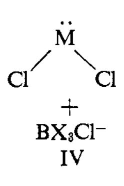
I



II



III



IV

where M = Ge or Sn and X = F or Cl.

The molecular weight data agree with I, II, or III; unless MCl_2 exists as a high polymer in sulfolane, the data are not consistent with IV. Additional evidence against structure IV is the lack of a significant infrared

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(1) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

(2) M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, **88**, 301 (1966), and references therein.

(3) (a) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963); (b) A. C. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963); (c) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

(4) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

(5) A. Tchakirian, *Compt. Rend.*, **192**, 233 (1931).

(6) Conductivity data indicate that tetraphenylarsonium chloride is completely dissociated in tetramethylene sulfone (sulfolane): R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

(7) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 86. (b) Far-infrared spectra were obtained on Nujol mulls between polyethylene plates.