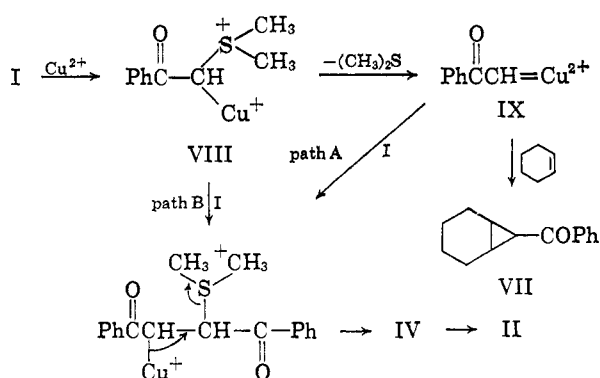


Scheme II



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 Brønsted¹ or Lewis² 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 $\text{Sn} \rightarrow \text{B}$ and $\text{Ge} \rightarrow \text{B}$ donor-acceptor bonds. For such compounds only σ donation can be involved.

Salts containing GeCl_3^- and SnCl_3^- were prepared by adding $(\text{C}_6\text{H}_5)_4\text{AsCl}$ or $(\text{CH}_3)_4\text{NCl}$ to HCl solutions of divalent germanium⁵ or tin. Good C, H, N, and Cl analyses were obtained on the compounds. Molecular weight information was as follows. Calcd for $(\text{C}_6\text{H}_5)_4\text{AsGeCl}_3$ (one-half formula weight):⁶ 281.

(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).

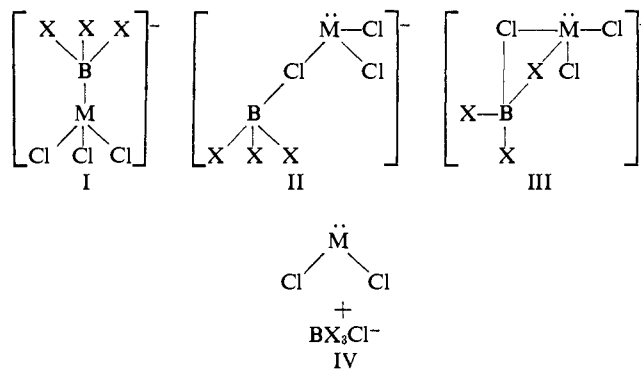
(4) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

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

Found (cryoscopic, sulfolane): 276. Calcd⁶ for $(\text{C}_6\text{H}_5)_4\text{AsSnCl}_3$: 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 $(\text{C}_6\text{H}_5)_4\text{AsMCl}_3$ (*ca.* 0.075 mmole; $\text{M} = \text{Sn}$ 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: $(\text{C}_6\text{H}_5)_4\text{AsSnCl}_3 \cdot \text{BF}_3$, 0.99:1; mol wt: calcd⁶ 338, obsd 308. $(\text{C}_6\text{H}_5)_4\text{AsSnCl}_3 \cdot \text{BCl}_3$, 1.04:1; mol wt: calcd⁶ 363, obsd 344. $(\text{C}_6\text{H}_5)_4\text{AsGeCl}_3 \cdot \text{BF}_3$, 0.99:1; mol wt: calcd⁶ 315, obsd 311. $(\text{C}_6\text{H}_5)_4\text{AsGeCl}_3 \cdot \text{BCl}_3$, 1.02:1, mol wt: calcd⁶ 340, obsd 343. $(\text{CH}_3)_4\text{NsnCl}_3 \cdot \text{BF}_3$, 0.95:1. Boron(11) nmr spectra of sulfolane solutions showed singlet absorptions at 19.1 ppm for $\text{Cl}_3\text{SnBF}_3^-$, and 19.0 ppm for $\text{Cl}_3\text{GeBF}_3^-$, relative to $\text{B}(\text{OCH}_3)_3$. 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: $\text{Cl}_3\text{SnBF}_3^-$, 267 and 294 cm^{-1} ; $\text{Cl}_3\text{SnBCl}_3^-$, 255 and 284 cm^{-1} ; $\text{Cl}_3\text{GeBF}_3^-$, 280 and 323 cm^{-1} ; and $\text{Cl}_3\text{GeBCl}_3^-$, 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



where $\text{M} = \text{Ge}$ or Sn and $\text{X} = \text{F}$ 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

(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.

absorption at 456 cm^{-1} for $(\text{CH}_3)_4\text{NMCl}_3 \cdot \text{BF}_3$ ($\text{M} = \text{Ge}$ or Sn). According to Waddington and Klanberg, such an absorption⁸ is characteristic of BF_3Cl^- which should be present in IV.

Structures II and III are more difficult to eliminate, but the following data indicate that they are unlikely. (1) Long-wavelength infrared spectra in the M-Cl stretch region exhibit only two bands, an observation consistent with the C_{3v} symmetry of I but not the C_{2v} symmetry of II or low symmetry of III. However, it is possible that the other bands expected for II and III are of low intensity or lie beyond the range of the instrument, 200 cm^{-1} . Upon coordination, there is very little shift in the M-Cl stretching vibrations which indicates that framework of the MCl_3^- is not greatly distorted as is required by structure III or similar multiple bridged structures. (2) Stoichiometry of formation was determined for two acids of varying strengths and at two different temperatures (-45 and 25°), but a residual affinity which is expected for the terminal chloride of structures II and III was not observed. (3) *n*-Butyltin trichloride in methylene chloride was exposed to an excess of BF_3 for 2 hr at -45° , and the BF_3 was quantitatively removed at this temperature; thus, a stable Sn-Cl-B bridge adduct was not formed. Structure III requires that the tin accept an electron pair from the halide attached to boron, and since *n*-butyltin trichloride is a Lewis acid it should form such compounds more readily than SnCl_3^- . The lack of $\mu\text{-SnClBF}_3$ in this system indicates that III is improbable.

The remaining alternative is structure I which contains germanium-boron or tin-boron donor-acceptor bonds. Thus, π bonding does not appear to be a necessary condition for complex formation with GeCl_3^- and SnCl_3^- . Another interesting characteristic of these metal bases is their lack of affinity for diborane under conditions which lead to boron halide addition. Precedent for this unusual order of affinity may be found in our previous work on the basicity of transition metal cyclopentadienyl hydrides.² Paradoxically, this order of affinity indicates Sn(II) is a hard base with boron acids, while previous synthetic studies indicate it is a soft base with transition metal acceptors. Softness and hardness are qualitative concepts which undoubtedly originate from a variety of factors.⁹ Thus, we cannot expect this classification to always hold when different bonding situations are compared. With transition metal acceptors back π bonding may account for the softness of SnCl_3^- , but this is not possible with the boron acids.

Acknowledgment. We thank Professor F. Basolo and Paul Poskozim for suggestions, and Glenn Mack and Professor Sheldon Shore for infrared and B^{11} nmr spectra. This research was supported by Grant GP-3804 from the National Science Foundation.

(8) (a) T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2339 (1960). (b) We have confirmed the presence of this band in the reaction product of $(\text{CH}_3)_4\text{NCl}$ with BF_3 .

(9) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

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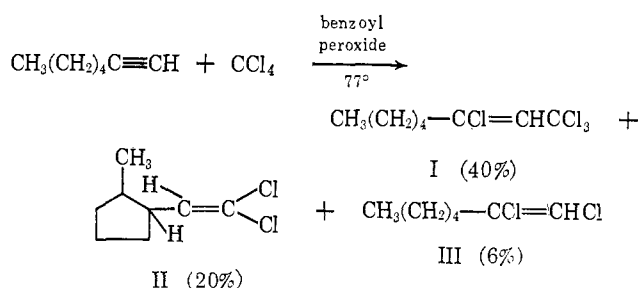
Free-Radical Isomerization.

A Novel Rearrangement of Vinyl Radicals

Sir:

Intramolecular 1,5-hydrogen migration¹ in carbon radicals has been proposed in various polymerization² and thermal decomposition reactions,³ but as yet no unequivocal case⁴ of open-chain alkyl radical isomerization in solution has been reported. Open-chain saturated alkyl radicals, unlike their cyclic analogs⁵ or corresponding oxygen⁶ and nitrogen⁷ radicals, do not readily abstract an internal 5-hydrogen atom. However, we wish to report that such rearrangement has now been observed with an open-chain vinyl radical.

The vinyl radical intermediate, formed by the peroxide-initiated addition of CCl_4 to 1-heptyne, has been found to abstract internal δ hydrogen, as shown by the major products isolated.



The nmr spectrum of the normal 1,2-addition product I, bp $90\text{--}92^\circ$ (3 mm), contained a triplet at τ 3.5 ($J = 0.7$ cps, 1 H) and a multiplet at τ 7.3 (2 H) in addition to numerous peaks in the τ 8.3–9.3 region. The infrared spectrum indicated olefin absorption at 1630 cm^{-1} . The absence of any additional vinyl hydrogen peak in the nmr spectrum as well as the absence of 1618 cm^{-1} band in the infrared absorption indicates no significant contamination of I with its allylic isomer $\text{CH}_3(\text{CH}_2)_4\text{CCl}_2\text{-CH=CCl}_2$ under our experimental conditions.

Besides the normal addition product, two lower boiling compounds were isolated. The more abundant product, II, bp $77\text{--}80^\circ$ (10.5 mm), consisted of two isomers in about 1.5:1 ratio as determined by vapor phase chromatography. The nmr spectrum of the major isomer showed a doublet at τ 4.35 ($J = 9.7$ cps, 1.0 H), a multiplet at τ 7.2 (1.0 H), broad absorption in the τ 7.8–8.8 region (7.2 H), and another doublet at τ 9.2 ($J = 6.5$ cps, 2.9 H). The other isomer had its low-field doublet displaced to τ 4.43 ($J = 9.1$ cps). The infrared spectrum of each isomer contained a sharp

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(2) V. Jaacks and F. R. Mayo, *J. Am. Chem. Soc.*, **87**, 3371 (1965), and references therein.

(3) A. Kossiakoff and F. Rice, *ibid.*, **65**, 590 (1943).

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(5) M. Fisch and G. Ourisson, *Chem. Commun.*, 407 (1965); J. G. Traynham and T. M. Couvillon, *J. Am. Chem. Soc.*, **87**, 5806 (1965).

(6) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *ibid.*, **83**, 2196 (1961); C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961); M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961).

(7) S. Wawzonek and P. J. Thelen, *ibid.*, **72**, 2118 (1950); E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).