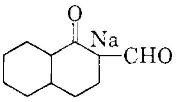
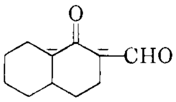
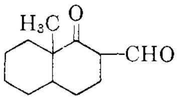


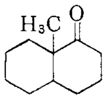
V



VI



VII



VIII

the 2-methylanilinomethylene[7] or the 2-isopropoxymethylene[5] derivative of decalone.

Further studies are in progress on the reactions of the dicarbanions of formylacetone, formyldecalone and other β-ketoaldehydes.

[7] A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1944).

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RECEIVED MARCH 26, 1962

CARBONIUM ION SALTS. IV. TETRAIODOBORATES[1]

Sir:

The literature on complexes of boron iodide is sparse. The single reference to iodoborate formation—a remarkably terse communication by Waddington[2]—gives no details of preparation or characterization, and the ammonia adduct reported by Besson[3] has been shown[4,5] not to exist. We wish to report that the method used for the preparation of tropenium chloroborate[6] and bromoborate[7] has yielded tropenium iodoborate, and to present evidence for the existence of triphenylcarbonium iodoborate.

Boron iodide reacts rapidly and smoothly with cycloheptatriene in dry methylene chloride (glove box; dry, O_2 free N_2 atmosphere) to give 60.6% tropenium iodoborate as a precipitate of brilliant yellow single crystals, m.p. 223°, ultraviolet spectrum (96% sulfuric acid)[8]: λ_{max} 268 (sh), 274 (4330), 280 mμ; (water)[9]: λ_{max} 275 (4380), 280 (sh). *Anal.* Calcd. for $C_7H_7BI_4$: $C_7H_7^+$, 14.9; B, 1.77; I, 83.28. Found[7]: $C_7H_7^+$, 14.8; B, 1.65; I, 83.32. The iodoborate is stable in a dry atmosphere and does not seem light sensitive; however, it is hygroscopic and darkens with liberation of hydrogen iodide on exposure to moist air. The compound is not decolorized by ice-cold water, in which it is sparingly soluble, and dissolves smoothly on warming to room temperature to give water-white solutions of tropenium ion, boric acid, and hydriodic acid. It is decomposed instantly by acetone to give scarlet tropenium iodide, m.p. 127°.[8,10] On attempted sublimation (85°, 0.2 mm.) the iodoborate decomposed slowly; a mixture of tropenium iodide and triiodide collected on the cold finger.

Reaction of boron iodide with triphenylmethyl iodide in methylene chloride (conditions as above, then precipitation with cyclohexane) gave dark, viciously hygroscopic, light sensitive crystals for which satisfactory analyses could not be obtained. The formation of triphenylcarbonium iodoborate in the methylene chloride solution is inferred from the following: (1) Addition of cycloheptatriene to a boron iodide–triphenylmethyl iodide solution in methylene chloride gives an instantaneous precipitate of 57% tropenium iodoborate of high purity and 95% triphenylmethane is isolated from the reaction solution. This rapid hydride exchange shows[6,7,8,11] the existence of an ionic triphenylcarbonium salt; the iodoborate ion is the most probable anionic species.[12] (2) B^{11} n.m.r. spectra[13] of boron iodide–triphenylmethyl iodide solutions in methylene chloride show a single resonance at $\delta = +112.2$ (relative to $(C_2H_5)_2O\cdot BF_3 = 0$) compared to a value of $\delta = +5.5$ for boron iodide. Triphenylcarbonium chloroborate ($\delta = -4.5$) and bromoborate ($\delta = +23.9$) in methylene chloride show similar shifts to higher field relative to the halides (BCl_3, $\delta = -45.6$; BBr_3, $\delta = -40.1$)[14] as do alkali metal haloborates in nitrobenzene.[15] The theoretical predictions of Landesman and Williams[15] that tetrahedral iodoborate ion should show a chemical shift greater than $\delta = +100$ (higher than any other known boron compound) are in agreement with the value observed for presumed triphenylcarbonium iodoborate.

[1] Supported by the Petroleum Research Fund.

[2] T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 315 (1960).

[3] A. Besson, *Compt. rend.*, **114**, 542 (1892).

[4] A. Joannis, *ibid.*, **135**, 1106 (1902).

[5] W. J. McDowell and C. W. Keenan, *J. Am. Chem. Soc.*, **78**, 2069 (1956).

[6] K. M. Harmon, A. B. Harmon and F. E. Cummings, *ibid.*, **83**, 3912 (1961).

[7] K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

[8] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *ibid.*, **79**, 4557 (1957), report λ_{max} 268 (sh), 273.5 (4350), 280 mμ for tropenium ion in this solvent.

[9] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954), report λ_{max} 275 (4350), 280 mμ (sh) for tropenium ion in this solvent.

[10] W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

[11] D. L. Pearson, Ph. D. Thesis, University of Washington, 1955; *Dissertation Abstr.*, **15**, 978 (1955).

[12] Under these conditions triphenylmethyl iodide and cycloheptatriene give a precipitate of only 1.5% tropenium triiodide in 24 hours.

[13] We are indebted to Dr. Robert E. Williams and the National Engineering Science Company, Pasadena, California, for determination of the B^{11} chemical shifts of the haloborates.

[14] T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[15] H. Landesman and R. E Williams, *J. Am. Chem. Soc.*, **83**, 2663 (1961).

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RECEIVED FEBRUARY 17, 1962

FORMATION OF BIS-(METHYLTHIO)-METHYLENE FROM METHYL ORTHOTHIOFORMATE AND POTASSIUM AMIDE

Sir:

Earlier work has provided evidence that a number of trisubstituted methanes, upon treatment with base, undergo α-elimination reactions yielding derivatives of methylene as reaction intermediates.[1] There is evidence that the α-dehydrohalogenations

[1] (a) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); (c) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959); J. Hine, R. J. Rosscup and D. C. Duffey, *ibid.*, **82**, 6120 (1960); (e) J. Hine and J. J. Porter, *ibid.*, **82**, 6178 (1960).

of bromodifluoromethane, chlorodifluoromethane and difluoroiodimethane are concerted one-step reactions[2] but that the α-dehydrohalogenations of chloroform and most other haloforms are stepwise processes involving the formation of small concentrations of reactive intermediate carbanions.[1a,3] We wish now to report that ethyl orthothioformate and methyl orthothioformate, with potassium amide in liquid ammonia, undergo essentially complete transformation to tris-(alkylthio)· methyl anions, which, more slowly, lose thioalkoxy anions to give intermediate bis-(alkylthio)-methylenes, some of which are transformed to tetrakis-(alkylthio)-ethylenes.

Both methyl and ethyl orthothioformate react with potassium amide in ammonia to give green solutions, which are similar in color to those that may be prepared from potassium amide and bis-(methylthio)-methane,[4] but which acquire a brownish color on standing for several hours. Such a solution, prepared from 11.7 g. (76 mmoles) of methyl orthothioformate and 150 mmoles of potassium amide in about 150 ml. of ammonia, was allowed to reflux for an hour before the ammonia was allowed to evaporate. From the residue was isolated 1.8 g. (12 mmoles) of methyl orthothioformate and 2.7 g. (13 mmoles—40% based on unrecovered orthothioformate) of tetrakis-(methylthio)-ethylene, m.p. 59–60°, reported m.p. 61.5°;[6] sole n.m.r.[7] band at 7.63 τ (in carbon tetrachloride). Tetrakis-(ethylthio)-ethylene, prepared analogously from ethyl orthothioformate, melted at 50–53° and showed no melting-point depression when mixed with tetrakis-(ethylthio)-ethylene prepared from tetrachloroethylene and sodium thioethoxide.[8] In at least one previously reported α-elimination the concentration of intermediate carbanion was large enough to observe directly.[9] In the present case there are two observations that show that the reactant is transformed almost quantitatively to its conjugate base. After the addition of one equivalent of potassium amide to solutions of orthothioformates the green color is made no more intense by the addition of further amide. Treatment of a freshly prepared solution of the tris-(methylthio)-methyl anion with methyl iodide leads to the formation of 75% of methyl orthothioacetate, b.p. 98.5–100° (11 mm.), $n^{24.5}_D$ 1.5680, $d^{24.5}_4$ 1.1197; molecular refractivity calcd. 49.21, found 49.22; sharp n.m.r.[7] absorption band at 8.20 τ and one with three times the integrated intensity at 7.92 τ (neat). *Anal.* Calcd. for $C_5H_{12}S_3$: C, 35.67; H, 7.19; S, 57.14. Found: C, 35.49; H, 7.42; S, 57.31.

The fact that tris-(alkylthio)-methyl anions may be generated in high concentrations is to be attributed to the relative ease of removal of a proton from orthothioformates[10,11] and to the difficulty of displacing thioalkoxy anions from saturated carbon atoms. The tetrakis-(alkylthio)-ethylenes formed in the reactions studied need not arise from the dimerization of bis-(alkylthio)-methylenes. They may just as plausibly be ascribed to the reaction of such a methylene with the much more abundant carbanions as shown below.

$$\begin{tikzcd}
(RS)_3CH + NH_2^- \arrow[r] & (RS)_3C^- \arrow[r] & RS\text{-}C\text{-}SR + RS^- \arrow[d, "(RS)_3C^-"] \\
& (RS)_2C{=}C(SR)_2 + RS^- & (RS)_3C{-}C(SR)_2^- \arrow[l]
\end{tikzcd}$$

In view of the difficulty of displacing thioalkoxy anions from saturated carbon, an alternate mechanism involving the formation of the intermediate pentakis-(alkylthio)-ethane by the nucleophilic attack of tris-(alkylthio)-methyl anions on orthothioformate molecules seems improbable.

Acknowledgment.—We wish to acknowledge the support of this investigation by the U. S. Army Research Office (Durham).

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[2] J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957); J. Hine and D. C. Duffey, *ibid.*, **81**, 1131 (1959); J. Hine and A. D. Ketley, *J. Org. Chem.*, **25**, 606 (1960).

[3] J. Hine and S. J. Ehrenson, *J. Am. Chem. Soc.*, **80**, 824 (1958).

[4] We have alkylated such a solution of bis-(methylthio)-methane with propyl bromide and obtained the dimethyl mercaptal of butyraldehyde. The first report of such a reaction was by Arens, Fröhling and Fröhling,[5] who did not state what specific compounds they studied.

[5] J. F. Arens, M. Fröhling and A. Fröhling, *Rec. trav. chim.*, **78**, 663 (1959).

[6] B. Fetkenheuer, H. Fetkenheuer and H. Lecus, *Ber.*, **60**, 2535 (1927).

[7] A Varian A-60 instrument was used.

[8] P. Claesson, *J. prakt. Chem.*, [2] **15**, 193 (1877).

[9] C. G. Swain and E. G. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

[10] *Cf.* L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26**, 3158 (1961); S. Oae, W. Tagaki and A. Ohno, *J. Am. Chem. Soc.*, **83**, 5036 (1961).

[11] When triphenylmethane is added to a green solution containing two equivalents of bis-(methylthio)-methane per equivalent of potassium amide the solution becomes red. The red color is not discharged by the addition of excess triethyl orthothioformate. We therefore conclude that both of the sulfur compounds are weaker acids than triphenylmethane.

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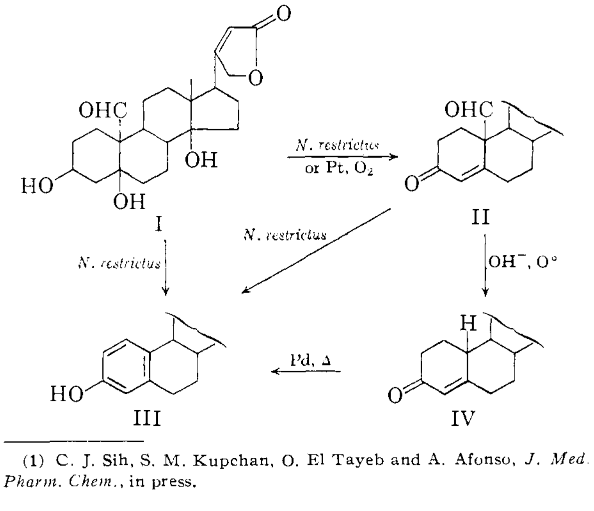
RECEIVED MARCH 7, 1962

MICROBIOLOGICAL TRANSFORMATIONS. II. THE AROMATIZATION OF RING A OF STROPHANTHIDIN

Sir:

A recent paper described the conversion of strophanthidin (I) to the anhydrostrophanthidone II by *Chaetomium globosum*.[1] We report herewith the transformation of I to II and thence to the new phenol III by *Nocardia restrictus*.



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[1] C. J. Sih, S. M. Kupchan, O. El Tayeb and A. Afonso, *J. Med. Pharm. Chem.*, in press.