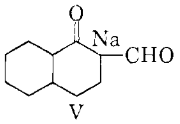
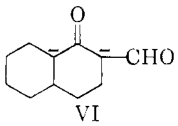
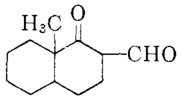


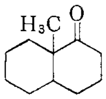
V



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).

DEPARTMENT OF CHEMISTRY
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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 $(C_2H_5)_2O{\cdot}BF_3{=}O$) 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).

DEPARTMENT OF CHEMISTRY
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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).