lected using a Dean–Stark separator (0.60 g., 90%). A portion of the toluene solution of di-*n*-butyltin, exposed to air for 1 day, rapidly turned to a white solid which had the properties of di-*n*-butyltin oxide.

Anal. Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.73.

Reaction of Di-n-butyltin Dihydride with Bis(tri-n-butyltin) Oxide. Di-*n*-butyltin dihydride (2.35 g., 0.0100 mole) was heated with bis(tri-*n*-butyltin) oxide (5.96 g., 0.0100 mole) for 9 hr. at 100° with less than 5% of gas evolved based on the hydride hydrogen and the recovery of water (0.0105 mole) as a distillate. The nearly colorless liquid remaining in the flask was mainly octa-*n*-butyltritin as shown by its molecular weight and bromine titration.

Anal. Calcd. for $C_{32}H_{72}Sn_3$: mol. wt., 813. Found: mol. wt. (thermistor osmometer, 0.098 *m* in toluene), 748.

Bromine titration showed 100% of the expected based on 2 moles of bromine per mole of octa-*n*-butyltritin. Attempted distillation gave a colorless liquid as the distillate and a yellow-green viscous liquid remaining in the flask. The colorless liquid had the properties of hexa-*n*-butylditin, which had previously been prepared.

Anal. Calcd. for $C_{24}H_{54}Sn_2$: Sn, 40.92; mol. wt., 580. Found: Sn, 41.00; mol. wt. (thermistor osmometer, 0.070 *m* in toluene), 559.

Upon mixing the two liquid reactants at room temperature, a reaction occurred in which a solid was formed. An infrared spectrum of the mixture taken after mixing showed the presence of tri-*n*-butyltin hydride by the Sn–H absorption at 1814 cm.$^{-1}$ and the complete loss of di-*n*-butyltin dihydride which shows Sn–H absorption at 1835 cm.$^{-1}$. The mixture was taken up in anhydrous ether and filtered giving a white solid, di-*n*-butyltin oxide (97%), as the residue.

Anal. Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.50.

Upon evaporation of the solvent, tri-*n*-butyltin hydride (71%) was recovered. Since it was now evident that the water-forming reaction taking place at 100° involved tri-*n*-butyltin hydride and di-*n*-butyltin oxide that reaction was carried out separately.

Reaction of Tri-n-butyltin Hydride with Di-n-butyltin Oxide. Tri-*n*-butyltin hydride (7.26 g., 0.0250 mole) was heated with di-*n*-butyltin oxide (3.11 g., 0.0125 mole) for 26 hr. at 100°. No gas was evolved, and water[17] (0.0129 mole) was obtained as a distillate. Octa-*n*-butyltritin remained in the flask.

Anal. Calcd. for $C_{32}H_{72}Sn_3$: C, 47.27; H, 8.93; Sn, 43.80. Found: C, 47.24; H, 8.79; Sn, 44.00.

Another similar preparation was used to obtain the bromine titration for tin–tin bonds and the molecular weight. Bromine titration showed 92% of that expected based on 2 moles of bromine per mole of octa-*n*-butyltritin. The molecular weight (by thermistor osmometer, 0.058 *m* in toluene) was found to be 789 (calculated for octa-*n*-butyltritin, 813).

Visible absorption spectra, using a Bausch and Lomb Spectronic 20 colorimeter, were taken in the range of 400–975 mμ. Hexa-*n*-butylditin was transparent throughout the entire range. Di-*n*-butyltin showed one absorption maximum at 820 mμ, whereas octa-*n*-butyltritin showed one absorption maximum at 750 mμ.

Reaction of Di-n-butyltin Dihydride with Di-n-butyltin Dimethoxide. When di-*n*-butyltin dihydride (2.35 g., 0.0100 mole) and di-*n*-butyltin dimethoxide (2.95 g., 0.0100 mole) were mixed, an exothermic reaction occurred giving a clear, homogeneous product. Within 10 min. of mixing, an infrared spectrum was taken showing complete loss of Sn–H absorption at 1835 cm.$^{-1}$ and appearance of a new, single, strong Sn–H absorption at 1785 cm.$^{-1}$. In addition, strong absorption was found in the 3000–3500-cm.$^{-1}$ region which was not shown by either of the starting materials. Upon standing for 2 hr. at room temperature, no gas was evolved, and a yellow color developed in the mixture, which appeared to separate into two layers. About 1 day later, at 1 mm., 0.23 g. (36%) of methanol was collected in a trap at −70°. The condensate was a volatile liquid having the odor of and an infrared spectrum identical with that of an authentic sample of methanol. Over a period of several days additional methanol was collected for an over-all yield of 66%. A small portion of the yellow product upon exposure to air for several days was converted to di-*n*-butyltin oxide.

Anal. Calcd. for $C_8H_{18}OSn$: Sn, 47.69. Found: Sn, 47.59.

Carbonium Ion Salts. VIII. Synthesis of Iodoborates and an Improved Route to Triphenylmethyl Iodide[1,2]

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Tropenium and triphenylcarbonium iodoborates have been prepared; these are the first characterized salts of this anion to be reported. The formation of the tropenium salt is an example of hydride ion transfer from carbon to metal. The ^{11}B spectra of tetrahaloborate anions have been studied in the course of this work, and an excellent route to triphenylmethyl iodide has been developed.

The literature on complexes of boron iodide is sparse. Besson[3] reported several adducts with ammonia, but later workers[4,5] showed that these were really amides. Boron iodide does not form a complex with pyridine but instead gives a dipyridyldiiodoboron cation.[6] A recent report[7] indicates that boron iodide and phosphorus triiodide combine in a 1:1 ratio, but the structure of the product is unknown. Waddington[8] has reported sparingly on the synthesis of tetraalkylammonium and pyridinium iodoborates in liquid hydrogen iodide solvent, but details of experimentation and characterization have not been forthcoming.

We have previously reported the synthesis of tropenium chloroborate[9] and bromoborate[10] by reaction of cycloheptatriene with boron halide. Similarly reaction of boron iodide with cycloheptatriene in methylene chloride or cyclohexane solvent gives high yields of tropenium iodoborate. The iodoborate forms as brilliant yellow microneedles which melt at 223°. These crystals are not very soluble in ice-cold water, but dissolve smoothly on warming to room temperature (in oxygen-free water) to give colorless solutions of tropenium ion, hydriodic acid, and boric acid. Acetone instantly decomposes the compound with the concurrent formation of tropenium iodide. Crystals of tropenium iodoborate are quite stable in a dry, oxygen-free atmosphere, but decompose with liberation of iodine on exposure to the air. The compound does not seem to be particularly light sensitive, but was protected from light during synthesis and storage as a routine precaution.

Triphenylcarbonium iodoborate was prepared by reaction of triphenylmethyl iodide with boron iodide in methylene chloride, followed by precipitation with hydrocarbon solvent. The crystals of this compound are a rusty black; this is surprising in light of the bright yellow color of other salts of this cation. Triphenylcarbonium iodoborate is viciously hygroscopic and is sensitive to light and oxygen: it is much harder to handle than the tropenium compound. The crystals begin to decompose at 148° and melt at 150–152°. The behavior of the crystals on melting is unsettling; they first become colorless, and then melt to a bright green liquid. At present these observations are unexplained.

Solutions of triphenylcarbonium iodoborate in methylene chloride give instantaneous and complete hydride exchange[11] with cycloheptatriene to give tropenium iodoborate and triphenylmethane; it has been previously demonstrated[11,12] that such facile hydride exchange shows the presence of a highly ionized triphenylcarbonium ion salt in solution. The

BI$_4^-$ anion is transferred intact in this chemical reaction.

Triphenylmethyl iodide is a troublesome compound; it darkens with liberation of iodine when exposed to light, forms the peroxide on contact with oxygen, undergoes homolysis to iodine and hexaphenylethane in nonpolar solvents, reacts irreversibly with water to form the carbinol, and is reduced to triphenylmethane by hydrogen iodide liberated in this hydrolysis. The synthesis reported below circumvents these pitfalls and gives material of high quality in good yield. The method has been adapted from the directions of Dauben, et al.,[13] for triphenylcarbonium perchlorate and fluoroborate, which in turn were derived from the work of Hofmann and Kirmreuther,[14] and consists of the reaction of triphenylcarbinol with 48% aqueous hydriodic acid under conditions which are outlined in detail in the Experimental section.

Experimental

Eastman Kodak Co. White Label methylene chloride and cyclohexane were purified and dried in the manner previously described[9]; Phillips pentane (99 mole %) was purified in a manner identical with the cyclohexane. Eastman Kodak Co. White Label acetic anhydride was distilled immediately before use. All solvents were freed of oxygen by bubbling a stream of highly purified nitrogen through a stirred (magnetic pea) portion of the solvent contained in a ground-glass bottle fitted with a gas delivery head; 30 min. of this treatment gives solvent that will remain colorless when saturated with anhydrous hydrogen iodide. Cycloheptatriene[15] was distilled under nitrogen and stored in the glove box. Eastman Kodak White Label triphenylcarbinol was treated with Norit in benzene and recrystallized from this solvent. Baker and Adamson reagent grade 48% hydriodic acid was stored under nitrogen and was colorless.

All operations with exception of the initial precipitation of triphenylmethyl iodide were carried out in a glove box. The nitrogen atmosphere of the box was freed of moisture by circulation over phosphorus pentoxide and of oxygen by circulation through hot copper: a positive pressure of nitrogen was maintained at all times. All operations were carried out under red light. Glassware and utensils were rigorously dried in an oven at 120° and were allowed to stand in the glove box overnight before use to remove adsorbed oxygen.

Spectra were recorded on a Cary Model 13 spectrophotometer; melting points were determined on a Fisher-Johns block (in the box) and are corrected. ^{11}B n.m.r. spectra were recorded on a Varian 4300 spectrophotometer at 12.8 Mc.

Boron Iodide. Boron iodide was purchased from the Kern Chemical Co. and was rated as being 99.9% pure. It was a light violet color from trace amounts of iodine. The ampoule was opened in the glove box and the iodide was dissolved in pentane. This solution was shaken with mercury and then filtered through a fritted glass filter to remove mercuric iodide. Aliquots of the resulting water-white pentane solution were

(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) E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **15**, 182 (1960).
(7) R. F. Mitchell, J. A. Bruce, and A. F. Armington, *Inorg. Chem.*, **3**, 915 (1964).
(8) T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 315 (1960).
(9) K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961); *ibid.*, **86**, 5511 (1964).
(10) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).
(11) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).
(12) (a) H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1954, p. 18-O; (b) H. J. Dauben, Jr., L. R. Honnen, and D. L. Pearson, unpublished work in Ph.D. Theses of L. R. H., 1960, and D. L. P., 1955, University of Washington.

(13) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
(14) K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4856 (1909).
(15) Gift of the Shell Chemical Corp. This material contains 10% toluene.

pipetted into reaction vessels and the pentane was removed *in vacuo*. Boron iodide was thus obtained as completely colorless, transparent plates which melted sharply at 48.0–48.5° to a water-white liquid.[16] On cooling this liquid recrystallized at 48.5–48.0° to white plates; this melting and recrystallizing process could be repeated many times within the same half-degree range without observable decomposition.

Triphenylmethyl Iodide. Triphenylcarbinol (3.23 g., 12.4 mmoles) was placed in a 100-ml., pear-shape flask equipped with a side arm bearing a 10/30 standard taper joint and containing a glass magnetic stirring pea. The flask was fitted with an inlet–outlet head equipped with stopcocks, and was evacuated overnight at 0.1 mm. to remove most of the air trapped among the crystals; nitrogen was bled into the flask when it was removed from the pump. Purified nitrogen was then passed through the flask by means of the head; when the side arm was opened the exit stopcock was closed, thus directing a stream of nitrogen out of the side arm and preventing entrance of the outside atmosphere. The side arm was fitted with a rubber dam, and acetic anhydride (50 ml.) was injected with a syringe. The flask was warmed with a hot-air blower and the solution was stirred until the carbinol dissolved. The flask was cooled for 1 min. with an ice bath, and then 48% hydriodic acid (3.0 ml., 17 mmoles) was added dropwise by syringe (glass needle). Nitrogen flow, cooling, and stirring were maintained at all times. When addition of hydriodic acid was complete the rubber dam was removed and the reaction solution was quickly decanted from the precipitated iodide. The solid was washed with acetic anhydride (syringe) until the wash solvent was colorless (5 × 20 ml.), the side arm was stoppered (Kel-F grease), and the flask was evacuated through the head to remove the bulk of the residual solvent. The flask was then transferred to the glove box and the contents were dried *in vacuo* to yield 68.7% triphenylmethyl iodide (3.18 g., 8.53 mmoles) as golden microprisms, m.p. 132–133°,[17] visible spectrum (96% sulfuric acid)[18] λ_{max} 404 and 432 mμ (ϵ 38,100).

Anal. Calcd. for $C_{19}H_{15}I$: I, 34.28; $(C_6H_5)_3C$, 65.72. Found: I, 34.31; $(C_6H_5)_3C$, 65.2.

There is a fine point between enough hydriodic acid and too much. With too great an excess of acid the solution blackens and the yield is poor; if severe darkening is observed, immediate decantation and washing is in order.

Reaction of Cycloheptatriene with Boron Iodide in Methylene Chloride. Cycloheptatriene (0.207 g., 2.02 mmoles) was added dropwise with swirling to a water-white solution of boron iodide (0.73 g., 1.86 mmoles) in methylene chloride (15 ml.). A yellow precipitate formed immediately and the solution became light orange in color. After 2 hr. the solution was decanted and the solid was washed with cyclohexane (3 × 10 ml.) and dried *in vacuo* to yield 61.4% tropenium iodoborate (0.69 g., 1.13 mmoles) as yellow needles, m.p. 223°, ultraviolet spectrum (96% sulfuric acid)[19]

λ_{max} 268 (sh), 274 (ϵ 4330), and 280 mμ; (water)[20] λ_{max} 275 (ϵ 4380) and 280 (sh) mμ.

Anal. Calcd. for $C_7H_7BI_4$: C_7H_7, 14.94; B, 1.77; I, 83.28. Found: C_7H_7, 14.8; B, 1.65; I, 83.32.

When the washings were added to the mother liquor a second crop of yellow needles formed; these were examined under the polarizing microscope and found to be well formed single crystals, m.p. 223°. This second crop represented a yield of 12.9% tropenium iodoborate (0.146 g., 0.24 mmoles) which raised the total yield to 74.3%.

When the yellow needles of tropenium iodoborate were contacted with acetone they immediately turned to scarlet tropenium iodide, m.p. 127°.[21]

Reaction of Cycloheptatriene with Boron Iodide in Cyclohexane. Cycloheptatriene (0.207 g., 2.02 mmoles) was added to a water-white solution of boron iodide (0.66 g., 1.68 mmoles) in cyclohexane (15 ml.); a yellow precipitate formed at once. The flask was allowed to stand overnight during which time the amount of solid increased; the solvent remained water white. The solvent was decanted and the solid was washed with cyclohexane (3 × 25 ml.) and dried *in vacuo* to yield 71.4% tropenium iodoborate (0.73 g., 1.20 mmoles) as yellow microneedles, m.p. 223°, ultraviolet spectrum (96% sulfuric acid)[19] λ_{max} 268 (sh), 274 (ϵ 4340), and 280 mμ.

Anal. Found: C_7H_7, 14.9; I, 83.47.

Ultraviolet spectral analysis[9] of the mother liquor showed the presence of 8.4% unreacted cycloheptatriene (0.016 g., 0.17 mmole).

Triphenylcarbonium Iodoborate. A solution of boron iodide (1.09 g., 2.79 mmoles) in pentane (7.5 ml.) was added to a solution of triphenylmethyl iodide (1.20 g., 3.22 mmoles) in methylene chloride (15 ml.). The mixture became deeply colored, and dark needles formed. Cyclohexane (50 ml.) was added and the amount of precipitate increased markedly. The solvent was decanted and the crystals were dried *in vacuo* to yield 91.0% triphenylcarbonium iodoborate (1.93 g., 2.54 mmoles) as rusty black needles, m.p. 150–152° (decomposition begins about 148°), visible spectrum (96% sulfuric acid)[18] λ_{max} 404 and 432 (ϵ 35,800) mμ.

Anal. Calcd. for $C_{19}H_{15}BI_4$: I, 66.64. Found: I, 66.29.

Reaction of Cycloheptatriene with Triphenylcarbonium Iodoborate in Methylene Chloride. A solution of boron iodide (0.18 g., 0.46 mmole) in methylene chloride (10 ml.) was added to a solution of triphenylmethyl iodide (0.17 g., 0.46 mmole) in methylene chloride (10 ml.). Cycloheptatriene (0.09 g., 0.88 mmole) was added, and an immediate precipitation of yellow crystals occurred. The solvent was decanted and the solid was washed with cyclohexane (3 × 15 ml.) and dried *in vacuo* to yield 67.8% tropenium iodoborate (0.19 g., 0.31 mmoles) as yellow needles, m.p. 223°. The mother liquor was extracted with dilute thiosulfate and then with water, and the combined aqueous solutions were back extracted with methylene chloride.

(16) W. C. Schumb, E. L. Gamble, and M. D. Banus, *J. Am. Chem. Soc.*, 71, 3225 (1949), report m.p. 49.4–50.4°, with concurrent iodine formation.

(17) M. Gomberg, *ibid.*, 22, 757 (1900), reports m.p. 135° dec.

(18) We have found[10] the spectrum of the triphenylcarbonium ion in this solvent to be λ_{max} 405 and 432 mμ (ϵ 38,400).

(19) H. J. Dauben, Jr., *et al.*,[11] report the spectrum of tropenium ion in this solvent as λ_{max} 268 (sh), 274 (ϵ 4350), and 280 mμ.

(20) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 76, 3203 (1954), give the spectrum of tropenium ion in this solvent as λ_{max} 275 (ϵ 4350) and 280 (sh) mμ.

(21) W. von E. Doering and L. H. Knox, *ibid.*, 79, 352 (1957), report m.p. 127°.

The combined organic layers were dried over sodium sulfate and concentrated *in vacuo* to a tan solid. This was washed with pentane through a short column of alumina; evaporation of the pentane yielded 95% crude triphenylmethane (0.107 g., 0.427 mmole) as off-white crystals, m.p. 87–90°. Recrystallization from methanol gave white needles, m.p. 93°.[22]

Discussion

In an earlier paper[10] on bromoborates we pointed out that arguments against the possible formation of the bromoborate ion based on steric crowding around boron or insufficient Lewis acidity of boron bromide had been discounted by a variety of experimental evidence prior to the actual synthesis of the ion itself. It has not been possible, however, to predict with assurance whether or not the iodoborate ion would be stable, since relatively little is known about the complexing strength of boron iodide, and the steric problem is more demanding than in the bromine case.[23]

The synthesis and characterization of compounds containing the iodoborate anion[2,8] resolve the question of its possible existence and complete the series of simple tetrahaloborate anions. The iodoborate anion does not seem markedly less stable than the other haloborate anions. Actually, tropenium iodoborate seems more stable on heating than the bromoborate; the iodoborate melts sharply at 223°, while the bromoborate shows considerable loss of boron bromide with concurrent sublimation of yellow tropenium bromide when heated on the melting point block. On attempted sublimation (70–100°; 0.1 mm.) tropenium fluoroborate fails to sublime, the chloroborate sublimes unchanged, and the bromoborate gives a pure sublimate of tropenium bromide. Under these conditions the iodoborate decomposes slowly and a mixture of tropenium iodide and triiodide collects on the cold finger. The reaction of tropenium iodoborate with water appears to be smoother and less exothermic than that of the bromoborate, but unless chilled water is used enough heat is generated to cause decomposition with iodine formation.

(22) A. Kekule and A. Franchimont, *Ber.*, **5**, 907 (1872), report m.p. 92.5°.

(23) Using reported values for the trigonal and tetrahedral covalent radii of boron,[24] the B–I bond in boron iodide,[25] and the covalent radius of iodine corrected for electronegativity contractions[26] we calculate the I–I distance in boron iodide to be 3.64 Å. and in the iodoborate anion to be 3.59 Å. Both differ considerably from the value of 4.30 Å. which is twice the van der Waals radius of iodine. It would appear that both boron iodide and the iodoborate ion suffer from steric crowding, but that it is not much worse in the ion than in the parent halide.

(24) (a) K. Hedberg, *J. Am. Chem. Soc.*, **74**, 3486 (1952); H. A. Levy and L. O. Brockway, *J. Chem. Soc.*, 2085 (1937).

(25) M. A. Ring, J. D. H. Donnay, and W. S. Koski, *Inorg. Chem.*, **1**, 109 (1962).

(26) C. A. Coulson, "Valence," Oxford University Press, London, 1952.

The preparation of triphenylcarbonium iodoborate has made it possible to compare the [11]B n.m.r. spectra of a series of identical, highly soluble haloborates.[27] Table I lists the spectra of the four boron halides and

Table I. [11]B N.m.r. Spectra of Boron Halides and Haloborate Anions

Boron halide	δ	Haloborate anion	δ	$\Delta\delta$
BF_3	−9.4	BF_4^-	1.4	10.0
BCl_3	−45.6	BCl_4^-	−4.5	41.1
BBr_3	−40.1	BBr_4^-	23.9	74.0
BI_3	5.5	BI_4^-	112.2	106.7

the corresponding triphenylcarbonium haloborates[2,9,10,13] in methylene chloride solvent. The chemical shift values are taken relative to a value of zero for boron fluoride etherate. Triphenylcarbonium iodoborate shows a single sharp resonance at δ 112.2 indicative of a single, highly shielded boron species in solution, and in good agreement with the theoretical predictions of Landesman and Williams[28] that a tetrahedral iodoborate anion should show a chemical shift greater than δ 100. This is the highest chemical shift known for a boron compound. It is also of interest to note the regularity of the change $\Delta\delta$ (*cf.* Table I) between adjacent pairs of halogens, *i.e.*, 31.1 between F and Cl, 32.9 between Cl and Br, and 32.7 between Br and I.

In both methylene chloride and cyclohexane solvent the yields of tropenium iodoborate from the reaction of cycloheptatriene with boron iodide approach the theoretical limit of a 75% yield based on boron iodide. The total lack of polymerization of cycloheptatriene and the high degree of conversion in these reactions indicate that they proceed by hydride transfer from carbon to boron for reasons that we have discussed before.[9,10] This is particularly true in the cyclohexane reaction, where no solvent cocatalysis is possible. Since almost all of the iodine in the original boron iodide is in the precipitate, the boron that remains is in a highly reduced condition; we assume that boron hydride products in these reactions are consumed by excess cycloheptatriene in hydroboration reactions.

(27) We are indebted to Dr. Robert E. Williams, Dr. Herbert Landesman, and the National Engineering Science Co., Pasadena, Calif., for the determination of n.m.r. spectra.

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