

was allowed to stir for *ca.* 15 hr. and was then filtered to remove the chromium salts. The resulting filtrate was evaporated under vacuum, furnishing a green-white oil. The oil was dissolved in ether; the ethereal solution was washed with water, and was then dried with magnesium sulfate. Infrared spectroscopic analysis indicated a material comparable with that obtained on ozonolysis of 1,5,5-trimethylcyclohexene. The oil was used directly in the preparation of the methyl esters XV and XVI.

**2,2-Dimethylheptan-6-on-1-oic Acid Methyl Ester and 4,4-Dimethylheptan-6-on-1-oic Acid Methyl Ester.**—To the crude 2,2-dimethylheptan-6-on-1-oic acid and 4,4-dimethylheptan-6-on-1-oic acid obtained above was added an ethereal solution of diazomethane (prepared<sup>40</sup> by the addition of 2.0 g. of N-methyl-N-nitroso-N'-nitroguanidine to a solution containing 6 ml. of 50% potassium hydroxide and 40 ml. of ether, followed by distillation into a flask cooled in a Dry Ice bath). The ether was allowed to evaporate and the resulting oil was separated by vapor phase chromatography. The product mixture was separated into two components which were collected and analyzed by infrared and nuclear magnetic resonance spectroscopy.

The infrared spectrum of the second component was found to be identical with the authentic sample of 4,4-dimethylheptan-6-on-1-oic acid methyl ester synthesized as described above, as was its retention time on a 10-ft. Carbowax column in a vapor phase chromatograph. The nuclear magnetic resonance spectrum was comparable, but because of poor resolution could not be compared exactly.

The first component had an infrared spectrum similar to the one described above, but it differed in the fingerprint region. The nuclear magnetic resonance spectrum was essentially identical with that obtained above; however, there was a 5-min. difference in retention time at 150° on a 10-ft. Carbowax column in a vapor phase chromatograph. The first component was therefore identified as 2,2-dimethylheptan-6-on-1-oic acid methyl ester.

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>: C, 64.49; H, 9.74. Found: C, 63.80; H, 9.92.

**Acknowledgment.**—This work was supported in part by a grant from the Army Research Office (Durham).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVEY MUDD COLLEGE, CLAREMONT, CALIFORNIA]

## Carbonium Ion Salts. VII. Synthesis of Tropenium Chloroborate and Related Reactions<sup>1,2</sup>

BY KENNETH M. HARMON, ANN B. HARMON, AND FRANK E. CUMMINGS<sup>3</sup>

RECEIVED JULY 9, 1964

This paper reports the synthesis of tropenium chloroborate and the characterization of triphenylcarbonium chloroborate as easily preparable, reasonably stable salts of the BCl<sub>4</sub><sup>-</sup> anion. Some reactions of boron chloride, boron bromide, and stannic chloride with organic hydride donors are discussed which show that carbon-to-metal halide hydride transfer is the source of carbonium ions in certain metal halide-hydrocarbon reactions.

There has been considerable interest in compounds containing the tetrachloroborate anion<sup>4</sup>; however, with the exception of Lappert's<sup>4c</sup> synthesis of pyridinium chloroborate from pyridinium chloride and boron chloride in methylene chloride, the routes to simple chloroborate salts have involved high temperatures and pressures,<sup>4d</sup> long milling of solids,<sup>4h</sup> or liquid hydrogen chloride solvent,<sup>4g</sup> and the products often give unsatisfactory analyses. Muetterties<sup>4i</sup> reports the preparation of cesium chloroborate by reaction of cesium chloride and boron chloride in a nitrobenzene slurry but finds that stoichiometric material is best prepared by use of a stainless steel pressure reaction vessel.

We find that the reaction of boron chloride with cycloheptatriene in methylene chloride solvent at room temperature proceeds smoothly to give tropenium chloroborate of high purity. The reaction is not accompanied by any observed decomposition of cycloheptatriene, and the crystalline product is isolated by removal of mother liquor with a pipet, washing with solvent, and drying *in vacuo*. Tropenium chloroborate prepared in this manner consists of transparent single needles, m.p. 119°. These crystals are not particularly hygroscopic,

but become coated with an opaque coat of boric acid on exposure to the atmosphere. The chloroborate dissolves slowly in cold water to give water-white solutions of tropenium ion, boric acid, and hydrogen chloride. The crystals can be kept for a long time in a dry atmosphere without any apparent change; the compound does not appear to be light sensitive like tropenium chloride or hydrogen dichloride.<sup>5</sup>

Tropenium chloroborate can also be prepared by reaction of boron chloride with cycloheptatriene in cyclohexane or by mixing the reactants neat, but the products are not as satisfactory. Reaction of tropenium chloride with boron chloride in methylene chloride affords tropenium chloroborate of good quality and confirms the ionic nature of the compound, but the difficulties inherent in the handling of tropenium chloride<sup>6</sup> obviate this as a useful route to the chloroborate. Addition of *t*-butyl chloride to the reaction of cycloheptatriene and boron chloride in methylene chloride increases the yield, but the crystal size and quality of the product are not quite as good as in the reaction without *t*-butyl chloride cocatalyst.

Wiberg<sup>6</sup> has reported a complex of boron chloride with triphenylmethyl chloride with correct analyses for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>CCl<sub>2</sub>·BCl<sub>3</sub>; this material is stable to 200°. We find that addition of boron chloride to a colorless solution of triphenylmethyl chloride in methylene chloride gives a deep red solution from which the 1:1 adduct is precipitated by cyclohexane as a yellow crystalline solid. In methylene chloride solvent this compound undergoes instantaneous hydride transfer with cycloheptatriene to give tropenium chloroborate and triphenylmethane; the material is thus an ionic salt<sup>7</sup> and contains the BCl<sub>4</sub><sup>-</sup>

(1) Supported by the Petroleum Research Fund and the National Science Foundation.

(2) Reported in preliminary form in a communication: K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

(3) American Chemical Society, Petroleum Research Fund Scholar, 1960; National Science Foundation Scholar, 1961, 1962.

(4) (a) D. R. Martin, *Chem. Rev.*, **42**, 581 (1948); (b) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956); (c) M. F. Lappert, *Proc. Chem. Soc.*, 121 (1957); (d) E. I. Muetterties, *J. Am. Chem. Soc.*, **79**, 6563 (1957); (e) A. B. Burg and E. R. Birnbaum, *J. Inorg. Nucl. Chem.*, **7**, 146 (1958); (f) D. E. Burge, H. Freund, and T. H. Norris, *J. Phys. Chem.*, **63**, 1969 (1959); (g) T. C. Waddington and F. Klanberg, *Naturwiss.*, **20**, 578 (1959); *J. Chem. Soc.*, 2329, 2332 (1960); (h) W. Kynaston, B. E. Larcombe, and H. S. Turner, *ibid.*, 1772 (1960); (i) E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **12**, 355 (1960); (j) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2319 (1961).

(5) K. M. Harmon and S. Davis, *J. Am. Chem. Soc.*, **84**, 4359 (1962).

(6) E. Wiberg and U. Heubaum, *Z. anorg. allgem. Chem.*, **222**, 98 (1935).

anion which may be transferred intact in a chemical reaction.

The yields of tropenium ion from the reactions of cycloheptatriene with boron chloride are much less than when boron bromide<sup>8</sup> or boron iodide<sup>10</sup> is used. Since the mechanism of these oxidations is open to conjecture,<sup>2,8</sup> it is of interest to see how other changes in the metal halide or the carbonium ion progenitor affect the course of such reactions.

Boron fluoride reacts to a very limited extent with cycloheptatriene; treatment of a cyclohexane solution of cycloheptatriene with boron fluoride gas for 2 hr. does not produce any observable precipitate, and ultraviolet spectral analysis of the reaction solution shows quantitative recovery of starting material. Stannic chloride also fails to convert cycloheptatriene to tropenium ion in cyclohexane, even with a reaction time of several weeks. Some other reaction may occur, since only 84% of the initial cycloheptatriene is recovered from the reaction solution, but the yield of tropenium ion is negligible.

Boron bromide, however, reacts smoothly with cycloheptatriene in cyclohexane to give yields of tropenium ion in excess of 70%. The product separates slowly from the water-white mother liquor as a white microcrystalline powder which at a first approximation<sup>11</sup> is tropenium bromoborate. The reaction solution contains an extremely reactive species which is rapidly converted to white polymer on contact with the atmosphere, but this solution appears to keep indefinitely without visible darkening or decomposition in the absence of air and moisture.

Boron bromide also reacts rapidly with trianisylmethane in cyclohexane to give high yields of trianisylcarbonium bromoborate. Trianisylmethane is also converted to the ion by boron bromide in methylene chloride but concurrent Friedel-Crafts polymerization makes it difficult to determine the degree of conversion.

Cycloheptatriene is converted to tropenium hexachlorostannate by reaction with stannic chloride in methylene chloride, but the reaction differs from any of the cycloheptatriene reactions listed above in that it is accompanied by extensive polymerization and decomposition of the cycloheptatriene. The yield of tropenium ion in this reaction is not great, and the salt must be freed from much dark, amorphous solid by repeated washings with solvent followed by recrystallization from 12 *N* hydrochloric acid.

### Experimental

Eastman Kodak practical grade methylene chloride and acetonitrile were prepared as previously reported.<sup>12</sup> Eastman Kodak

(7) The argument for this has been discussed in detail<sup>8</sup> and is based on the fact<sup>9</sup> that only highly ionized triphenylcarbonium ion salts undergo this hydride transfer.

(8) K. M. Harmon and A. B. Harmon, *J. Am. Chem. Soc.*, **83**, 865 (1961).

(9) (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr., L. R. Honnen, and D. L. Pearson, unpublished work in Ph. D. Theses of L. R. H. (1962) and D. L. P. (1955), University of Washington.

(10) K. M. Harmon and F. E. Cummings, *J. Am. Chem. Soc.*, **84**, 1751 (1962).

(11) The analyses of this material indicate a composition quite close to that of C<sub>7</sub>H<sub>7</sub>BBr<sub>4</sub> (see Experimental). Tropenium bromoborate, however, dissolves in cold water to give clear, water-white solutions<sup>8</sup> while the product of this reaction dissolves in water to give greenish solutions with some undissolved, amorphous material which appears to form on solution rather than to be in the original precipitate.

(12) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Am. Chem. Soc.*, **84**, 3349 (1962).

White Label cyclohexane was purified and dried in the same manner as the methylene chloride. Eastman Kodak White Label *t*-butyl chloride was distilled before use. Cycloheptatriene<sup>13</sup> was distilled under nitrogen, passed over alumina under nitrogen, and stored under nitrogen in a brown bottle until used. This material contains 10% toluene by v.p.c. Matheson anhydrous boron fluoride was passed through a column of Drierite before entering the reaction vessel. Trona boron chloride was used directly from a steel cylinder; when liquid was required this was condensed in a graduated pear-shape flask fitted with a three-necked adaptor bearing compensated dropping funnels with which solvents or reactants could be introduced into the reaction vessel. The system was operated at all times under positive pressure of dried nitrogen. Trona boron bromide was distilled from mercury under nitrogen and stored over mercury in the glove box. Baker and Adamson reagent grade stannic chloride was distilled from phosphorus pentoxide and stored in the glove box. Baker and Adamson reagent grade sulfuric acid was used for spectral solutions.

All glassware was dried in an oven at 120° overnight and stored in a desiccator or in the glove box. Reactions were carried out either in all-glass systems with positive nitrogen pressure or in the glove box. Solvents were redistilled (methylene chloride from phosphorus pentoxide, cyclohexane from calcium hydride) into the reaction vessel or into dried bottles to be taken into the glove box.

Weights were recorded with a Mettler H-5 balance. Melting points were taken on a Fisher-Johns block and are corrected. Ultraviolet spectra were recorded with a Cary Model 13 spectrophotometer.

**Reaction of Cycloheptatriene with Boron Chloride in Methylene Chloride.**—Cycloheptatriene (0.90 g., 8.80 mmoles) in methylene chloride (15 ml.) was added to a solution of boron chloride (1.5 g., 13 mmoles) in methylene chloride (15 ml.); a light yellow color appeared in the solution. In 1 hr. small white needles began to separate from a light red, clear solution. After 24 hr. the mother liquor was removed by pipet from a quantity of white needles, which were washed with methylene chloride (3 × 15 ml.) and cyclohexane (3 × 15 ml.) and dried *in vacuo* to yield 13.1% tropenium chloroborate (0.28 g., 1.15 mmoles) as transparent single needles, m.p. 119–120°; ultraviolet spectrum (96% sulfuric acid)<sup>14</sup> λ<sub>max</sub> 269 (sh), 274 (4350), 280 mμ.

*Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>BCl<sub>4</sub>: B, 4.44; Cl, 58.19; C<sub>7</sub>H<sub>7</sub>, 37.38; neut. equiv., 48.76. Found<sup>8</sup>: B, 4.23; Cl, 58.33; C<sub>7</sub>H<sub>7</sub>, 37.4; neut. equiv., 49.15.

**Reaction of Cycloheptatriene with Boron Chloride and *t*-Butyl Chloride in Methylene Chloride.**—Cycloheptatriene (0.90 g., 8.80 mmoles) and *t*-butyl chloride (0.85 g., 9.20 mmoles) in methylene chloride (15 ml.) were added to a solution of boron chloride (1.5 g., 13 mmoles) in methylene chloride (15 ml.) and the mixture was allowed to stand at room temperature for 24 hr. The mother liquor was withdrawn by pipet and the crystals remaining were washed with methylene chloride (3 × 15 ml.) and cyclohexane (3 × 15 ml.) and dried *in vacuo* to yield 29.0% tropenium chloroborate (0.619 g., 2.54 mmoles) as colorless plates, m.p. 119–121°; ultraviolet spectrum (96% sulfuric acid)<sup>14</sup> λ<sub>max</sub> 268 (sh), 274 (4370), 280 mμ; (water)<sup>15</sup> λ<sub>max</sub> 275 (4270), 280 (sh) mμ.

**Reaction of Cycloheptatriene with Boron Chloride in Cyclohexane.**—Cycloheptatriene (0.90 g., 8.80 mmoles) in cyclohexane (15 ml.) was added to a frozen solution of boron chloride (1.5 g., 13 mmoles) in cyclohexane (15 ml.). The mixture was thawed and swirled while warming to room temperature; a light yellow color appeared in the solution and a small quantity of light yellow fluffy precipitate formed. This turned white in a short time, and over the next 24 hr. a quantity of white powder deposited in the flask. The mother liquor was removed by pipet and the solid washed with cyclohexane (3 × 15 ml.) and dried *in vacuo* to yield 6.14% tropenium chloroborate of 94.7% purity (0.138 g., 0.54 mmole); ultraviolet spectrum (96% sulfuric acid)<sup>14</sup> λ<sub>max</sub> 268 (sh), 274 (4120), 280 mμ. The mother liquor was freed of boron chloride by warming and shaking with water; quantitative spectral analysis<sup>16</sup> showed the presence of 75.2% recovered cycloheptatriene. The salt produced in this reaction was not completely

(13) Gift of the Shell Chemical Co.

(14) In this solvent the spectrum of tropenium ion is λ<sub>max</sub> 269 (sh), 274 (4350), 279.5 mμ.<sup>9a,12</sup>

(15) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954), give λ<sub>max</sub> 275 (4350), 280 (sh) mμ for tropenium ion in water.

(16) We find the spectrum of cycloheptatriene in cyclohexane to be λ<sub>max</sub> 262 (3300) mμ.

soluble in water, but left a slight amorphous residue which appeared polymeric.

**Reaction of Cycloheptatriene with Boron Chloride (Neat).**—Cycloheptatriene (2.70 g., 26.4 mmoles) was added to liquid boron chloride (4.5 g., 39 mmoles); the mixture darkened at once and a butter-yellow solid separated. The reaction was held at 0° for 24 hr.; after this time a cake of tan solid had formed and no free liquid could be observed. Excess boron chloride and cycloheptatriene were removed *in vacuo* and the solid triturated with methylene chloride (2 × 50 ml.) which gave a dirty brown solution and a gray powder. The powder was separated by filtration and dissolved in water where quantitative spectral analysis showed a yield of 16.6% tropenium ion (0.396 g., 4.35 mmoles);  $\lambda_{\max}$  275, 280 (sh)  $\mu\mu$ .<sup>15</sup> The methylene chloride solution was concentrated to give a quantity of amorphous material; repeated recrystallizations from benzene-pentane gave a white powder with a broad band at 248  $\mu\mu$  in acetonitrile. This spectrum suggests a conjugated diene polymer<sup>17</sup> but does not suggest aromatic character.

**Reaction of Tropenium Chloride with Boron Chloride in Methylene Chloride.**—Tropenyl methyl ether<sup>15</sup> (0.171 g., 1.40 mmoles) was dissolved in methylene chloride (100 ml.) and dry hydrogen chloride passed over the surface of the solution, which became deep yellow in color. No precipitate formed.<sup>18</sup> Boron chloride gas was then passed over the solution with the immediate formation of white needles. The addition was continued until precipitation ceased; the solvent was removed by pipet, and the crystals dried *in vacuo* to give 34.0% tropenium chloroborate (0.119 g., 0.49 mmole) with a 1% enrichment of the chloride; ultraviolet spectrum (96% sulfuric acid)<sup>14</sup>  $\lambda_{\max}$  269 (sh), 274 (4420), 280  $\mu\mu$ .

*Anal.* Found<sup>8</sup>: B, 4.44; Cl, 57.32; C<sub>7</sub>H<sub>7</sub>, 38.0; neut. equiv., 49.48.

**Triphenylcarbonium Chloroborate.**—Triphenylmethyl chloride<sup>19</sup> (m.p. 109–111°, 5.85 g., 21.0 mmoles) in methylene chloride (20 ml.) was added to a solution of boron chloride (2.25 g., 21 mmoles) in methylene chloride (10 ml.) to give a deep red solution. This solution was taken up in a pipet and discharged beneath the surface of cyclohexane (70 ml.) to yield a bright yellow precipitate. This product was washed with cyclohexane (3 × 30 ml.) and dried *in vacuo* to give 78.8% triphenylcarbonium chloroborate as brilliant yellow microcrystals; visible spectrum (96% sulfuric acid)<sup>20</sup>  $\lambda_{\max}$  405, 432 (38, 200)  $\mu\mu$ .

*Anal.* Calcd. for C<sub>14</sub>H<sub>15</sub>BCl<sub>4</sub>: B, 2.73; Cl, 35.85; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C, 61.44; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>COH, 65.74. Found<sup>8</sup>: B, 2.40; Cl, 34.86; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C, 61.1; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>COH, 65.85.

**Reaction of Triphenylcarbonium Chloroborate with Cycloheptatriene in Methylene Chloride.**—Cycloheptatriene (0.90 g., 8.80 mmoles) was added dropwise to a deep red solution of triphenylcarbonium chloroborate (2.20 g., 5.55 mmoles) in methylene chloride (10 ml.). The color of the solution was instantly discharged and a white precipitate appeared. Pentane (10 ml.) was added to aid in settling the precipitate, the solution decanted, and the solid washed with pentane (3 × 50 ml.) and dried *in vacuo* to yield 100% tropenium chloroborate (1.36 g., 5.55 mmoles) as a white, microcrystalline powder; ultraviolet spectrum (96% sulfuric acid)<sup>14</sup>  $\lambda_{\max}$  268 (sh), 274 (4340), 280  $\mu\mu$ ; this shows 37.3% tropenium ion; calcd. for C<sub>7</sub>H<sub>7</sub>BCl<sub>4</sub>; 37.38.

The colorless mother liquor and combined washings were concentrated by rotary evaporation to a white solid which smelled of cycloheptatriene. Cycloheptatriene was removed *in vacuo* to yield 86.6% triphenylmethane (1.17 g., 4.81 mmoles), m.p. 90–92° (reported<sup>21</sup> 92.5°). Recrystallization from methanol raised the m.p. to 93°.

**Reaction of Cycloheptatriene with Boron Fluoride in Cyclohexane.**—Cycloheptatriene (0.11 g., 1.09 mmoles) was dissolved in cyclohexane (25 ml.) and a slow stream of dry boron fluoride passed over the surface of the solution for 2 hr. A faint tinge of yellow color appeared in the first few seconds; this did not deepen nor did any visible precipitate form. Dry nitrogen was then

bubbled through the solution until the exit gas ceased to fume. The solvent was decanted and the flask dried *in vacuo*; a faint white film was then seen below the original solution level. This was dissolved in water where quantitative spectral analysis<sup>15</sup> indicated a yield of 0.58% tropenium ion (0.58 mg., 6.4  $\mu$ moles). Spectral analysis of the reaction solution showed a quantitative recovery of cycloheptatriene.

**Reaction of Cycloheptatriene with Stannic Chloride in Cyclohexane.**<sup>22</sup>—Cycloheptatriene (0.53 g., 5.20 mmoles) was dissolved in cyclohexane (50 ml., oxygen-free), and stannic chloride (1.41 g., 5.30 mmoles) added; nothing happened. The reaction was allowed to stand for 17 days; after this time the solution was still water-white and no precipitate had formed. The solution was transferred to another flask, and the reaction flask washed with cyclohexane and dried *in vacuo*. The flask was then rinsed with 96% sulfuric acid; quantitative spectral analysis of this acid solution<sup>14</sup> showed a yield of 0.0011% tropenium ion (5.24  $\mu$ g., 0.057  $\mu$ mole). A small aliquot of the reaction solution was withdrawn and analyzed spectrally; it showed a peak at 258  $\mu\mu$  imposed on a high end absorption. If taken as cycloheptatriene this spectrum would indicate the presence of 5.7 mmoles. The combined reaction solution and washings were shaken with water to remove stannic chloride; quantitative spectral analysis<sup>15</sup> showed the presence of 83.8% recovered cycloheptatriene,  $\lambda_{\max}$  262  $\mu\mu$ .

**Reaction of Cycloheptatriene with Boron Bromide in Cyclohexane.**<sup>22</sup>—A solution of cycloheptatriene (0.90 g., 8.80 mmoles) in cyclohexane (15 ml.) was added to a solution of boron bromide (2.60 g., 10.4 mmoles) in cyclohexane (15 ml.). The reaction solution became cloudy at once, and slowly deposited a white, microcrystalline powder; the supernatant liquid remained water-white. After 1 week the solution was carefully decanted from the solid, and the solid washed with cyclohexane (2 × 10 ml.) and dried *in vacuo* to yield 71.3% tropenium ion (0.570 g., 6.27 mmoles) contained in 2.63 g. of tropenium bromoborate slightly enriched with tropenium bromide.

*Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>BBR<sub>4</sub>: B, 2.57; Br, 75.81; C<sub>7</sub>H<sub>7</sub>, 21.6. Found<sup>8</sup>: B, 2.35; Br, 75.27; C<sub>7</sub>H<sub>7</sub>, 22.5.

The mother liquor showed a single, exceptionally sharp spike at 256  $\mu\mu$  in the ultraviolet. Upon the slightest contact with the atmosphere this peak dropped sharply and a white opaque material coated the walls of the cell. This white material was soluble in 96% sulfuric acid in which it showed a strong peak at 247  $\mu\mu$  and a lower pair of peaks at 280 and 285  $\mu\mu$ .

**Reaction of Cycloheptatriene with Stannic Chloride in Methylene Chloride.**—Cycloheptatriene (0.68 g., 6.70 mmoles) was dissolved in methylene chloride (10 ml.) and stannic chloride (1.81 g., 6.80 mmoles) added. The solution became yellow at once and tan precipitate began to form within 15 min. After 6 hr. the dark brown mother liquor was decanted from a quantity of light brown solid; this solid was washed with methylene chloride (3 × 15 ml.) and dried *in vacuo* to yield 16.4% tropenium ion (0.997 g., 1.10 mmoles) contained in 0.281 g. of tropenium hexachlorostannate. Recrystallization of the reaction product from 12 *N* hydrochloric acid gave white cubes of tropenium hexachlorostannate; these turn black at 252° and melt at 256–257°<sup>23</sup>; ultraviolet spectrum (96% sulfuric acid)<sup>14</sup>  $\lambda_{\max}$  269 (sh), 274 (8700), 280  $\mu\mu$ .

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>SnCl<sub>6</sub>: C<sub>7</sub>H<sub>7</sub>, 35.48. Found: C<sub>7</sub>H<sub>7</sub>, 35.5.

**Reaction of Trianisylmethane with Boron Bromide in Methylene Chloride.**<sup>22,24</sup> Trianisylmethane<sup>25</sup> (0.0875 g., 0.261 mmole) was dissolved in cyclohexane (15 ml.) and boron bromide (0.13 g., 0.52 mmole) added. A white precipitate formed at once; in 1 to 2 min. this redissolved with concurrent formation of an orange precipitate. After a total reaction time of 5 min. the mother liquor was removed and the solid washed with cyclohexane (3 × 10 ml.) and dried *in vacuo*. The orange solid weighed 0.1617 g., and visible spectral analysis<sup>27</sup> in acetonitrile showed it to contain 44.7% trianisylcarbonium ion by weight. The yield of trianisylcarbonium ion is thus 83.2% (0.0723 g., 0.217 mmole).

(22) All operations carried out in glove box under nitrogen atmosphere.

(23) D. Bryce-Smith and N. A. Perkins, *Chem. Ind. (London)*, 1022 (1959), report m.p. 252° dec.

(24) With J. W. Breslow.

(25) White needles from methanol, m.p. 47.5–49° (reported<sup>26</sup> 45–47°).

(26) A. Baeyer and V. Villiger, *Ber.*, **35**, 1197 (1902).

(27) We have determined the visible spectrum of the trianisylcarbonium ion in acetonitrile to be  $\lambda_{\max}$  483 (73,600)  $\mu\mu$ .

(17) R. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950).

(18) Some tropenium hydrogen dichloride may form in this process; however, the chloride is the main species present in the solution as shown by the deep yellow C–T absorption.<sup>12</sup> Solutions of tropenium hydrogen dichloride in methylene chloride are colorless.<sup>5</sup>

(19) W. E. Bachmann, "Organic Syntheses," Coll. Vol. 111, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 841.

(20) We have determined<sup>8</sup> the spectrum of triphenylcarbonium ion in this solvent to be  $\lambda_{\max}$  405, 432 (38, 400)  $\mu\mu$ .

(21) A. Kekulé and A. Franchimont, *Ber.*, **5**, 907 (1872).

A portion of the orange solid was pumped overnight at room temperature to remove excess boron bromide; this left trianisylcarbonium bromoborate as light orange-red microcrystals, m.p. (gas evolution and dec.) 90–105°, visible spectrum (acetonitrile)<sup>27</sup>  $\lambda_{\text{max}}$  483 (74,000) m $\mu$ . *Anal.* Calcd. for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>BBr<sub>4</sub>: (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C, 50.22. Found: (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C, 50.4.

A portion of the trianisylcarbonium bromoborate was dissolved in acetonitrile; addition of ether gave a bright red precipitate of trianisylcarbonium bromide, visible spectrum (acetonitrile)<sup>27</sup>  $\lambda_{\text{max}}$  483 (73,700) m $\mu$ . *Anal.* Calcd. for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>Br: (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C, 80.71. Found: (*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>C, 80.7.

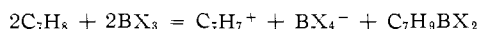
### Discussion

The four tetrahaloborate anions have now all been prepared, and while bromo- and iodoborates are still regarded as chemical oddities, chloroborates are becoming a more familiar class of compounds. Interest in compounds of the chloroborate anion should turn in the future from synthesis to physical chemical studies of bonding and stability, and to investigations of the anion as a catalyst carrier and a reaction intermediate.

The carbonium ion salts of the chloroborate anion reported herein may well find utility in such studies. They are easily prepared, and the tropenium salt in particular forms excellent crystals which separate from the reaction solution in a pure state and need no further treatment or recrystallization. Tropenium chloroborate is quite stable, and can be stored and handled with relatively mild precautions against moisture; it is not light or oxygen sensitive.

Triphenylcarbonium chloroborate was actually the first salt of this anion to be isolated and analyzed, but it was not so recognized at the time.<sup>6</sup> It is more sensitive to moisture than tropenium chloroborate, but no more so than other salts of the triphenylcarbonium ion. It is very soluble in organic solvents such as methylene chloride; this property has already been utilized<sup>10</sup> to determine definitive <sup>11</sup>B n.m.r. spectra of the chloroborate anion.

The reaction of boron bromide with cycloheptatriene (TrH) in methylene chloride has been discussed previously. Four possible reaction paths were proposed<sup>2,8</sup>: (1) direct hydride transfer from TrH to BX<sub>3</sub>, followed by disproportionation of HBX<sub>3</sub><sup>-</sup> to BX<sub>4</sub><sup>-</sup> and HBX<sub>2</sub>; (2) addition of BX<sub>3</sub> to TrH to form a diene cation which then takes hydride from TrH; (3) reaction of BX<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub> to give a cationic species (not necessarily free CH<sub>2</sub>Cl<sup>+</sup>) which abstracts hydride from TrH; or (4) adds to TrH to give a diene cation which then accepts hydride from TrH. The reaction of cycloheptatriene with boron bromide in methylene chloride has a 2:2 stoichiometry; *i.e.*, if either reagent is in excess the reaction proceeds until 50% of the other reagent is consumed.<sup>28</sup> This would be in accord with reaction path 1 if the liberated HBX<sub>2</sub> hydroborates cycloheptatriene. The over-all reaction would be:



Unfortunately, reaction path 2 would possess the same stoichiometry and indeed in the first approximation would produce the same products. Neither reaction path 3 nor 4 would be limited to a 50% consumption of BX<sub>3</sub>; however, path 4 could only convert 50% of the initial cycloheptatriene to the ion.

(28) Consumption of cycloheptatriene is occasionally slightly higher, but the 50% limit on conversion of boron bromide to bromoborate in this system seems rigidly fixed.

It is clear that this reaction system leaves something to be desired in the matter of simplicity. Similarly, no real conclusions can be drawn from the boron chloride-cycloheptatriene reaction in methylene chloride, since the yields are quite low.

The reactions of metal halides with cycloheptatriene in cyclohexane are another matter. At the outset reaction paths 3 and 4 can be eliminated since there is no solvent cocatalysis, and rigorous purification of materials will reduce cocatalysis by water or hydrogen halide to a minimum. This leaves only direct interaction of metal halide and cycloheptatriene by paths 1 and/or 2 as the source of tropenium ion in these systems.

Boron fluoride reacts to a very limited extent with cycloheptatriene in cyclohexane, and boron chloride does little better. Boron bromide, however, converts over 70% of the available cycloheptatriene to tropenium ion. Since reaction path 2 consumes two cycloheptatrienes for each tropenium ion produced, path 1 must account for a minimum of 42.6% out of the total yield of 71.3% tropenium ion in this reaction, or 59.8% of the ion produced. This minimum figure assumes no hydroboration of cycloheptatriene by reduced boron products. The high yield of tropenium ion, coupled with the total lack of polymer formation in the water-white mother liquor (*cf.* discussion below), indicates that direct hydride transfer is the main source of tropenium ion in this reaction.

Since most of the bromine introduced into the reaction as boron bromide is in the precipitate, there must be a highly reduced boron species in the mother liquor; we believe that the reactive substance in the cyclohexane solution remaining after this reaction is an alkylborane arising from hydroboration of cycloheptatriene by such reduced boron species. A clarification of the role of hydroboration in the reaction of cycloheptatriene with boron bromide in cyclohexane and methylene chloride and an explanation for the apparent differences in these two systems must await identification of the soluble products. Attempts to isolate these species or to convert them to boronic acids have resulted to date only in the separation of intractable polymers that contain boron and have an ultraviolet spectrum suggesting a conjugated seven-membered diene.<sup>17</sup>

Further support for this type of direct hydride transfer is given by the reaction of trianisylmethane with boron bromide in cyclohexane. Here path 2 should not be operative since the substrate is not an olefin, and the rapid conversion of the methane to trianisylcarbonium ion in 83.2% yield is best accounted for by direct hydride transfer from carbon to metal.

Stannic chloride fails to produce tropenium ion by reaction with cycloheptatriene in cyclohexane. West<sup>29</sup> has shown that tin halides will add to bicycloheptadiene in hydrocarbon solvent to give products stable below 0°. We have not ruled out the possibility of such addition taking place with cycloheptatriene, but if it does occur it does not lead to ion formation in this solvent, and probably (see below) does not take place through a cationic intermediate. In methylene chloride stannic chloride reacts with cycloheptatriene with much concurrent polymerization. Colclough and Dainton<sup>30</sup> have shown that stannic chloride cannot polymerize styrene

(29) F. M. Rabel and R. West, *J. Am. Chem. Soc.*, **84**, 4169 (1962).

(30) R. O. Colclough and F. S. Dainton, *Trans. Faraday Soc.*, **54**, 886 (1958).

in nitrobenzene in the absence of cocatalyst, such as water or alkyl halide, and that in carbon tetrachloride, where the dielectric constant is too low to allow any ion formation, only water is an effective cocatalyst. In 1,2-dichloroethane, however, there is polymerization in the absence of any other added substance due to solvent cocatalysis (1,2-dichloroethane is also an effective cocatalyst in nitrobenzene). Methylene chloride has a dielectric constant (9.08 at 25°) similar to that of 1,2-dichloroethane (10.2 at 25°) and should also be a cocatalytic solvent for cationic polymerization. We believe that the reaction of stannic chloride with cycloheptatriene in methylene chloride proceeds mainly by reaction path 4, and that the generation of diene carbonium ions in cycloheptatriene solutions will always lead to much cationic polymerization in addition to ion formation. This is supported by the observation that conversion of cycloheptatriene to tropenium ion by sulfuric acid<sup>9b</sup> and perchloric acid is accompanied by extensive polymerization of the triene.

The reaction of boron halides with cycloheptatriene goes more rapidly in methylene chloride than in cyclohexane. This might be due to solvent cocatalysis; certainly *t*-butyl chloride appears to act as a cocatalyst with boron chloride.<sup>31</sup> However, the reaction of boron chloride with cycloheptatriene in the presence of *t*-butyl chloride is accompanied by much darkening of the solution and concurrent polymerization of cycloheptatriene. Since neither boron bromide nor chloride produces polymerization or decomposition of cycloheptatriene<sup>32</sup> in

(31) Coleclough and Dainton<sup>30</sup> found that *t*-butyl chloride is  $1.43 \times 10^4$  times as effective a cocatalyst as 1,2-dichloroethane for the polymerization of styrene by stannic chloride in nitrobenzene.

(32) These reaction solutions become colored (yellow to red) but this is attributed to the C-T absorptions of tropenium halide<sup>12</sup> rather than to de-

methylene chloride in the absence of cocatalyst, we conclude that the cocatalytic activity of the solvent is negligible, and that the increase in rate of these reactions in going from hydrocarbon to chlorocarbon solvent is caused by a lowering of the energy of the first, ion-forming hydride transfer step by the more polar solvent.

A note should be made of the work of Joy and Lappert<sup>33</sup> who find that refluxing a neat mixture of boron chloride and cycloheptatriene leads to the formation of benzylboron dichloride. Under the conditions of our reactions we find no aromatic product. Since they did not look for tropenium salt products, it cannot be said at this time whether they produced benzylboron dichloride concurrently with, subsequently to, or instead of tropenium chloroborate.

The work reported herein, coupled with studies on triarylmethanes to be reported shortly, establishes the existence of carbon-to-metal hydride transfer reactions as a source of carbonium ions in the reactions of certain hydrocarbons with metal halides, and has laid a foundation for more detailed studies, currently in progress, of the scope, limitations, and mechanisms of such reactions.

**Acknowledgment.**—We wish to thank Dr. Hyp J. Dauben, Jr., who encouraged us in the early stages of this work and jointly developed the mechanistic discussion with us, Drs. L. R. Honnen and M. F. Lappert for discussions and suggestions, and the many students at Harvey Mudd College who have assisted in parts of the work.

composition of cycloheptatriene. Solutions of pure tropenium haloborates in methylene chloride are also colored unless excess boron halide is present to suppress dissociation of the anion.

(33) F. Joy and M. F. Lappert, *Proc. Chem. Soc.*, 353 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK, STONY BROOK, NEW YORK]

## Stable Free Radicals. I. Isolation and Distillation of 1-Ethyl-4-carbomethoxypyridinyl

BY EDWARD M. KOSOWER<sup>1</sup> AND EDWARD J. POZIOMEK<sup>2</sup>

RECEIVED AUGUST 14, 1964

The preparation of the stable free radical, 1-ethyl-4-carbomethoxypyridinyl, by reduction of the corresponding pyridinium iodide with zinc or magnesium and its isolation in pure form by distillation under high vacuum are described. In acetonitrile, the radical has  $\lambda_{\text{max}}$  (m $\mu$ ) 6326 ( $\epsilon$  83), 3950 ( $\epsilon$  4700), 3040 ( $\epsilon$  11,300), and 2080 ( $\epsilon$  concentration dependent). The structure of the radical is proved through the identity of the spectrum with that of radical produced in quantitative electrochemical reduction, by elemental analysis, and by its magnetic properties, including high-resolution e.s.r. spectra and magnetic susceptibility which indicates 93% radical in the pure material at 25°. Infrared and visible spectra demonstrate that the radical at 77°K., a sapphire-blue solid, is identical with the radical at 298°K., an emerald-green liquid. The radical reduces methylviologen dication to the cation radical, abstracts halogen rapidly from such halocarbons as dibromomethane, trichloromethane, and tetrachloromethane, and reacts rapidly with oxygen. Other physical and chemical properties are described. The stability of the radical is attributed to steric hindrance to dimerization and to an intrinsic factor related to delocalization and the presence of electronegative atoms (nitrogen and oxygen) and summarized as decreased "electron availability."

The first stable organic free radical, triphenylmethyl, was prepared by Gomberg in 1900.<sup>3</sup> A modest number of other stable free-radical types have been discovered in the succeeding five decades.<sup>4</sup> In the last 15 years,

(1) Alfred P. Sloan Fellow 1960–1964.

(2) (a) Secretary of the Army Research and Study Fellow 1962–1963.

(b) Support from the Department of Defense through Contract DA-49-083 OSA-2615 is gratefully acknowledged.

(3) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); *Ber.*, **33**, 3150 (1900).

(4) *Cf.*, for example, the list given by G. W. Wheland in "Resonance in

the combination of electron spin resonance (e.s.r.) techniques with careful methods of reduction (or oxidation) has led to an enormous increase in the number and variety of stable free radicals. However, largely because of preparative accessibility, most of the radicals reported have been charged species, either monoanions or monocations. The only reasonably simple *neutral* stable free radicals which have been investigated have

*Organic Chemistry*," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 391.