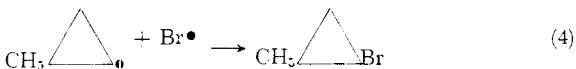
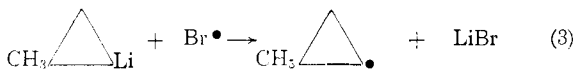
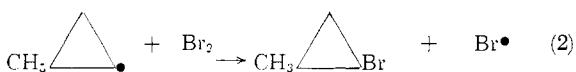
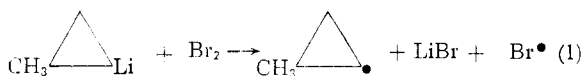


least as easy as in the case of open-chain secondary alkylolithiums).

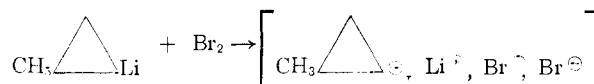
The possibility of a free cyclopropyl radical intermediate is more easily envisioned, and finds analogy in the recently discovered free-radical brominolysis of organomercurials.<sup>14</sup> A free-radical



process might be a chain reaction, as shown in reactions 1-4, in which case a competitive stereospecific reaction (possibly  $S_N2$ ) would be required to account for the partial retention of configuration observed (Table I). Alternatively, a free-radical cage reaction, using only steps 1 and 4 might account for part or all of the retention obtained. A difficulty of the free-radical possibilities is that they do not readily account for the effect of ether in reducing the stereospecificity.

The possibility that bromine initially oxidizes the lithium reagent to a carbonium ion, followed

(14) F. R. Jensen and L. H. Gale, *J. Am. Chem. Soc.*, **82**, 148 (1960).



by collapse within the resulting ion cluster, would account for partial retention of configuration and would predict the effect of added ether correctly. Better solvation of the ions in ether would lead to longer ion lifetimes and lower probability of retention upon collapse. An argument against the carbonium ion intermediate is the strong tendency of cyclopropyl cations to undergo ring opening.<sup>15</sup> There is at least one case known, however, in which such a ring opening may be slow in comparison with reaction of the cation with a nucleophile.<sup>16</sup> A final choice of the mechanism of brominolysis must await the results of further experiments.

**Acknowledgment.**—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We wish also to express our gratitude to the Sloan Foundation for support during the fall of 1959.

(15) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(16) R. Pettit, *ibid.*, **82**, 1972 (1960). The author chooses to regard his elegant case, which involved replacement of amino with chlorine in the presence of nitrous acid and chloride ion, as in  $S_N1$  reaction rather than a "free carbonium ion" reaction. Because  $S_N1$  reactions appear most often to be carbonium ion-pair reactions,<sup>17</sup> we feel that his result is suggestive of a slow ring opening of a cyclopropyl cation, whether the reaction be  $S_N1$  or  $S_N1$ .

(17) (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 294; (b) D. E. Applequist and J. D. Roberts, *Chem. Revs.*, **54**, 1073 (1954).

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

## Carbonium Ion Salts. I. Tropenium and Trityl Bromoborates<sup>1</sup>

BY KENNETH M. HARMON AND ANN B. HARMON

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Reaction of boron bromide with cycloheptatriene either neat or in  $\text{CH}_2\text{Cl}_2$  gives good yields of tropenium (cycloheptatrienylium) ion. The initial product is tropenium bromoborate,  $\text{C}_7\text{H}_7\text{BBr}_4$ ; composition confirmed by analysis and spectra. Properties (high m.p., soluble in polar, insol. in non-polar solvents), reactions (converted to tropenium bromide ( $\text{TrBr}$ ) by ether trituration or sublimation), and direct synthesis from  $\text{TrBr}$  and  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  indicate a salt of  $\text{Tr}^+$  and  $\text{BBr}_4^-$ . Reaction consumes 50% of available  $\text{BBr}_3$ ; *t*-BuBr raises yield of neat reaction but has no effect in  $\text{CH}_2\text{Cl}_2$ . Alternative reaction paths are discussed. Reaction of  $(\text{C}_6\text{H}_5)_3\text{CH}$  with  $\text{BBr}_3$  in cyclohexane or  $\text{CH}_2\text{Cl}_2$  gives 6-26%  $(\text{C}_6\text{H}_5)_3\text{C}^+$  by spectra;  $\text{BBr}_3$  and  $(\text{C}_6\text{H}_5)_3\text{CBr}$  in these solvents give 80-90% yields of triphenylmethyl bromoborate,  $\text{C}_6\text{H}_5)_3\text{C}^+\text{BBr}_4^-$ , a yellow, crystalline salt. Hydride exchange between triphenylmethyl bromoborate and cycloheptatriene in methylene chloride gives high yields of tropenium bromoborate and triphenylmethane.

We have previously reported<sup>2</sup> that the action of boron bromide on a mixture of cycloheptatriene and *t*-butyl bromide yields a white tropenium (cycloheptatrienylium) salt presumed to be tropenium bromoborate,  $\text{C}_7\text{H}_7^+\text{BBr}_4^-$ , on the basis of spectral analysis. Subsequent investigation has shown that the reaction of boron bromide, either neat or in methylene chloride, gives good yields of

this compound. The elemental analysis, quantitative ultraviolet spectrum, physical and chemical properties, and alternative synthesis from tropenium bromide and boron bromide are consonant with a formulation as a salt of the tropenium cation and the bromoborate anion. This reaction is of interest as a source of the little-known bromoborate anion, as a convenient synthetic route to tropenium bromide, and as a possible example of a novel hydride transfer reaction.

Until recently no evidence for the formation of the bromoborate anion had been reported,<sup>3,4</sup>

(1) Supported by grants from the Petroleum Research Fund and the Claremont Graduate School; presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 12, 1960, Abstracts of Papers, p. 4-P.

(2) (a) H. J. Dauben, Jr. and K. M. Harmon, Abstracts, 134th Meeting, American Chemical Society, Chicago, Ill., Sept. 8, 1958, p. 35-P; (b) K. M. Harmon, Ph.D. Thesis, University of Washington, 1958, *Dissertation Abstr.*, **19**, 1563 (1959).

(3) D. R. Martin, *Chem. Revs.*, **42**, 581 (1948).

(4) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 760.

and only a few examples of boron bromide acting as an acceptor toward bromine had been observed.<sup>3,5</sup> This failure of boron bromide to act as an acceptor toward bromine or bromide has been explained<sup>3,6</sup> on the basis of steric crowding around the boron atom, and as a result of the low electronegativity of bromine which might lower the acceptor strength of boron bromide in comparison to boron fluoride. However, it has been shown<sup>7</sup> that boron bromide undergoes rapid exchange with radioactive bromine which suggests that the steric factor is not a prohibitive one, and recent chemical evidence<sup>8</sup> has shown that both boron bromide and boron chloride are better acceptors than boron fluoride. This latter observation has been theoretically explained<sup>9</sup> as a result of loss of resonance energy in trigonal boron fluoride when converted to a tetrahedral configuration.

Whether or not complexing between boron bromide and bromine or bromide is theoretically reasonable, few examples of it appear in the literature. Tarible has reported<sup>10</sup> compound formation between boron bromide and phosphorus pentabromide and Frazer, Gerrard and Patel<sup>11</sup> suggest from infrared data that bromine in phosphorus oxybromide acts as a donor toward boron bromide. Fairbrother<sup>5</sup> found evidence for reaction between triphenylmethyl bromide and boron bromide but did not isolate any products. Lappert<sup>12</sup> has reported the preparation of pyridinium bromoborate, but gives no experimental or analytical details. Kynastron, Larcombe and Turner<sup>13</sup> report a preparation of ammonium bromoborate and give infrared data; their analytical figures, however, indicate considerable excess ammonium bromide in the product. The preparation of tropenium and triphenylmethyl bromoborates reported in this work supports theoretical arguments and experimental evidence for the existence of the bromoborate anion; these compounds are the first reasonably tractable, stoichiometric bromoborates to be characterized and reported.

**Results.**—The hydride exchange reaction between cycloheptatriene and triphenylmethyl carbonium ion first reported by Dauben and Pearson<sup>14</sup> has been extended to the preparation of a number of other aromatic carbonium ion species.<sup>2,14-16</sup> In an attempt to find a more convenient hydride acceptor the use of *t*-butylcarbonium ion was investigated. Dauben and Harmon<sup>2</sup> have shown that

*t*-butyl halides react with cycloheptatriene in sulfur dioxide to give low yields of tropenium salts, and that higher yields are obtained when a solution of the corresponding mercuric halide in ether is used instead of sulfur dioxide. Dauben and Honnen<sup>15</sup> have shown that *t*-butyl fluoride and boron fluoride in pentane react with cycloheptatriene to give tropenium fluoborate. A paper discussing these and related reactions is in preparation.<sup>17</sup> This paper also includes the first evidence that a Lewis acid, stannic chloride, may effect hydride abstraction from cycloheptatriene in the absence of a carbonium ion source such as *t*-butyl halide (*cf.* D. Bryce-Smith and N. A. Perkins, *Chemistry & Industry*, 1022 (1959), for a different interpretation of results obtained from the use of *t*-butyl chloride and stannic chloride).

The use of boron bromide as a catalyst in the reaction of cycloheptatriene and *t*-butyl bromide was next investigated. It was found that addition of boron bromide to a mixture of cycloheptatriene and *t*-butyl bromide resulted in an exothermic reaction and the formation of a gray, fuming solid which could be converted to tropenium bromide by trituration with ether or by addition of an acetonitrile solution to a large excess of ether. Attempted sublimation of the reaction product gave tropenium bromide and boron bromide. Addition of a minimum amount of ether to an acetonitrile solution of the material gave a white solid; ultraviolet spectral analysis of this substance agrees with a formulation as C<sub>7</sub>H<sub>7</sub>BBr<sub>4</sub>. Moderation of this reaction with methylene chloride solvent gave a much cleaner, crystalline product.

It was found that boron bromide will react with cycloheptatriene to give tropenium bromoborate in the absence of *t*-butyl bromide. When the reaction is run in methylene chloride at fairly high dilutions large, well-formed crystals are produced, with the correct elemental analysis and ultraviolet spectrum for C<sub>7</sub>H<sub>7</sub>BBr<sub>4</sub>. At higher concentrations the yield is increased, but the crystals formed are much smaller in size due to the rapidity with which they are produced. Conversion of boron bromide to bromoborate ion does not exceed 50%; however, with excess boron bromide at least 60% of the cycloheptatriene may appear as tropenium ion.

Tropenium bromoborate is a colorless, crystalline compound; it reacts slowly with moist air but is less hygroscopic than tropenium bromide. It dissolves slowly in water at 0° but dissolves rapidly at room temperature to give clear solutions. It is slightly soluble in methylene chloride, insoluble in hydrocarbons, converted to tropenium bromide by ether (slowly) and acetone (rapidly), and soluble with loss of boron bromide in alcohols or acetonitrile. It may be recrystallized from nitrobenzene as white needles which show a slight (2-3%) enrichment of tropenium bromide. Large needles of tropenium bromoborate melt at 170-173° with prior sublimation of tropenium bromide, but the melting point is not a satisfactory criterion of identity as it is affected by crystal size and history of sample. We have used quantitative ultraviolet spectra in 96% sulfuric acid to "fingerprint" the

(17) H. J. Dauben, Jr., K. M. Harmon and L. R. Honnen, *J. Org. Chem.*, in preparation.

- (5) F. Fairbrother, *J. Chem. Soc.*, 503 (1945).  
 (6) D. R. Martin, *Chem. Revs.*, **24**, 461 (1944).  
 (7) Ya. A. Fielkov and Yu. P. Nazarenko, *Izvest. Akad. Nauk, S. S. S. R., Otdel. Khim. Nauk*, 590 (1950); *C. A.*, **45**, 6025d (1951).  
 (8) (a) H. C. Brown and R. R. Holmes, *THIS JOURNAL*, **78**, 2173 (1956); (b) N. N. Greenwood and P. G. Perkins, *J. Chem. Soc.*, 1141 (1960); (c) W. Dutton, W. G. Paterson and M. Onyszczuk, *Proc. Chem. Soc.*, 149 (1960).  
 (9) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).  
 (10) J. Tarible, *Compt. rend.*, **116**, 1521 (1883).  
 (11) M. J. Frazer, W. Gerrard and J. K. Patel, *J. Chem. Soc.*, 726 (1960).  
 (12) M. F. Lappert, *Proc. Chem. Soc.*, 121 (1957).  
 (13) W. Kynastron, B. E. Larcombe and H. S. Turner, *J. Chem. Soc.*, 1772 (1960).  
 (14) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *THIS JOURNAL*, **79**, 4557 (1957).  
 (15) L. R. Honnen, Ph.D. Thesis, Univ. of Washington, 1960.  
 (16) H. J. Dauben, Jr., and L. R. Honnen, *THIS JOURNAL*, **80**, 5570 (1958).

compound, since the absorption of tropenium ion in this solvent has been carefully determined,<sup>14</sup> and tropenium ion is completely stable in sulfuric acid.<sup>2</sup> The bromoborate ion is decomposed by sulfuric acid with liberation of hydrogen bromide, and shows no ultraviolet absorption in this medium.

Tropenium bromide dissolves in methylene chloride to give a bright orange solution.<sup>18</sup> Addition of boron bromide to such a solution causes the disappearance of this color and the formation of a white precipitate of tropenium bromoborate. The large quantity of solvent needed in this reaction leads to a lower yield (about 39%) than in the reaction of cycloheptatriene with boron bromide since tropenium bromoborate is moderately soluble in methylene chloride.

The reaction of triphenylmethane and boron bromide was investigated to determine the versatility of this reagent in forming carbonium ions. Triphenylmethane reacts slowly with boron bromide in cyclohexane or methylene chloride; in four weeks 26% of the triphenylmethane was oxidized to triphenylmethyl carbonium ion. No triphenylmethyl salt was isolated from these reactions. The carbonium ion formed was assayed by hydrolysis followed by solution of triphenylcarbinol in sulfuric acid and spectral analysis.

Triphenylmethyl bromide reacts readily with boron bromide in cyclohexane or methylene chloride to give nearly quantitative yields of triphenylmethyl bromoborate, a yellow, crystalline salt. Elemental analysis, ultraviolet spectra and quantitative conversion to triphenylcarbinol agree with the assigned formulation. Triphenylmethyl bromoborate is much more sensitive to moisture than is the tropenium salt; it fumes in air and rapidly turns white. The compound is fairly soluble in methylene chloride, insoluble in hydrocarbons, and reacts violently with even ice-cold water. It may be recrystallized by slow addition of cyclohexane to a methylene chloride solution as yellow needles which are somewhat more tractable than the microcrystalline reaction product, presumably due to lowered surface area. Triphenylmethyl bromoborate melts at 150°.

Addition of cycloheptatriene to a preformed solution of triphenylmethyl bromoborate in methylene chloride gives an immediate precipitate of tropenium bromoborate in 83.9% yield, and triphenylmethane can be isolated from the reaction solution in quantitative amounts.

### Experimental

Eastman Kodak Co. practical grade cyclohexane, methylene chloride and acetonitrile were refluxed with phosphorus pentoxide, and distilled from phosphorus pentoxide directly into the reaction vessel at all times. Baker and Adamson reagent grade anhydrous ether and benzene were stored over sodium wire and transferred with a pipet. Trona boron bromide was stored in a brown bottle over mercury, and distilled into the reaction vessel from mercury through an all-glass apparatus. This apparatus consists of a small Claisen-Vigreux distilling head and two fraction cutters<sup>19</sup>

(18) K. M. Harmon and D. A. Davis, unpublished work. This color is due to a band at 401  $m\mu$  (1100) which appears in this solvent in addition to the expected tropenium ion spectra at 277  $m\mu$  (4200). We attribute this band to charge-transfer, in ion-pairs, and feel that it is the absorption responsible for the unexplained yellow color of solid tropenium bromide.

mounted one above the other. The upper has a chamber made from a 15-ml. graduated centrifuge tube and is used as a holding chamber or for measuring large samples, while the lower has a chamber made from a 1-ml. graduated pipet and is used for accurate measurement of small samples. Ground glass joints are sealed with Teflon sleeves and all stopcocks contacted by boron bromide are Teflon. The system is purged with dry nitrogen before use, and dry nitrogen is passed through the lower cutter over the delivery tip whenever flasks are being changed. Eastman Kodak Co. white label *t*-butyl bromide was distilled prior to use and stored in a brown bottle; Eastman white label triphenylcarbinol was used without purification except as noted below. Cycloheptatriene was generously furnished by the Shell Chemical Corp.; this material is 92% pure, the remainder being toluene. Cycloheptatriene was rendered colorless by chromatography over alumina, distilled under nitrogen, and stored in the dark at 0° until used.

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet spectra were taken with a Beckman DU using silica cells. Baker and Adamson reagent grade 96% sulfuric acid was used to prepare spectral solutions.

**Reaction of Cycloheptatriene and *t*-Butyl Bromide with Boron Bromide (Neat).**—Cycloheptatriene (1.00 g., 10.0 mmoles)<sup>20</sup> and *t*-butyl bromide (1.50 g., 11.0 mmoles) were mixed, the flask was cooled in an ice-water-bath, and excess boron bromide (10.5 ml.) added. An exothermic reaction occurred and a cream-colored precipitate formed; the supernatant solution was colorless. Excess boron bromide was removed by pumping at room temperature until, after one hour, a pink paste remained in the flask. Trituration with ether (1 × 25 ml.) removed the reddish color and left a gray solid which fumed when exposed to air. This was further triturated with ether (3 × 25 ml.) to give 63.1% crude tropenium bromide (1.08 g., 6.31 mmoles) as a yellow-green powder, m.p. 190°. Sublimation (105°, 0.5 mm.) gave yellow crystals of tropenium bromide, m.p. 203°; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{max}$  268 (shoulder), 273.5  $\mu$  (4380), 280  $m\mu$  (reported: m.p. 203°, ultraviolet spectrum (96% sulfuric acid)<sup>14</sup>:  $\lambda_{max}$  268 (shoulder), 273.5  $\mu$  (4350), 280  $m\mu$ ). Boron bromide was recovered from a Dry Ice trap in the vacuum line.

In another reaction, cycloheptatriene (1.00 g., 10.0 mmoles) and *t*-butyl bromide (1.20 g., 8.80 mmoles) were treated with excess boron bromide (20.0 ml.) and the reaction mixture pumped at room temperature overnight to give 4.00 g. of gray powder. A portion of this was dissolved in acetonitrile and reprecipitated by addition of an equal volume of ether as a white powder; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{max}$  268 (shoulder), 273.5 (4140), 280  $m\mu$ ; this shows 20.6% tropenium ion; calcd for  $C_7H_7BBR_4$ :  $\lambda_{max}$  268 (shoulder), 273.5 (4350), 280  $m\mu$ ; 21.6% tropenium ion.

Attempted sublimation of the white material (100°, 1 mm.) gave bright yellow crystals of tropenium bromide, m.p. 203°. A solution of the gray powder in acetonitrile was added to a large excess of ether to give a precipitate of tropenium bromide as a yellow powder, m.p. 200°; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{max}$  268, 273.5 (4400), 280  $m\mu$ .

**Reaction of Cycloheptatriene and *t*-Butyl Bromide with Boron Bromide in Methylene Chloride.**—Cycloheptatriene (1.00 g., 10.0 mmoles) and *t*-butyl bromide (1.37 g., 10.0 mmoles) were dissolved in methylene chloride (20 ml.) and boron bromide (2.60 g., 10.4 mmoles) added dropwise. A precipitate of small white needles appeared at once. The reaction was allowed to stand for 2 hours; during this time the quantity of precipitate increased slightly and larger needles formed. The solvent was removed with a pipet and the crystals washed with methylene chloride (4 × 25 ml.) and dried *in vacuo* to give 44.4% presumed tropenium bromoborate (1.87 g., 4.44 mmoles) as a white, microcrystalline powder; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{max}$  268 (shoulder), 273.5  $\mu$  (4280), 280  $m\mu$ ; this shows 21.3% tropenium ion; calcd for  $C_7H_7BBR_4$ : 21.6% tropenium ion.

(19) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 28-29.

(20) Weights of cycloheptatriene given are the actual weight of 92% cycloheptatriene employed; the number of mmoles is the actual number of mmoles of cycloheptatriene contained in the sample.

(21) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **76**, 3203 (1954).

When this white powder was heated on the melting point block a yellow, crystalline substance sublimed onto the upper glass; this was presumed to be tropenium bromide since it melted at 204°. The dark residue decomposed slowly but did not melt. A sample of the white powder was sublimed (100°, 1 mm.) to give yellow crystals of tropenium bromide, m.p. 203°.

**Reaction of Cycloheptatriene with Boron Bromide (Neat).**—Cycloheptatriene (0.40 g., 4.00 mmoles) was placed in a small flask and boron bromide (3.90 g., 15.6 mmoles) added. A vigorous exothermic reaction took place which was controlled by use of an ice-water bath; when reaction was complete a brown solid remained in the flask. This solid was triturated with ether (3 × 15 ml.) to give a gray powder which fumed in air. The gray powder was dissolved in the minimum amount of acetonitrile and added to ether (500 ml.) to give a yellow precipitate of tropenium bromide in 43.8% yield (0.30 g., 1.75 mmoles); ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268 (shoulder), 273.5 (4250), 280  $m\mu$ .

**Reaction of Cycloheptatriene with Boron Bromide in Methylene Chloride.**—Cycloheptatriene (1.50 g., 15.0 mmoles) was dissolved in methylene chloride (200 ml.) and boron bromide (2.60 g., 10.4 mmoles) added. The solution became light yellow in color, and in a few minutes fine white needles began to form on the walls of the reaction flask. In one hour these had grown to a thick mass of well-formed white needles up to an inch in length; examination with the polarizing microscope showed these to be single crystals. They retained their crystal form for about 15 minutes between microscope slides, but gradually became moist and lost definition on longer exposure to the air. The solution was removed with a pipet and the crystals washed with methylene chloride (4 × 50 ml.) and dried *in vacuo* to give 52.7% tropenium bromoborate<sup>22</sup> (1.15 g., 2.74 mmoles) as white needles. When these needles are heated on the melting point block they slowly diminish in size while a yellow sublimate—presumed to be tropenium bromide—collects on the upper glass. The unchanged portion of the needles melts at 173° dec. Ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268 (shoulder), 273.5 (4370), 280  $m\mu$ ; this shows 21.7% tropenium ion; calcd. for  $C_7H_7BBr_4$ : 21.6% tropenium ion.

A weighed portion of the crystals was hydrolyzed by addition of ice-cold de-ionized water in a system sealed to prevent loss of hydrogen bromide. The crystals did not react rapidly with cold water, but dissolved without decomposition on warming to room temperature to give a clear, colorless solution; this solution was transferred to a volumetric flask, brought to volume, and used for analysis. Boron was determined by the mannitol method as boric acid<sup>23</sup>; the solution was brought to pH 7<sup>24</sup> by addition of dilute sodium hydroxide (carbonate free), an excess of mannitol added, and the hydrogen ion liberated from the mannitol-boric acid complex titrated to pH 7. Carbon dioxide must be rigorously excluded; for this purpose the titrating vessel was blanketed with nitrogen during titrations. A Beckman Zeromatic pH meter was used to follow the titrations. The neutralization equivalent was determined by adding excess mannitol and phenolphthalein to a sample and titrating to a pink color.<sup>24</sup> Bromine was determined by the Volhard method.

*Anal.* Calcd for  $C_7H_7BBr_4$ : B, 2.57; Br, 75.81; neut. equiv., 84.32 (5 × neut. equiv. = mol. wt., 421.61). Found: B, 2.46; Br, 75.60; neut. equiv., 84.47 (mol. wt., 422.35).

(22) Since the exact stoichiometry of the reaction is not known, the yield is calculated on a possible conversion of one-half of the boron bromide to bromoborate (see Discussion).

(23) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1911, pp. 588-590.

(24) The hydrolysis reaction of tropenium bromoborate is:  $C_7H_7BBr_4 + 3H_2O = H_3BO_3 + C_7H_7^+ + 4Br^- + 3H^+$ . Titration to pH 7 neutralizes the hydrobromic acid (strong), 99% of the tropenium ion ( $pK_a$   $1.8 \times 10^{-9}$ ),<sup>20</sup> and 1% of the boric acid ( $pK_a$   $5.5 \times 10^{-10}$ ). Addition of mannitol followed by titration to pH 7 effectively gives the amount of boric acid. For the total neutralization equivalent it is necessary to titrate to phenolphthalein end-point. Trityl bromoborate hydrolyzes by the equation  $(C_6H_5)_3CBBR_4 + 4H_2O = (C_6H_5)_3COH$  (insoluble) +  $4H^+$  +  $H_3BO_3$  +  $4Br^-$ . Titration to pH 6 neutralizes hydrobromic acid and leaves boric acid unaffected—addition of mannitol and titration to pH 7 then measures boric acid.

In another reaction cycloheptatriene (1.50 g., 15.0 mmoles) was dissolved in methylene chloride (30 ml.) and boron bromide (2.60 g., 10.4 mmoles) added. The solution turned yellow at once, and a mass of small white needles formed rapidly; under the microscope they appeared as well-formed single crystals which slowly decomposed in air. The reaction was allowed to stand for 15 minutes, then the solvent was removed with a pipet and the crystals washed with methylene chloride (4 × 25 ml.) and dried *in vacuo* to give 100% tropenium bromoborate<sup>22</sup> (2.19 g., 5.20 mmoles), white needles, m.p. 173-174° dec.; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268 (shoulder), 273.5 (4370), 280  $m\mu$ .

*Anal.* Calcd. for  $C_7H_7BBr_4$ : B, 2.57. Found: B, 2.60.

**Reaction of Cycloheptatriene and Boron Bromide in Methylene Chloride (1:2 Ratio).**—Cycloheptatriene (0.50 g., 5.00 mmoles) was dissolved in methylene chloride (15 ml.) and boron bromide (2.86 g., 11.4 mmoles) added. The reaction stood for 1 hour, then the solvent was removed by dropper, the crystalline precipitate washed with methylene chloride (4 × 25 ml.) and dried *in vacuo* to give tropenium bromoborate (1.22 g., 2.90 mmoles) as a white crystalline powder; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268 (shoulder), 273.5 (4350), 280  $m\mu$ . This is a 58.0% yield based on available cycloheptatriene, 25.4% based on available boron bromide and 50.8% based on consumption of one-half of the boron bromide.

**Reaction of Tropenium Bromide and Boron Bromide in Methylene Chloride.**—Tropenium bromide was prepared by hydride exchange between cycloheptatriene and triphenylmethyl bromide in liquid sulfur dioxide.<sup>14</sup> A solution was prepared of tropenium bromide (0.177 g., 1.04 mmoles) in methylene chloride (400 ml.) by shaking a weighed excess of the salt with the solvent, then filtering and weighing the undissolved portion. This solution was a bright orange color characteristic of tropenium bromide in this solvent. Boron bromide (0.52 g., 2.08 mmoles) was added dropwise with swirling. As the addition progressed the orange color of the solution lightened and a white precipitate appeared; when addition was complete the solution was colorless and a white, curdy precipitate had formed. The solvent was siphoned from the flask, the precipitate washed with methylene chloride (3 × 50 ml.) and dried *in vacuo* to give 39.0% tropenium bromoborate (0.17 g., 0.40 mmole) as a white powder, m.p. 171-173° dec.; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268 (shoulder), 273.5 (4430), 280  $m\mu$ ; this shows 21.9% tropenium ion; calcd. for  $C_7H_7BBr_4$ : 21.6% tropenium ion.

**Reaction of Triphenylmethane and Boron Bromide in Methylene Chloride.**—Triphenylmethane was obtained as a by-product of the preparation of tropenium bromide.<sup>14</sup> It was recrystallized from methanol, then leached with 70% sulfuric acid on a fritted glass filter until the acid wash was colorless, washed with water, dilute bicarbonate, water again, dried, and dissolved in benzene. The benzene solution was passed through a short alumina column and concentrated *in vacuo*. The white, solid residue was recrystallized from methanol to give triphenylmethane free of triphenylcarbinol, m.p. 92.5° (reported<sup>25</sup> m.p. 92.5°).

Triphenylmethane (1.2712 g., 5.20 mmoles) was dissolved in methylene chloride (15 ml.) to give a colorless solution, and boron bromide (1.30 g., 5.20 mmoles) added. The solution darkened at once to a red-brown color typical of solutions of triphenylmethylcarbonium ion. After the solution had stood for 40 minutes, distilled water (5 ml.) was added; the color of the solution disappeared and a white precipitate formed. The solvents were removed *in vacuo* and the solid residue transferred to a fritted glass funnel and leached with 70% sulfuric acid until no more color was extracted from the solid by the acid. A quantitative spectrum of the yellow sulfuric acid solution<sup>26</sup> showed 6.7%

(25) Aug. Kekule and A. Franchimont, *Ber.*, **5**, 907 (1872).

(26) The visible spectrum of triphenylmethylcarbonium ion in 70% sulfuric acid was determined by dissolving weighed samples of triphenylcarbinol in this solvent. The carbinol used for this purpose was recrystallized from benzene, passed through an alumina column in benzene solvent, and again recrystallized from benzene to give white prisms, m.p. 162°, (reported<sup>27</sup> m.p. 162-162.5°). The values obtained were  $\lambda_{\max}$  405 (37,300), 432  $m\mu$  (38,400). Since this carbinol gave an identical spectrum in 96% sulfuric acid it is assumed that the carbinol is completely converted to the ion in both media, and the values given above were used for quantitative calculations in this work.

triphenylmethylcarbonium ion (0.0838 g., 0.35 mmole). The solid remaining on the filter was washed with water, dilute bicarbonate, water again, dried, and dissolved in benzene. The benzene solution was passed through an alumina column and concentrated *in vacuo* to give 89.4% recovered triphenylmethane (1.1369 g., 4.65 mmoles) as a white powder, m.p. 93°. Total recovery of triphenylmethyl species was 96.0%.

**Reaction of Triphenylmethane with Boron Bromide in Cyclohexane.**—Triphenylmethane (1.3885 g., 5.68 mmoles) was dissolved in cyclohexane (15 ml.) to give a colorless solution, and boron bromide (1.43 g., 5.72 mmoles) added. The solution turned orange at once, then clouded and began to deposit an orange precipitate. The reaction was allowed to stand in a desiccator for four weeks, during which time the amount of precipitate slowly increased. The solvent was then removed with a pipet and transferred to another flask; as the solution contacted the air a heavy yellow precipitate formed in the second flask. The solvent was again removed, and the two portions of yellow, fuming solid treated with water to give white solids. These were combined and dried *in vacuo*, and dissolved in 70% sulfuric acid to give a yellow solution. Quantitative spectral analysis of this solution showed 26.8% triphenylmethylcarbonium ion (0.371 g., 1.53 mmoles).

**Reaction of Triphenylmethyl Bromide with Boron Bromide in Cyclohexane.**—Triphenylmethyl bromide was prepared by the method of Bachmann<sup>28</sup> and was recrystallized from benzene to which a few drops of acetyl bromide had been added; the crystals so obtained were crushed and dried to give a white powder, m.p. 152° (reported<sup>28</sup> 152°).

Triphenylmethyl bromide (1.59 g., 4.92 mmoles) was dissolved in cyclohexane (50 ml.); gentle warming was used to speed solution. The solution was cooled to room temperature and boron bromide (1.22 g., 4.90 mmoles) was added dropwise. An immediate heavy yellow precipitate formed about the drops of boron bromide, trapping boron bromide within the mass of the solid. The precipitated material was agitated with a stirring rod to break up these globules; dry nitrogen was passed over the reaction vessel during this stirring. More precipitate formed as the trapped boron bromide was stirred into the solution. The flask was stored in a desiccator overnight. After this time the reaction appeared to be complete and a quantity of yellow-orange solid remained. This was broken up under the solvent with a stirring rod (nitrogen) to give a yellow-orange micro-crystalline powder, the solvent removed with a pipet, and the powder washed with cyclohexane (4 × 50 ml.) and dried *in vacuo* to give 95.0% triphenylmethyl bromoborate (2.56 g., 4.44 mmoles), m.p. 148–150°. This material is extremely sensitive to atmospheric moisture; it fumes and turns white after a brief exposure; visible spectrum (96% sulfuric acid)<sup>28</sup>:  $\lambda_{\max}$  405, 432  $\mu$  (38,600); this shows 42.6% triphenylmethylcarbonium ion; calcd. for  $C_{19}H_{15}BBr_4$ : 42.4% triphenylmethylcarbonium ion.

A weighed portion of the crystals was hydrolyzed with ice-cold de-ionized water in a sealed system; much fuming was noted and a white solid formed. This was triturated thoroughly with de-ionized water and the combined washings filtered through fritted glass into a volumetric flask, brought to volume, and used for analysis. Boron was determined by the mannitol method<sup>29</sup> after first bringing the solution to pH 7<sup>24</sup> by addition of base. Bromine was determined by the Volhard method. The white residue of triphenylcarbinol was washed on the filter and dried to give a white powder, m.p. 162° (reported<sup>27</sup> 162–162.5°).

*Anal.* Calcd. for  $C_{19}H_{15}BBr_4$ : B, 1.89; Br, 55.71;  $(C_6H_5)_3COH$ , 45.37. Found: B, 1.90; Br, 54.42;  $(C_6H_5)_3COH$ , 45.42.

**Reaction of Triphenylmethyl Bromide with Boron Bromide in Methylene Chloride.**—Triphenylmethyl bromide (2.90 g., 8.98 mmoles) was dissolved in methylene chloride (20 ml.) to give a pale yellow solution, and boron bromide (2.16 g., 8.65 mmoles) added dropwise. With the first drop of boron bromide the solution turned deep red-brown in color. The reaction stood overnight in a desiccator; after this time a small quantity of crystalline material had

been deposited in the flask. The solvent was carefully transferred to a dried flask by pipet and the residue solid dried *in vacuo* to give 9.1% trityl bromoborate as a yellow powder, m.p. 150° (0.45 g., 0.78 mmole). Cyclohexane (10 ml.) was added to the methylene chloride reaction solution with swirling; a mass of small, well-formed yellow-orange needles formed at once. The solvent was removed by pipet and the crystals washed with cyclohexane (4 × 25 ml.) and dried *in vacuo* to give 68.0% triphenylmethyl bromoborate (3.38 g., 5.89 mmoles) as small orange needles, m.p. 150°; total yield was 77.1%.

**Hydride Exchange between Triphenylmethyl Bromoborate and Cycloheptatriene in Methylene Chloride.**—Triphenylmethyl bromide (4.61 g., 14.3 mmoles) was dissolved in methylene chloride to give a very pale yellow solution. Boron bromide (3.38 g., 13.5 mmoles) was added dropwise and the solution became a dark red-orange. Cycloheptatriene (1.43 g., 14.3 mmoles) was added with swirling. A white precipitate formed with the first drop of cycloheptatriene, and when addition was complete a heavy precipitate had settled to the bottom of the flask and the solution was again a light yellow color. The solution was withdrawn with a pipet and the white solid washed with methylene chloride (5 × 50 ml.) and dried *in vacuo* to give 83.9% tropenium bromoborate as a white, microcrystalline powder; ultraviolet spectrum (96% sulfuric acid):  $\lambda_{\max}$  268, 273.5 (4420), 280  $\mu$ .

The methylene chloride washings were combined with the reaction solution, extracted with water, dried over sodium sulfate, and concentrated *in vacuo* to give a quantitative recovery (3.31 g., 13.5 mmoles) of crude triphenylmethane, m.p. 87–88°. Recrystallization from methanol gave white needles of triphenylmethane in 70.5% yield (2.33 g., 9.56 mmoles), m.p. 92–93° (reported<sup>25</sup> 92.5°).

**Discussion.**—On the basis of this work, and in consideration of previous experimental evidence,<sup>7,12,13</sup> there appears to be no doubt of the existence of the bromoborate anion, nor of the ability of boron bromide to complex with bromide ion. The similarity of the infrared spectrum of solid tropenium bromide<sup>21</sup> to that of the perchlorate<sup>2b,30</sup> or to that of tropenium bromide in hydrobromic acid solution<sup>31</sup> shows that tropenium bromide is ionized even in the crystal. Thus when boron bromide is added to tropenium bromide in solution reaction must take place with either the tropenium cation or the bromide anion, since no covalent compound is present. Tropenium ion is not attacked by electrophilic reagents such as hot, concentrated sulfuric acid, and may be recovered unchanged after treatment with 20% fuming sulfuric acid at 100° for one week or with excess bromine in concentrated sulfuric acid at 200° for five days.<sup>2,30</sup> It is not reasonable to believe that boron bromide attacks tropenium ion, and the reaction between tropenium bromide and boron bromide must consist of attack on bromide ion by boron bromide to give a  $BBr_4^-$  entity. The lack of color of solid tropenium bromoborate suggests that no free bromide ion is present, since tropenium bromide and substituted tropenium bromides<sup>2b</sup> are brilliant yellow compounds—presumably due to charge transfer. Whether or not the four bromines in the bromoborate anion are arranged in a regular tetrahedron about the boron atom is a question still to be resolved. Dr. W. G. Sly of these laboratories is initiating an X-ray diffraction study of the compound in an attempt to answer this question.

There appears to be no reason to believe that triphenylmethyl bromoborate does not also possess

(27) Hg. Frey, *Ber.*, **28**, 2517 (1895).

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

(29) H. Schwarz, *Ber.*, **14**, 1520 (1881).

(30) D. L. Pearson, Ph.D. Thesis, Univ. of Washington, 1955; *Dissemination Abstr.*, **15**, 978 (1955).

(31) W. G. Fateley and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957).

a bromoborate anion, but there is greater possibility of an alternative structure than in the tropenium case. As noted above, tropenium bromide is ionized in the crystal; however, pure triphenylmethyl bromide, like the chloride, is a colorless compound which dissolves in non-polar solvents to give colorless, non-conducting solutions in which ionization does not occur.<sup>32</sup> Thus it might be possible to picture triphenylmethyl bromoborate as a complex between boron bromide and covalent triphenylmethyl bromide in which no  $BBr_4^-$  anion was formed. The solubility properties and the brilliant yellow color of triphenylmethyl bromoborate in the solid state and in solution are typical of salts of this cation such as the perchlorate or fluoroborate. However, the most convincing evidence for the existence of the bromoborate anion in triphenylmethyl bromoborate is the hydride exchange reaction with cycloheptatriene in methylene chloride. Triphenylmethyl bromide gives slow and incomplete hydride exchange with cycloheptatriene in solvents such as acetonitrile<sup>15,30</sup> and does not react at all with cycloheptatriene in methylene chloride in which triphenylmethyl halides are not ionized,<sup>15</sup> while in sulfur dioxide reaction is rapid and quantitative.<sup>14</sup> Ionic triphenylmethyl perchlorate and fluoroborate, on the other hand, react rapidly with cycloheptatriene in any solvent in which they are sufficiently soluble. Thus the rapid hydride exchange between triphenylmethyl bromoborate and cycloheptatriene in methylene chloride indicates that a highly ionized triphenylmethylcarbonium ion species is present. The tropenium bromoborate does not arise from dissociation of triphenylmethyl bromoborate into triphenylmethyl bromide and boron bromide followed by reaction of boron bromide with cycloheptatriene. The reaction of boron bromide with cycloheptatriene in methylene chloride at these concentrations is slow, and never consumes more than 50% of available boron bromide, while the reaction of cycloheptatriene with triphenylmethyl bromoborate is essentially instantaneous and proceeds in over 80% yield. Also, no mechanism other than hydride exchange could account for the high yield of triphenylmethane isolated from this reaction.

The ease of formation and apparent stability of carbonium ion bromoborates as contrasted to inorganic analogs<sup>3,6,33</sup> may be due to some stabilizing effect of the large cation, as suggested by Lappert.<sup>12</sup> A similar effect is found in the chloroborates; inorganic chloroborates are usually formed with high temperatures<sup>34</sup> or long reaction times,<sup>13</sup> alkyl chlorides and benzyl chloride do not react with boron chloride, and acetyl chloride forms only a low-melting, unstable compound.<sup>35</sup> However, triphenylmethyl chloride and boron chloride form a bright yellow compound of reasonable stability—melting point greater than 200°—with the correct analysis for the chloroborate.<sup>36</sup>

(32) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 53-56.

(33) E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **12**, 355 (1960).

(34) E. L. Muetterties, *THIS JOURNAL*, **79**, 6563 (1957).

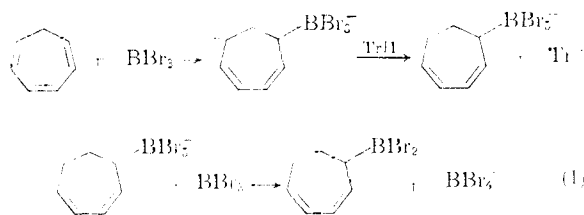
(35) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956).

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

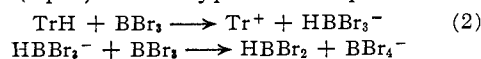
In the absence of specific evidence for special stabilization of the bromoborate anion by carbonium ions, we suggest that the ease of preparation of these salts is at least partially due to the fact that the reactants may be brought together in homogeneous solution and in an environment of low basicity. Muetterties has observed a similar effect in the preparation of alkali metal chloroborates in nitrobenzene solution.<sup>33</sup>

The reaction of boron bromide with cycloheptatriene offers a simple route to tropenium bromide. Tropenium bromide has been prepared by pyrolysis of 1,6-dibromo-2,4-cycloheptadiene in 60% yield,<sup>21,37</sup> by treatment of the isocyanate derived from cycloheptatriene-7-carboxylic acid with hydrogen bromide in 90% yield,<sup>38</sup> and by hydride exchange with trityl bromide in sulfur dioxide in 96% yield.<sup>2</sup> Since the boron bromide reaction does not require the preparation of any starting material and the bromoborate may be converted to the bromide by simple ether trituration or sublimation, the lower yields may be compensated for by the ease of preparation. For preparation of the bromide without isolation of the bromoborate it is not necessary to purify commercial cycloheptatriene with care, nor to rigorously protect boron bromide from the atmosphere. We wish to point out that while this reaction may find use where fairly large quantities of tropenium bromide are required, as in synthetic work, for quantitative conversion of cycloheptatriene to tropenium bromide of extreme purity the hydride exchange technique is still preferred.

The mechanism of the reaction between boron bromide and cycloheptatriene is of considerable interest, but full understanding must depend upon the identification of other products. It is possible that boron bromide adds to cycloheptatriene (eq. 1), followed by hydride abstraction from cycloheptatriene (TrH) by the cycloheptadienyl carbonium ion species so formed and loss of a bromide



anion from the diene product to boron bromide to give the bromoborate anion. An alternative route would be direct hydride abstraction by boron bromide (eq. 2). The hypothetical species  $HBBr_2^-$



could either disproportionate to  $BBr_3$  and  $B_2H_6$  as has been observed for  $HBCl_2$ ,<sup>39</sup> or could react further with cycloheptatriene. Either reaction 1 or 2 as written would convert 50% of available boron bromide to bromoborate ion, in agreement with experiment; however, complete disproportionation

(37) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **79**, 352 (1957).

(38) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021 (1956).

(39) H. C. Brown and P. A. Tierney, *THIS JOURNAL*, **80**, 1552 (1958); *J. Inorg. Nucl. Chem.*, **9**, 51 (1959).

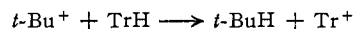
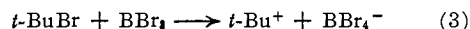
tionation of  $\text{HBr}_2$  would allow conversion of 75% of the boron bromide. Conversion of more than 50% of cycloheptatriene to tropenium ion has been observed, but not to an extent that would rule out path 1. Experiments designed to isolate the boronic acid derived from a possible cycloheptadienylboron dibromide intermediate or  $\text{HBr}_2$  as an etherate by the methods used for  $\text{HBCl}_2$  by Brown and Tierney<sup>39</sup> are being investigated in an attempt to resolve this issue.

Kursanov and Vol'pin<sup>40</sup> have obtained low yields of tropenium ion by treatment of cycloheptatriene with boron fluoride or aluminum chloride, and suggest a hydride transfer mechanism such as 2 for these reactions. However, they report that extensive polymerization lowered yields and made workup difficult. This is in contrast to the clean, rapid reaction of boron bromide with cycloheptatriene and suggests that boron fluoride and aluminum chloride may react primarily by addition 1 accompanied by polymerization while boron bromide reacts to an appreciable extent by hydride abstraction 2. In the reaction of boron bromide with triphenylmethane no additive mech-

(40) D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk. S. S. S. R.*, **113**, 339 (1957); *C. A.*, **51**, 14572f (1957).

anism such as 1 is reasonable, and the fact that the triphenylmethylcarbonium ion is produced is indicative of the ability of boron bromide to abstract hydride from an organic molecule.

When *t*-butyl bromide is present, two other paths are possible: abstraction of bromide from *t*-butyl bromide by boron bromide to give *t*-butylcarbonium ion, followed by hydride transfer from cycloheptatriene to *t*-butylcarbonium ion (eq. 3), or



addition of *t*-butylcarbonium ion (formed as in 3) to cycloheptatriene, followed by hydride transfer to the cycloheptadienyl carbonium ion so formed. Yield data indicate that either or both of these may occur to some extent in neat boron bromide, but are not important in methylene chloride solution.

The preparation and properties of other carbonium ion haloborates are presently under investigation.

**Acknowledgment.**—We wish to thank Dr. Hyp J. Dauben, Jr., for many helpful discussions of this work, and Mr. Ronald Schwartz for technical assistance.

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## Small-Ring Compounds. XXXI. Cyclobutane Derivatives from Adducts of Cyclohexenylacetylene and Fluorochloroethylenes<sup>1</sup>

BY CLAY M. SHARTS<sup>2</sup> AND JOHN D. ROBERTS

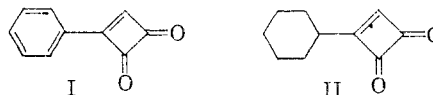
RECEIVED AUGUST 30, 1960

Cycloadditions of 1-ethynylcyclohex-1-ene with trifluorochloroethylene and difluorodichloroethylene gave 1,1,2-trifluoro-2-chloro- (IV) and 1,1-difluoro-2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XI), respectively. Both IV and XI were hydrolyzed by sulfuric acid to the corresponding monoketones, 2-fluoro-2-chloro- and 2,2-dichloro-3-(cyclohex-1-enyl)-cyclobutenones. With iodide and ethoxide ions IV or XI appeared to give  $\text{S}_{\text{N}}2'$  displacement products. Diels-Alder adducts were obtained from IV and maleic anhydride or dicarbethoxyacetylene. The triethylamine-catalyzed rearrangement of XI at 150° gave 1,1-difluoro-2,4-dichloro-3-(cyclohex-1-enyl)-cyclobutene (XXXI), but at 180° an unexpected elimination rearrangement led to 2-fluoro-1,3-dichloro-5,6,7,8-tetrahydronaphthalene (XXXIII).

The synthesis of substituted fluorinated cyclobutanes and cyclobutenes by cycloaddition reactions between fluorinated alkenes and appropriately substituted alkenes and alkynes provides a method of synthesis of useful intermediates that can often be converted to novel non-fluorinated four-membered carbon-ring compounds.<sup>3</sup> Thus several phenylcyclobutenones have been prepared from cycloadducts of phenylacetylene and various fluorochloroethylenes.<sup>4,5</sup>

Of particular interest is the product from hydrolysis of the cycloadduct from trifluorochloro-

ethylene and phenylacetylene: phenylcyclobutadienoquinone (I), a bright, yellow compound rather more stable than would be expected for a substance with its considerably strained ring system.<sup>6,7</sup>



In an effort to evaluate the influence of the phenyl group on the properties of the cyclobutadienoquinone ring in I, we have assayed the preparation of cyclohexylcyclobutadienoquinone (II) by way of the cycloadducts from 1-ethynylcyclohex-1-ene with trifluorochloroethylene and difluorodichloroethylene. The plan was to utilize the cyclohexenyl group to facilitate the addition reaction<sup>3</sup> and the formation of the cyclobutadienoquinone, and sub-

(1) Supported in part by the National Science Foundation.

(2) General Electric Co. Fellow, 1957-1958.

(3) J. D. Roberts and C. M. Sharts in A. C. Cope, "Organic Reactions," in press.

(4) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *J. Am. Chem. Soc.*, **75**, 4765 (1953).

(5) (a) E. F. Jenny and J. D. Roberts, *ibid.*, **78**, 2005 (1956); (b) E. F. Silversmith and J. D. Roberts, *ibid.*, **78**, 4023 (1956), and **80**, 4083 (1958); (c) E. F. Silversmith, Y. Kitahara and J. D. Roberts, *ibid.*, **80**, 4088 (1958); (d) E. F. Silversmith, Y. Kitahara, M. C. Caserio and J. D. Roberts, *ibid.*, **80**, 5840 (1958); (e) S. L. Manatt, Ph.D. Thesis, California Institute of Technology, 1959.

(6) E. J. Smutny and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 3420 (1955).

(7) E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).