

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

The Configurational Stability of *cis*- and *trans*-2-Methylcyclopropyllithium and Some Observations on the Stereochemistry of their Reactions with Bromine and Carbon Dioxide

BY DOUGLAS E. APPLEQUIST AND ALAN H. PETERSON

RECEIVED JULY 14, 1960

Exchange of *cis*- or *trans*-2-methylcyclopropyl bromide with isopropyllithium in media varying from pure pentane to 66% ether-34% pentane gives lithium reagents which have been shown by brominolysis studies not to undergo *cis-trans* isomerization at rates comparable with destruction of the lithium reagents by side reactions. The lithium reagents react stereospecifically with carbon dioxide to give carboxylic acids, but react with bromine to give bromides with only partial retention of configuration, the amount depending in part upon the solvent. The mechanism of the brominolysis is discussed.

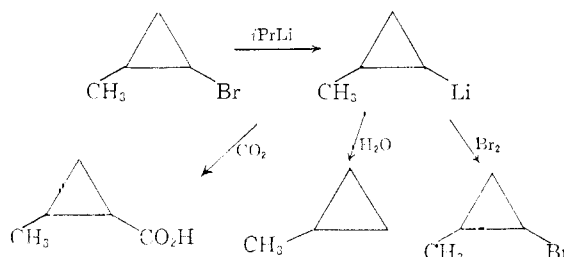
Introduction

In a previous publication¹ it was shown that a cyclopropyl radical, as generated by the brominative decarboxylation of silver 2-methylcyclopropanecarboxylate in carbon tetrachloride at room temperature, is incapable of maintaining a pyramidal configuration. This result was taken to mean that if a free radical is normally pyramidal, then a change of hybridization of the orbital bearing the odd electron from sp^3 to sp^2 is not sufficient to introduce an appreciable barrier to inversion.

The above experiment is in contrast with the effects of hybridization change on configurational stabilities of carbanions: It is known from many examples² that vinyl-type lithium reagents hold their configurations under conditions where saturated alkylolithiums rapidly suffer racemization or epimerization at the carbon bearing the metal, the contrast being especially marked in media containing ether.²ⁱ If one makes the reasonable assumption^{2h} that these isomerizations proceed by reversible dissociations to carbanions followed by slow inversions through planar (from alkylolithiums) or linear (from vinylolithiums) transition states, then the results may be rationalized in terms of the greater energy difference associated with movement of the unshared electron pair from an sp^2 orbital to a p orbital (required in the postulated transition state) than is required to change an sp^3 electron pair to p . This interpretation of the behavior of lithium reagents is supported by the recent report of Miller and Lee³ that methoxide-catalyzed proton exchange of *cis*-1,2-dibromoethene is much faster than *cis* to *trans* isomerization.

Before the configurational instability of the cyclopropyl radical can be considered a characteristic of a free radical formed at an originally sp^2 carbon (and thus to be in contrast with the behavior of anions), it is desirable to demonstrate (1) that vinyl radicals also do not retain geometrical con-

figuration and (2) that cyclopropyl anions exhibit the behavior of vinyl anions which we have above attributed (perhaps mistakenly) to a hybridization effect. The present research is a test of the latter point. The *cis*- and *trans*-2-methylcyclopropyllithiums have been generated by exchange of the previously known bromides¹ with isopropyllithium under various conditions of solvent and temperature and the resulting solutions have been analyzed by brominolysis and carbonation.



There are already some data in the literature relevant to the configurational stability of the cyclopropyl carbanion. Walborsky and Hornyak⁴ found that the anion derived by reaction of 2,2-diphenylcyclopropyl cyanide with base is incapable of maintaining optical activity. The cyano group in this case would be expected to stabilize the planar form by resonance, so the result does not reveal configurational instability of a simple cyclopropyl anion. Cope, Trumbull and Trumbull,⁵ on the other hand, have found stereospecific base-catalyzed rearrangements of *cis*- and *trans*-stilbene oxides to desoxybenzoin and diphenylacetaldehyde, respectively. The suggested mechanism was a proton abstraction followed by a proton or phenyl migration to the carbanionic center. The intermediacy of carbanions was not established, but if correct the carbanions must maintain pyramidal configurations in order to account for stereospecificity, in spite of the resonance stabilization available to the planar form in this case. Walborsky and Impastato⁶ have recently reported that the exchange reaction of 1-bromo-1-methyl-2,2-diphenylcyclopropane with butyllithium in 50% ether-25% benzene-25% petroleum ether at 6° followed by methanolysis gave 1-methyl-2,2-diphenylcyclopropane with over-all 60% retention

(4) H. M. Walborsky and F. M. Hornyak, *ibid.*, **77**, 6026 (1955).(5) A. C. Cope, P. A. Trumbull and E. R. Trumbull, *ibid.*, **80**, 2844 (1958).(6) H. M. Walborsky and F. J. Impastato, *ibid.*, **81**, 5835 (1959).

(6a) H. M. Walborsky, private communication.

(1) D. E. Applequist and A. H. Peterson, *J. Am. Chem. Soc.*, **82**, 2372 (1960).(2) (a) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (b) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958); (c) A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954); (d) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957); (e) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951); (f) D. Y. Curtin, H. W. Johnson and E. G. Steiner, *ibid.*, **77**, 4566 (1955); (g) A. N. Nesmeyanov, A. E. Borisov and N. V. Novikova, *Doklady Akad. Nauk, S.S.S.R.*, **119**, 504, 712 (1958); (h) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950); (i) D. Y. Curtin and W. J. Koehl, Jr., *Chemistry & Industry*, 262 (1960).(3) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

of configuration. A certain amount of configurational stability of the lithium reagent is a probable explanation of this result, although it was not known how much of the lithium reagent, if any, was still present when the methanol was added after the 35 min. reaction time. Since then, it has been found that carbonation of the same lithium reagent gives high yields of acid with clean retention of configuration, in agreement with the experiments reported here.^{6a} Finally, it has been shown that N-alkylethylenimines, which are isoelectronic with cyclopropyl carbanions, have unusually high energy barriers for inversion at nitrogen.⁷

Experimental⁸

Isopropylolithium.—Solutions of isopropylolithium in pentane were prepared by a modification of the method of Gilman.⁹ In a typical run, 1.4 g. (0.20 g. atom) of lithium wire and 7.85 g. (0.10 mole) of 2-chloropropane was heated under reflux in 120 ml. of dry, olefin-free pentane for 8 hr. The cooled reaction mixture was filtered to give a colorless solution of isopropylolithium. Such solutions were found to be stable for several days when stored at -20° .

The approximate concentration of isopropylolithium was determined by a modification of Gilman's procedure¹⁰ for the determination of lithium reagents in ether. The total base in a 5.00-ml. aliquot of the isopropylolithium solution was determined by titration to the phenolphthalein end-point with 0.100 *M* hydrochloric acid. The base remaining in a 10.00-ml. aliquot after coupling of the isopropylolithium with allyl bromide was similarly determined. The difference in the molarity of the base found in the two titrations was considered to be the concentration of isopropylolithium.

In a typical determination, 10.00 ml. of isopropylolithium solution (0.351 *M* in total base) was pipetted into a solution of 2.33 g. (0.019 mole) of allyl bromide (Eastman Kodak Co. white label) and 34 g. of dry ether in a 125 ml. erlenmeyer flask flushed with dry nitrogen. The reaction mixture became opalescent immediately. The solution was swirled intermittently for 12 minutes at room temperature, approximately 20 ml. of water was added, and the mixture was titrated to the phenolphthalein end-point with 0.100 *M* hydrochloric acid (9.80 ml.). The molarity of the isopropylolithium solution found by this procedure was 0.253 (= 0.351 - 0.098).

Reaction of Isopropylolithium with Bromine.—With the aid of a capillary dropper, a solution of 0.0835 g. (0.000994 mole) of cyclohexane in 0.50 ml. of pentane was added to 5.00 ml. of 0.299 *M* (0.368 - 0.069) isopropylolithium solution in the apparatus used for exchange reactions (see below). The solutions were mixed thoroughly and two 0.375-ml. samples were dropped into solutions of 10 drops of bromine in 0.30 ml. of pentane cooled in a Dry Ice-acetone-bath under a flow of dry nitrogen. Excess bromine was destroyed by the addition of 10 drops of cyclohexane to each of the cold solutions.

To the remaining solution in the reaction vessel was added 0.283 ml. of anhydrous ether to obtain the solvent mixture used by Letsinger^{2b} (about 6% ether by volume). Two samples were taken and treated as before.

To the remaining solution was added 7.80 ml. of ether to obtain a solution 66% ether by volume. Two samples were taken and treated as before. The first sample was taken as soon as the solution was well mixed and the second was taken a few minutes later.

(7) (a) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956); (b) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1958); (c) A. Loewenstein, J. F. Neumer and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3599 (1960).

(8) Infrared spectra were measured on a Perkin-Elmer model 21B spectrophotometer with sodium chloride optics. Gas chromatography was done with a Perkin-Elmer model 154B vapor fractometer, using helium as the carrier gas.

(9) (a) H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941); (b) H. Gilman, W. Langham and F. W. Moore, *ibid.*, **62**, 2327 (1940).

(10) R. G. Jones and H. Gilman, in R. Adams, "Organic Reactions," Vol. 6, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 353.

The samples were analyzed by vapor phase chromatography on a didecyl phthalate column (55° , 84 ml. of helium per minute, 0.020-ml. sample). The yields of isopropyl bromide obtained in the three solvents (in the order of sample removal) were 91 and 85% in pentane, 54 and 55% in 6% ether, and 37 and 22% in 66% ether. Cyclohexane served as an internal standard, and corrections were made for the different thermal conductivities of cyclohexane and isopropyl bromide and for the small amount of cyclohexane present in commercial cyclohexane. The analysis for isopropyl bromide was shown to give an average error of about 3% when sample concentration and recorder sensitivity were varied over the ranges typically employed. Peak areas were measured with a planimeter.

Exchange Reactions.—All parts of the apparatus used for the exchange reactions of isopropylolithium with 2-methylcyclopropyl bromide were dried at 110° , assembled hot, and cooled while a stream of dry nitrogen (Matheson, prepurified) passed through. A 10-ml. distillation flask with side arm was used as the reaction vessel. Samples were removed through a capillary tube (0.5-mm. inside diameter) secured in the neck of the reaction flask by a rubber stopper and bent in the shape of an inverted letter J. The longer arm (30 cm.) was inserted nearly to the bottom of the reaction flask and the shorter arm (9 cm.) was enclosed in a nitrogen-flushed glass jacket, open at the bottom so that a 4-ml. sample vial could be inserted. A small positive pressure of nitrogen was maintained in the reaction flask and was increased to force the solution in the reaction vessel to flow through the capillary tube to the sample vial. The pressure was adjusted so that the number of drops (40 drops per ml.) falling into the sample vial could be counted. When the pressure was released, the solution in the capillary tube drained back into the reaction vessel. Under conditions where the exchange reaction occurred rapidly, a larger (5 cm.) diameter jacket was used around the capillary outlet so that two sample vials could be moved back and forth to collect alternate drops.

In a typical run, a solution of 0.0898 g. (6.65×10^{-4} mole) of *cis*-2-methylcyclopropyl bromide and 0.0849 g. (1.01×10^{-3} mole) of cyclohexane in 0.50 ml. of pentane was added to 5.00 ml. of 0.335 *M* (0.394 - 0.059) isopropylolithium in pentane at 26° . Samples of the reaction mixture (0.375 ml., 15 drops) were forced through the capillary tube by nitrogen pressure and dropped into bromine solutions (10 small drops of bromine in 0.30 ml. of pentane, cooled in a Dry Ice-acetone-bath under a flow of dry nitrogen) at various times. Excess bromine was destroyed with 7 drops of cyclohexane. Samples of 0.25 ml. (10 drops) of the reaction mixture were similarly dropped into 0.075 ml. of water. The samples were analyzed on a didecyl phthalate column (55° , 82 ml. of helium per minute, 0.020-ml. samples). The areas of the isopropyl bromide (6.6 min.), cyclohexane (8.8 min.), *trans*-2-methylcyclopropyl bromide (16.9 min.) and *cis*-2-methylcyclopropyl bromide (22.9 min.) peaks were measured with a Keuffel and Esser model 4236 planimeter. The number of moles of each bromide was calculated from the equation $M_i = (A_i T_i M_s) / A_s$, where A_i and A_s are the areas of the bromide and cyclohexane peaks, M_i and M_s are the number of moles of bromide and cyclohexane, and T_i is the thermal factor taken as 1.068 for isopropyl bromide and 1.21 for *cis*- and *trans*-2-methylcyclopropyl bromide. A correction for cyclohexane present in commercial cyclohexane was applied. The difference between the number of moles of the cyclopropyl bromides found after bromine treatment and the number found after water treatment was taken to be the total amount of *cis*- and *trans*-2-methylcyclopropylolithiums. The validity of the assumption that the cyclopropylolithium reagents react quantitatively with bromine to give bromides is uncertain, but the qualitative correctness is supported by the high yields of bromides obtained in some cases after short reaction times (Table I). Deviation of these yields from 100% represent maximum deviation of the brominolysis yields from quantitative, of course.

Carbonation of 2-Methylcyclopropylolithium from *cis*-2-Methylcyclopropyl Bromide.—A solution of 0.1113 g. (8.24×10^{-4} mole) of *cis*-2-methylcyclopropyl bromide, 0.0950 g. (1.13×10^{-3} mole) of cyclohexane, 0.33 ml. of ether and 0.50 ml. of pentane was added to 5.00 ml. of 0.220 *M* (0.269 - 0.049) isopropylolithium solution in pentane at 0° . Samples were dropped into bromine and water and analyzed as before. It was found that a 73% yield of cyclo-

TABLE I
COMPOSITION AND MAXIMUM YIELDS OF 2-METHYLCYCLO-
PROPYL BROMIDES FROM BROMINOLYSIS OF LITHIUM RE-
AGENTS OBTAINED BY EXCHANGE

Run	Ex- change condi- tions ^a	Starting bromide	<i>cis</i> product, %	Max. yield of bro- mides, %	Period of observn., min.
1	A	<i>cis</i>	52.4 ± 2.1 ^b	66	2-100
2	A	<i>trans</i>	19.6 ± 0.7	88	3-200
3	B	<i>cis</i>	82.5 ± 5.7	43	15-680 ^c
4	B	<i>trans</i>	20.0 ± 1.5	62	15-75
5	C	<i>cis</i>	48.9 ± 1.8	31	3-43
6	C	<i>trans</i>	26.0 ± 1.1	30	3-70 ^c
7	D	<i>cis</i>	93 ± 3	64	60-600
8	D	<i>trans</i>	4.4 ± 0.6	71	120-650

^a A refers to exchanges in 6% ether-94% pentane at 0°; B is the same medium at -70°. C is 66% ether-34% pentane at 0°; D is pure pentane at room temperatures, 26-32°. ^b The errors shown are average deviations from the mean of 3-6 measurements made during the time period shown in the last column. ^c These runs were continued until no significant yields of bromides could be obtained on brominolysis.

propyllithiums was obtained (along with 17% of unreacted *cis*-bromide) and that the bromides formed from the lithium reagents showed a *trans/cis* ratio of 0.63 ± 0.03.

The remainder of the reaction mixture was dropped into excess crushed Dry Ice. The solvent was removed on a steam-bath and the residue was dissolved in 2 ml. of dilute sulfuric acid. This aqueous solution was extracted 4 times with 1.5-2.0-ml. portions of carbon disulfide. The carbon disulfide solution was dried over anhydrous magnesium sulfate and reduced in volume on a steam-bath to a volume of about 1 ml. Vapor phase chromatography of this material on a didecyl phthalate column (170°, 52 ml. of helium per minute, 0.10 ml. samples) yielded 8 mg. (10%) of *cis*-2-methylcyclopropanecarboxylic acid (8.0 minutes). The stereoisomeric acids are not separated under these conditions. The infrared spectrum (carbon disulfide) was identical to that of pure *cis*-2-methylcyclopropanecarboxylic acid.¹ The estimated maximum contamination by *trans*-2-methylcyclopropanecarboxylic acid was 5%.

Carbonation of 2-Methylcyclopropyllithium from *trans*-2-Methylcyclopropyl Bromide.—A solution of 0.2083 g. (1.544×10^{-3} mole) of *trans*-2-methylcyclopropyl bromide, 0.0911 g. (1.085×10^{-3} mole) of cyclohexane, 0.625 ml. of ether and 0.50 ml. of pentane was added to 10.00 ml. of 0.534 *M* (0.590 - 0.056) isopropyllithium solution at 0°. Samples were dropped into bromine solution and water and analyzed as before. The yield of cyclopropyllithiums was 87% (no unreacted *trans*-bromide), and the *trans/cis* ratio of the brominolysis product was 4.95 ± 0.17. The carbonation was carried out in the same manner as used above for the *cis*-lithium reagent to give a 15% yield of acid whose infrared spectrum was indistinguishable from that of pure *trans*-2-methylcyclopropanecarboxylic acid.¹

Results and Discussion

At the outset of this research, brominolysis appeared to be the most attractive analytical method for a mixture of *cis*- and *trans*-2-methylcyclopropyllithiums, because the bromide mixture is easily analyzed by vapor chromatography and because it appeared likely that the brominolysis would be a stereospecific electrophilic substitution. It was furthermore expected that a combination of brominolysis and hydrolysis would provide additional checks on the exchange process by showing the amount of isopropyl bromide formed by exchange and the amount of isopropyllithium remaining unreacted at any given time, since isopropyl bromide can be determined simultaneously with the cyclopropyl bromides by vapor chroma-

tography. Only part of these expectations were realized. No useful information was obtained by isopropyl bromide analysis, because the reaction of isopropyllithium with bromine does not give a high yield of isopropyl bromide (see Experimental), and because isopropyl bromide is consumed by side reactions under the exchange conditions.¹¹ On the other hand, analysis of the mixture of *cis*- and *trans*-bromides obtained by brominolysis (corrected for unreacted starting bromide as determined by hydrolysis) proved very instructive. It was found in every case that a mixture of the two isomers was obtained, the composition of which varied somewhat erratically with the exchange solvent, the temperature of exchange and the starting isomer used (see Table I), but that the composition of the mixture showed no significant variation with time elapsed from the beginning of the exchange reaction, despite the fact that very different mixtures were obtained from starting *cis* and *trans* isomers. (The exchange reactions were complete within a few minutes in ether-containing media at 0°. Reactions in pentane and those run at -70° required several hours for completion. Completion was judged as having been reached when either the starting bromide or the isopropyllithium had been consumed, by exchange or otherwise.) The inescapable conclusion is that the *cis*- and *trans*-lithium reagents do not interconvert at a significant rate under any of the conditions studied (Table I, footnote *a*).

The lack of over-all stereospecificity in the exchange-brominolysis sequence must be attributed to either a non-stereospecific exchange reaction or a non-stereospecific brominolysis reaction or both. This question was settled by the carbonation experiments. Since the exchange-carbonation sequence gave an over-all complete retention of configuration (in 6% ether-94% pentane) from either *cis*- or *trans*-bromide,¹² it must be concluded that the brominolysis reaction is non-stereospecific and the exchange reaction is stereospecific.¹³

It is interesting to speculate on the reason for the non-stereospecificity of the brominolysis. While it is possible that the reaction is a mixture of concerted displacements, one with retention and one with inversion, this seems unlikely in view of the lack of non-stereospecific concerted displacements elsewhere in organic chemistry. Rather, it seems far more likely that a cation, radical or anion is intermediate in part or all of the reaction. Of these possibilities, the anion seems least probable in view of the above recorded failure to observe interconversion of the *cis*- and *trans*-lithium reagents (assuming that the dissociation of the cyclopropyllithiums to ions should be at

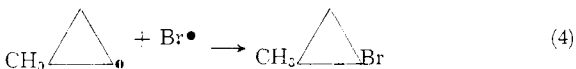
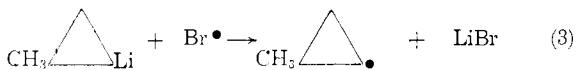
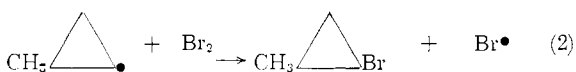
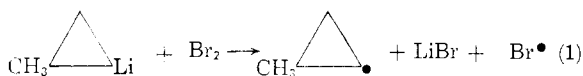
(11) Exact results of these analyses are to be found in the Ph.D. Thesis of A. H. Peterson, University of Illinois, 1960, from which thesis this paper has been abstracted.

(12) A preliminary report of this result appeared in ref. 1, footnote 15.

(13) The experiments reported here do not distinguish between two inversions or two retentions in the exchange-carbonation sequence, though the latter is certainly the more probable on the basis of existing analogy.³ Since the assignments of configuration of the bromides and acids are not completely certain,¹ the possibility even exists that one reaction of the exchange-carbonation sequence occurs with inversion and the other with retention.

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

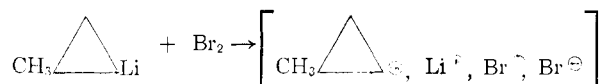
The possibility of a free cyclopropyl radical intermediate is more easily envisioned, and finds analogy in the recently discovered free-radical brominolysis of organomercurials.¹⁴ A free-radical



process might be a chain reaction, as shown in reactions 1-4, in which case a competitive stereospecific reaction (possibly S_E2) 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.¹⁵ 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.¹⁶ 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_Ni reaction rather than a "free carbonium ion" reaction. Because S_Ni reactions appear most often to be carbonium ion-pair reactions,¹⁷ we feel that his result is suggestive of a slow ring opening of a cyclopropyl cation, whether the reaction be S_Ni 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 Bromoborates¹

BY KENNETH M. HARMON AND ANN B. HARMON

RECEIVED JUNE 21, 1960

Reaction of boron bromide with cycloheptatriene either neat or in CH₂Cl₂ gives good yields of tropenium (cycloheptatrienylium) ion. The initial product is tropenium bromoborate, C₇H₇BBr₄; composition confirmed by analysis and spectra. Properties (high m.p., soluble in polar, insol. in non-polar solvents), reactions (converted to tropenium bromide (TrBr) by ether trituration or sublimation), and direct synthesis from TrBr and BBr₃ in CH₂Cl₂ indicate a salt of Tr⁺ and BBr₄⁻. Reaction consumes 50% of available BBr₃; *t*-BuBr raises yield of neat reaction but has no effect in CH₂Cl₂. Alternative reaction paths are discussed. Reaction of (C₆H₅)₃CH with BBr₃ in cyclohexane or CH₂Cl₂ gives 6-26% (C₆H₅)₃C⁺ by spectra; BBr₃ and (C₆H₅)₃CBr in these solvents give 80-90% yields of triphenylmethyl bromoborate, C₁₉H₁₅BBr₄, 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 reported² 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, C₇H₇⁺BBr₄⁻, 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,^{3,4}

(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.