ether to the residue from the distillation precipitated 1.73 g. (7.17 mmoles) of dibenzoylhydroxylamine.

Extraction of the filtrate with 5% hydrochloric acid gave 1.40 g. (11.5 mmole) of benzamide. Extraction with saturated sodium bicarbonate gave 1.09 g. (9.0 mmoles) of benzoic acid and 0.80 g. (3.32 mmoles) of dibenzoylhydroxylamine. They were separated by dissolving benzoic acid in hot water and filtering. Both were identified by mixed melting points and infrared spectra. Finally the extracted ether solution was dried over sodium sulfate and evaporated. A residue of 2.80 g. (11.7 mmoles) of hexachloroethane was identified. Hexachloroethane was immediately suspected because it sublimed readily into colorless rhombic crystals. The m.p. and mixed m.p. of sublimed material in a sealed tube was 185–187°.

Kinetics of Lossen Rearrangement.—Solutions of approximately 2.0×10^{-3} *M* hydroxylamine in toluene (or benzene) were prepared in a 200-ml. three-neck round-bottom flask to which were attached a thermometer, a reflux condenser and a sampling device with a capacity of 5.55 ml. The system was flushed with nitrogen and a Drierite drying tube was attached to the condenser. As soon as the solution started to reflux (heating mantle), a sample was taken. Subsequent samples were taken at known time intervals. The refluxing temperature was controlled to ±0.2°.

The samples or aliquots were quickly poured into 250-ml. iodine flasks which contained 1.0-ml. aliquots of 2.2×10^{-3} mole/l. aniline in toluene stock solution. To each flask 35 ml. of toluene was immediately added and with occasional shaking allowed to stand for more than 15 minutes. After five drops of methyl violet (0.2 g. of methyl violet in 100 ml. of chlorobenzene) was added, the excess aniline was titrated, with magnetic stirring, to a blue endpoint with standard 0.1 *N* perchloric acid in glacial acetic acid.[25] A typical rate curve, obtained by plotting the difference between the acid used in titration and that calculated as required for complete reaction, appears in Fig. 1.

Polymerization experiments were carried out in 5-ml. sealed degassed ampoules, using aliquots of standard solution of initiator in monomer, or, where the initiator showed a low room temperature solubility, by pipetting a standard solution of initiator in acetone into the ampule, evaporating the acetone, and adding a measured amount of monomer. In general, reactions were followed by opening the ampoules and determining the change in index of refraction, 1% polymerization corresponding to 9.4×10^{-4} and 5.7×10^{-4} unit, respectively, for methacrylate and styrene. The value for methacrylate is that of Walling and Briggs[23]; that for styrene was determined from a series of solutions of commercial polystyrene in monomer. The actual physical presence of polymer was demonstrated in many cases by adding some of the reacted mixture to methanol.

The copolymerization experiment (Table IV) was carried out on a larger sample containing 1:1 styrene-methyl methacrylate by volume. After 3 hours, the product was worked up essentially as described by Lewis and Mayo.[26] Analysis of the polymer showed C, 75.3; H, 7.67. The carbon analysis corresponds to 57 wt. % styrene, 43% methacrylate.

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(25) J. S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents," the G. Frederick Smith Chemical Co., Columbus, Ohio, 1952, p. 9.

(26) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Preparation and Characterization of Salts Which Contain the $B_{10}H_{13}$ Anion

BY M. FREDERICK HAWTHORNE, ANTHONY R. PITOCHELLI. R. DONALD STRAHM AND JOHN J. MILLER

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The $B_{10}H_{13}$ anion has been characterized by spectrophotometric means. Absorption maxima arise at two wave lengths, 267 and 335 mμ. Salts which contain this anion and alkali metal, tetraalkylammonium, alkyl-triphenylphosphonium, diethylammonium or triethylammonium cations have been prepared and their interconversion reactions examined.

The acidic behavior of decaborane in aqueous solution was recently recognized by Guter and Schaeffer[1] and ascribed to the operation of two distinct processes: direct ionization of decaborane as in (1) and the formation of an ion–dipole decaborane hydrate which is a strong acid(2).

$$B_{10}H_{14} + H_2O \rightleftarrows B_{10}H_{13}^{\ominus} + H_3O^{\oplus} \qquad (1)$$

$$B_{10}H_{14} + H_2O \rightleftarrows B_{10}\overset{\ominus}{H}_{14}\overset{\oplus}{O}H_2 \qquad (2)$$

$$B_{10}\overset{\ominus}{H}_{14}\overset{\oplus}{O}H_2 + H_2O \rightleftarrows B_{10}\overset{\ominus}{H}_{14}OH + H_3O^{\oplus}$$

Rationalization for the existence of the $B_{10}H_{13}$ anion may be found in the topological arguments of Lipscomb.[2]

Most recently Schaeffer and co-workers[3] have prepared the $B_{10}H_{13}$ anion in aqueous dioxane and aqueous acetonitrile by treatment of decaborane with sodium hydroxide and morpholine, respectively. These authors report two absorption maxima in the ultraviolet region which are characteristic of the $B_{10}H_{13}$ anion: 265 and 330 mμ. These results are in substantial agreement with our own. In addition to the $B_{10}H_{13}$ anion, Schaeffer, *et al.*,[3] have identified, by spectrophotometric means, the anion $B_{10}H_{15}O$ produced by the removal of a proton from the ion-dipole hydrate of decaborane as in (2) above. Under special circumstances we have also observed this species at 249 mμ.

Results and Discussion

Tetraalkylammonium Salts.—The addition of a diglyme solution of decaborane to an aqueous solution of tetramethylammonium hydroxide results in the immediate precipitation of a bright yellow, water-insoluble solid in essentially quantitative yield. Extension of this reaction to other tetraalkylammonium hydroxides gave similar insoluble materials whose elemental analyses (see Experimental) were in agreement with the following formulation where R = alkyl.

$$B_{10}H_{14} + R_4\overset{\oplus}{N}\overset{\ominus}{O}H \longrightarrow R_4\overset{\oplus}{N}B_{10}\overset{\ominus}{H}_{13} + H_2O$$

The ultraviolet absorption spectra of freshly prepared solutions of these salts in dry acetonitrile

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(1) G. A. Guter and G. W. Schaeffer, THIS JOURNAL, **78**, 3546 (1956); Abstracts of Papers, 131st Meeting, Am. Chem. Soc., Miami, Fla., p. 3R, 1957.

(2) W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958), suggests the possible removal of a bridge proton to produce a two center B–B bond. Some evidence for this is to be found in deuterium exchange studies of M. F. Hawthorne and John J. Miller, THIS JOURNAL, **80**, 754 (1958).

(3) G. W. Schaeffer, J. J. Burns, T. J. Klingen, L. A. Martincheck and R. W. Rozett, Abstracts of Papers, 135th Meeting, Am. Chem. Soc., Boston, Mass., 1959 p. 44M.

exhibited two absorption maxima: 267 mμ (ε 2,500) and 335 mμ (ε 1,730). Treatment of an ethereal slurry of these salts with aqueous hydrochloric acid resulted in the recovery of decaborane in low yields (20–30%). The solid salts are slowly oxidized in the air; more rapid air oxidation takes place in dilute solution.

Two additional procedures have been employed to prepare the tetramethylammonium salt. The first of these which is formally similar to that described above, involved the neutralization of decaborane with sodium hydroxide in aqueous ethanol followed by the addition of an aqueous solution of tetramethylammonium chloride. The insoluble tetramethylammonium salt immediately precipitated and was shown by its infrared spectrum to be identical with that prepared above.

$$B_{10}H_{14} + OH^{\ominus} \longrightarrow B_{10}H_{13}^{\ominus} + H_2O$$

$$B_{10}H_{12}^{\ominus} + (CH_3)_4\overset{\oplus}{N} \longrightarrow (CH_3)_4\overset{\oplus}{N}B_{10}H_{13}^{\ominus}\downarrow$$

The second method involved the conversion of tetramethylammonium chloride to the corresponding ilyde by reaction with phenyllithium.[4] Treatment of decaborane in diethyl ether solution with the ilyde produced the tetramethylammonium salt.

$$(CH_3)_4\overset{\oplus}{N} + C_6H_5Li \longrightarrow (CH_3)_3\overset{\oplus}{N}\overset{\ominus}{CH_2} + \overset{\oplus}{Li} + C_6H_6$$

$$(CH_3)_3\overset{\oplus}{N}\overset{\ominus}{CH_2} + B_{10}H_{14} \longrightarrow (CH_3)_4\overset{\oplus}{N}B_{10}\overset{\ominus}{H_{13}}$$

That the product was identical with that obtained by the methods described above was shown by infrared and ultraviolet absorption spectra.

In sharp contrast to the above results, it was found that the slow addition of aqueous tetramethylammonium hydroxide to a diglyme solution of decaborane produced a white precipitate in nearly quantitative yield. The ultraviolet spectrum of this material was not reproducible from run to run; the simple absorption maxima obtained varied from 249 mμ in one case to 275 mμ in another. These maxima may be assigned to the $B_{10}H_{15}O$ anion and an unidentified hydrolysis product, respectively.[3] The infrared spectra obtained from various samples of this product were similar to that of the tetramethylammonium salt of decaborane except that new bands were sometimes present in the O–H stretching region and always in the B–O region near 7μ. These white materials were unstable in the air and were often pyrophoric when dry. Elemental analyses were not conclusive. Treatment of decaborane with other quaternary ammonium hydroxides produced either the yellow or the white salt depending on the order of addition.

The dependence of product character upon the mode of addition of reagents is worthy of further consideration. In the case of the addition of the dry diglyme solution of decarobane to the aqueous quaternary ammonium hydroxide, reaction 1 occurs rapidly and, due to salt precipitation, irreversibly. On the other hand, the slow addition of aqueous quaternary ammonium hydroxide to the decaborane solution allows the decaborane solution to collect water. Reaction 2 and related hydrolysis reactions then become dominant and salts derived from these hydrolysis intermediates precipitate. This hypothesis was checked independently by the ultraviolet absorption spectra of the solutions produced by the addition of a twofold excess of aqueous tetramethylammonium hydroxide to aliquots of a solution of decaborane in 90% diglyme–10% water which had aged for various periods of time. Table I presents these data.

TABLE I

ULTRAVIOLET SPECTRA OF 5.4 × 10^{-4} M $B_{10}H_{14}$ SOLUTION IN 90% DIGLYME-10% WATER QUENCHED WITH TETRAMETHYLAMMONIUM HYDROXIDE, 25°C.

Time of aging, min.	Optical density, λ_{max} 335 mμ	Optical density, λ_{max} 249 mμ
Sample aged, then quenched		
6.6[a]	0.127	1.328
9.1	.067	1.530
12.5	.015	1.558
16.1	Nil	1.600
30.3	...	1.583
84.6	...	1.348
Sample quenched, then aged		
6.6[a]	0.127	1.328
27.0	.093	1.213
43.0	.083	1.154
50.1	.074	1.110
98.6	.043	0.912
156.5	.020	0.726

[a] Examination of this solution after 1,330 min. at 25° showed no absorption near 249 mμ but a single stable maximum at 275 mμ, O.D. 0.750, which remained constant for at least an additional 3,300 min.

Two anions are produced by neutralization of decaborane in aqueous diglyme. That two types of quaternary ammonium salts were isolated is, therefore, reasonable. Relatively large amounts of $B_{10}H_{13}$ anion (λ_{max} 335 mμ) are obtained when freshly prepared solutions of decaborane are neutralized, while the species (λ_{max} 249 mμ) derived from the ion–dipole reaction (2)[3] is produced almost exclusively after aging. The data above demonstrates that hydration of the $B_{10}H_{13}$ anion is less facile than hydration of decaborane itself. Further evidence that the production of $B_{10}H_{13}$ anion by bases is more rapid than hydration of decaborane is also provided. An intermediate of high stability (λ_{max} 275 mμ) is formed by aging the above neutralized samples.

Alkyl-triphenylphosphonium Salts.—Treatment of decaborane in diethyl ether solution with triphenylphosphine methylene[5] results in the immediate deposition of a bright yellow oil which crystallizes on standing. Recrystallization from methylene chloride–pentane produced nicely formed crystals, the ultraviolet spectrum of which displayed an absorption maximum at 338 mμ (ε 1,600) in acetonitrile solution. The shorter wave length band also characteristic of the $B_{10}H_{13}$ anion was obscured by the absorption of the methyltriphenylphosphonium ion. The salt was insoluble in water. Elemental analyses were in agreement[5] with the proposed structure. Treatment of decaborane with triphenylphosphine phenylmethylene $(C_6H_5)_3\overset{+}{P}\overset{-}{C}H$-

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(4) G. Wittig and M. Rieber, *Ann.*, **562**, 177 (1949).

(5) M. F. Hawthorne, THIS JOURNAL, **80**, 3480 (1958).

$$(C_6H_5)_3\overset{\oplus}{P}CH_3 \xrightarrow{C_6H_5Li} (C_6H_5)_3\overset{\oplus}{P}\overset{\ominus}{C}H_2 \xrightarrow{B_{10}H_{14}}$$
$$(C_6H_5)_3\overset{\oplus}{P}C\overset{\ominus}{H}_3B_{10}H_{13}$$

(C_6H_5) under identical conditions produced another yellow salt which absorbed at 338 mμ.

The sodium salt of decaborane was produced in aqueous alcoholic solution and treated with an aqueous solution of methyltriphenylphosphonium chloride. The methyltriphenylphosphonium salt precipitated immediately and was removed by extraction with methylene chloride. Infrared spectra proved it to be identical with the material described above. A similar reaction conducted by the addition of a methylene chloride solution of decaborane to an aqueous solution of methyltriphenylphosphonium hydroxide gave an identical product.

Amine Salts.—The reaction of excess decaborane with diethylamine in diethyl ether solution results in the formation of a light yellow crystalline solid. Elemental analysis of this material is in agreement with the formulation $(C_2H_5)_2NH_2B_{10}H_{13}$, and its ultraviolet absorption spectrum in acetonitrile contains the two maxima characteristic of the $B_{10}H_{13}$ anion.

In order to further confirm the identity of this compound as the diethylammonium salt of decaborane, a spectrophotometric titration of decaborane was carried out in acetonitrile solution with diethylamine. Table II presents the titration data obtained at 335 mμ. As seen by these results, the observed optical density becomes constant near a decaborane:amine ratio of unity.

TABLE II

SPECTROPHOTOMETRIC TITRATION OF 5.15 × 10^{-4} *M* $B_{10}H_{14}$ WITH DIETHYLAMINE IN ACETONITRILE

Point	Moles/l. × 10^6 Et_2NH added	$[Et_2NH]/[B_{10}H_{14}]$	O. D (335 mμ)
1	4.52	0.088	0.079
2	9.03	.175	.164
3	18.1	.351	.314
4	27.1	.526	.480
5	36.1	.701	.647
6	45.2	.877	.796
7	49.7	.964	.870
8	54.2	1.05	.904
9	72.2	1.40	.904
10	81.3	1.57	.904
11	135.5	2.63	.904

Conductometric titration of decaborane with diethylamine in acetonitrile and diglyme solvents produced data similar to that shown in Table II except that the end-point was not as well defined. This latter result was attributed to ion pair formation at the relatively high concentrations employed (0.3*M*).

Treatment of the diethylammonium salt with tetramethylammonium hydroxide in diglyme solution resulted in the immediate precipitation of the tetramethylammonium salt.

The reaction of decaborane with excess diethylamine produced another compound which appeared to have the composition $B_{10}H_{14}.2(C_2H_5)_2NH$. This compound and its reactions will be described at a later date.

Treatment of decaborane with triethylamine in diethyl ether produced a crystalline salt which exhibited an ultraviolet absorption spectrum characteristic of the $B_{10}H_{13}$ anion.

Alkali Metal Salts of Decaborane.—Decaborane in diethyl ether solution reacted instantaneously with aqueous sodium or potassium hydroxide solutions to produce yellow, ether-soluble salts. Since these salts could not be isolated from their ethereal solutions in the crystalline state, the sodium salt was characterized in solution by spectrophotometric titration of decaborane with standard sodium hydroxide solution in acetonitrile (4% volume)–diglyme (96% volume). The data are presented in Table III and prove that the $B_{10}H_{13}$ anion may be quantitatively produced under these conditions.

TABLE III

SPECTROPHOTOMETRIC TITRATION OF 5.04 × 10^{-4} *M* $B_{10}H_{14}$ WITH SODIUM HYDROXIDE IN ACETONITRILE (4% VOLUME)–DIGLYME (96% VOLUME)

NaOH added, moles/l. × 10^6	Moles NaOH/ moles $B_{10}H_{14}$	Optical density, 335 mμ
4.28	0.085	0.082
8.56	.148	.170
17.1	.339	.285
25.7	.509	.470
34.2	.678	.590
42.8	.850	.762
51.4	1.02	.882[a]
68.4	1.36	.882
85.6	1.68	.882

[a] Extinction coefficient 1750 at 335 mμ and 2490 at 267 mμ.

Infrared Characteristics of the $B_{10}H_{13}$ Anion.—The quaternary phosphonium, quaternary ammonium, diethylammonium and triethylammonium salts of decaborane contained bands at 4.05 and 5.25μ in the infrared which are attributed to terminal and bridge B–H stretching, respectively. No other bands were observed which might be called characteristic of the $B_{10}H_{13}$ anion.

Experimental

Materials.—Decaborane was sublimed before use. Acetonitrile was purified by distillation from phosphorus pentoxide followed by distillation from calcium hydride. Diglyme (diethylene glycol dimethyl ether) was purified by distillation *in vacuo* from lithium aluminum hydride and stored in sealed bottles. Other reagents were of high purity.

Ultraviolet and Infrared Spectra.—A model DK-1 Beckman recording spectrophotometer was employed for all ultraviolet measurements. A Perkin–Elmer model 21 infrared spectrophotometer equipped with sodium chloride optics was employed. The infrared spectra were obtained as Nujol mulls.

Preparation of Tetramethylammonium Decaborane Salt from Tetramethylammonium Hydroxide.—To 100 ml. of 1.0 *M* tetramethylammonium hydroxide in water was slowly added, with stirring, a solution of 12.2 g. (0.10 mole) of decaborane in 25 ml. of pure diglyme. The addition was carried out under nitrogen at ice-bath temperature. As each drop of decaborane solution was added, a voluminous yellow precipitate formed. Following the addition, the yellow salt was removed by filtration in a nitrogen atmosphere and washed with water. The product was dried *in vacuo*, m.p. >250°. The yield amounted to 17.0 g. (87%). The material was stored under nitrogen.

Anal. Calcd. for $C_4H_{25}B_{10}N$: C, 24.6; H, 13.0; B, 55.7. Found: C, 24.2; H, 12.8; B, 54.0.

Similar treatment of tetraethyl-, tetra-*n*-butyl- and triethyl-*n*-butylammonium hydroxides with decaborane produced yellow, water-insoluble salts of the same nature.

Preparation of tetramethylammonium decaborane salt from the ilyde.—Tetramethylammonium bromide (7.0 g., 0.05 mole) was placed in a seal-off bulb with 50 ml. of 0.97 *M* phenyllithium in diethyl ether. The bulb was evacuated, sealed and shaken at room temperature for 5 days. The bulb was then opened in the dry-box under nitrogen and added to a solution of 6.1 g. (0.05 mole) of decaborane in 100 ml. of diethyl ether. A yellow solid separated immediately and was removed by filtration. The crude product was washed with water, ethanol and diethyl ether. After drying *in vacuo*, the product weighed 8.7 g. (89% of theory) and was shown by infrared and ultraviolet spectra to be identical with the material described above.

Preparation of the Tetramethylammonium Salts of Partially Hydrolyzed Decaborane.—This reaction was carried out by the addition of 100 ml. of 1.0 *M* tetramethylammonium hydroxide to 12.2 g. of decaborane in 25 ml. of diglyme at zero degrees and under nitrogen. The white precipitated product was removed by filtration under nitrogen, washed with water and dried *in vacuo* (18.5 g., 95% of theory). Some samples of the product proved pyrophoric. The infrared and ultraviolet spectra of these materials are described in the body of the paper. The boron content of these products varied from 40 to 50%.

Spectrophotometric Examination of Aged Decaborane Solution in 90% Diglyme–10% Water Quenched with Tetramethylammonium Hydroxide at 25°.—A 5.4×10^{-3} *M* solution of decaborane was prepared in 90% diglyme–10% water (v./v.). As the decaborane was dissolved, a timer was started. A 1-ml. aliquot of the solution was transferred to a 10-ml. volumetric flask; the flask was filled nearly to the mark with the diglyme–water mixture; 0.4 *N* tetramethylammonium hydroxide was added from a 25-microliter pipet, the time was recorded, the volume was quickly adjusted to the mark, and the flask was well shaken. The final concentrations of the reagents were: decaborane, 5.4×10^{-4} *M;* tetramethylammonium hydroxide, about 1×10^{-3} *M.*

The ultraviolet spectrum of the final solution was rapidly scanned from 400–230 mμ on a Beckman model DK-1 spectrophotometer. This solution was then set aside, and periodically its ultraviolet absorption rechecked.

Other aliquots of the original decaborane solution were quenched with tetramethylammonium hydroxide at various intervals of time and ultraviolet spectra were scanned. These data are presented in Table I.

Reaction of Triphenylphosphine Methylene with Decaborane.—To 7.0 g. (2×10^{-2} mole) of methyl triphenylphosphonium bromide suspended in 100 ml. of diethyl ether was added 20 ml. of 0.97 *M* phenyllithium. The mixture was stirred under nitrogen for one hour. The resulting yellow solution was filtered through a dry glass wool plug into a solution of 2.4 g. (2×10^{-2} mole) of decaborane in 50 ml. of diethyl ether. A yellow oil which formed immediately crystallized on standing. The crystals were separated by filtration, washed with diethyl ether and weighed 5.85 g. (73% theory) after drying *in vacuo*. The crude product was recrystallized from methylene chloride–diethyl ether, m.p. 127–129°. The ultraviolet absorption spectrum was determined in acetonitrile solution; $\lambda_{\max}$ 338 mμ, ϵ 1.6×10^3, and other absorption due to the cation.

Anal. Calcd. for $C_{19}H_{31}B_{10}P$: C, 57.25; H, 7.84; B, 27.14; P, 7.77. Found: C, 56.8; H, 8.01; B, 25.9; P, 7.60.

Reaction of Methyltriphenylphosphonium Hydroxide with Decaborane.—One gram of sodium hydroxide was dissolved in 10 ml. of water and added to 1.7 g. of silver nitrate in 15 ml. of water. To this rapidly stirred solution was added 3.6 g. (1×10^{-2} mole) of methyltriphenylphosphonium bromide. Stirring was continued for one hour and the precipitated silver bromide was removed by filtration. The filtrate was then treated with a solution of 1.2 g. (1×10^{-2} mole) of decaborane in 20 ml. of methylene chloride. Immediately upon mixing, the organic layer became intensely yellow. The methylene chloride layer was washed once with water, dried over magnesium sulfate and evaporated to 5 ml. whereupon 5 ml. of diethyl ether was added. Yellow crystals separated upon standing, yield 1.5 g. (38% theory). That the product was identical to that described immediately above was shown by melting point, infrared and ultraviolet spectra.

Reaction of the Sodium Salt of Decaborane with Methyltriphenylphosphonium Chloride.—To 50 ml. of 0.20 *N* sodium hydroxide solution was added a solution of 1.2 g. (1×10^{-2} mole) of decaborane dissolved in 25 ml. of methylene chloride. The resulting mixture was stirred vigorously and 3.6 g. (1×10^{-2} mole) of methyltriphenylphosphonium chloride was added. The quaternary phosphonium salt immediately dissolved in the organic layer which, when worked up as described immediately above, produced 1.2 g. (30%) of yellow phosphonium salt which was identical to samples prepared by other routes.

Reaction of Triphenylphosphinephenylmethylene with Decaborane.—Eight and six-tenths grams of benzyl triphenylphosphonium bromide (2×10^{-2} mole) was employed in the procedure described above for the reaction of triphenylphosphine methylene with decaborane. After one recrystallization from ethylene chloride–diethyl ether, 4.2 g. (45% theory) of the benzyl triphenylphosphonium salt was obtained, m.p. 134–136°.

Anal. Calcd. for $C_{25}H_{35}B_{10}P$: C, 63.25; H, 7.43; B, 22.79; P, 6.53. Found: C, 62.95; H, 7.70; B, 21.50; P, 6.51.

Preparation of Diethylammonium Decaborane Salt.—In a typical preparation, 2.97 g. (4.06×10^{-2} mole) of diethylamine dissolved in 10 ml. of dry cyclohexane was added slowly, with stirring, to 5 g. (4.09×10^{-2} mole) of sublimed decaborane dissolved in 300 ml. of dry cyclohexane. The yellow precipitate which formed was isolated by filtration, washed with four portions of dry cyclohexane and dried *in vacuo;* yield 89.3%, m.p. 105° dec.

Anal. Calcd. for $C_4H_{25}NB_{10}$: C, 24.59; H, 12.81; N, 7.17; B, 55.43. Found: C, 25.55; H, 13.33; N, 7.02; B, 54.64.

The product could be purified either by recrystallization from methylene chloride or by vacuum sublimation at 80–90°.

Preparation of Triethylammonium Decaborane Salt.—A 4.0-g. sample of triethylamine (3.95×10^{-2} mole) dissolved in 10 ml. of dry benzene was added slowly, with stirring, to 5 g. of sublimed decaborane (4.09×10^{-2} mole) in 50 ml. of dry benzene. The resulting yellow solution was filtered and diethyl ether added to the filtrate, causing precipitation of 7.53 g. of a yellow crystalline solid. The sample was washed with three portions of dry ether and dried *in vacuo;* yield, 85.4%, m.p. 98° dec. The compound could also be prepared directly in diethyl ether.

Anal. Calcd. for $C_6H_{29}NB_{10}$: C, 32.26; H, 13.00; N, 6.30; B, 48.48. Found: C, 31.95; H, 12.75; N, 6.50; B, 48.05.

Spectrophotometric Titration of Decaborane with Diethylamine in Acetonitrile.—A 1.287×10^{-2} *M* stock solution of decaborane was prepared in acetonitrile. One milliliter aliquots of the solution were transferred to 25-ml. volumetric flasks.

A 2.257×10^{-3} *M* stock solution of diethylamine was prepared in acetonitrile. Each point on the titration curve was obtained by pipetting an aliquot of the diethylamine solution into one of the volumetric flasks, diluting to volume with acetonitrile and shaking well. At the instant the diethylamine solution was added to the decaborane, a timer was started.

The absorbance of the final solution was read immediately at the 335 mμ peak on a Beckman model DK-1 spectrophotometer. Since the absorbance decreases slightly with time, the optical density was extrapolated to mixing time. The size of the aliquot of diethylamine solution was increased for each succeeding point until several points beyond a 1:1 molar ratio of diethylamine to decaborane were obtained. Since the solvent contained a trace of base, a slight blank correction was made. A plot of optical density *vs.* $[Et_2NH]/[B_{10}H_{14}]$ gives the desired titration curve. These data are presented in Table II.

Spectrophotometric Titration of Decaborane with Sodium Hydroxide in 4% Acetonitrile–96% Diglyme.—The procedure employed in titrating decaborane with sodium hydroxide in 4% acetonitrile–96% diglyme (v./v.) was similar to that used in the preceding titration. One milliliter aliquots of a 1.260×10^{-3} *M* decaborane solution in acetonitrile were pipetted into 25-ml. volumetric flasks. Each flask in turn was filled nearly to the mark with diglyme. An aliquot of 0.017 *N* aqueous sodium hydroxide was quickly added from a micropipet, the timer was started, the volume adjusted to the mark, and the solution mixed well.

The absorbance of the final solution was read immediately at the 335 mμ maximum. Since the optical density at 335 mμ decreased more rapidly with this system, fast work and careful timing and extrapolation to zero or mixing time were important. The titration curve was plotted as before. These data are presented in Table III.

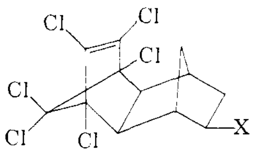
HUNTSVILLE, ALA.

COMMUNICATIONS TO THE EDITOR

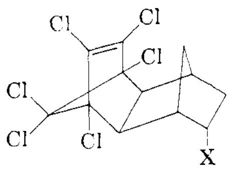
BRIDGED POLYCYCLIC COMPOUNDS. XII. A MECHANISM FOR THE HUNSDIECKER REACTION[1,2]

Sir:

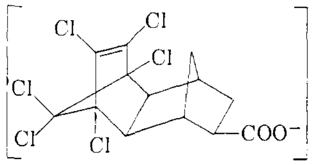
The Hunsdiecker reaction of bromine with the silver salts Ia and IIa gave a mixture of Ib and IIb, although the bromide formed by decomposition of the acyl peroxides III and IV in bromotrichloromethane was all *exo* (Ib). If the latter reaction reflects the stereochemistry of the reaction of the free radical V with bromine donors, some mechanism other than the reaction of V with bromine or acyl hypobromite must be involved in the Hunsdiecker reaction of Ia and IIa; a free radical is, however, generally accepted as the intermediate in this reaction.[3]



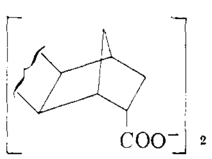
Ia, X = CO_2Ag
b, X = Br
c, X = CO_2H
d, X = COCl



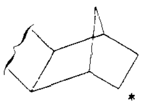
IIa, X = CO_2Ag
b, X = Br
c, X = CO_2H
d, X = COCl



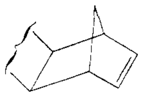
III



IV



V



VI

Ib (m.p. 178.5–179.2°) and IIb (m.p. 109.5–110.5°) result from the reaction of hexachlorocyclopentadiene with the mixture obtained by the Diels–Alder reaction of vinyl bromide and cyclopentadiene.[4] The *exo* bromide Ib also can be made by the addition of hydrogen bromide to Aldrin (VI). Ib and IIb were shown to be epimeric by dehydrobromination with alkali to VI. Ib and IIb were isolated from the reaction of Ia and IIa with bromine in carbon tetrachloride. The bromides were inert toward the reaction conditions and isolation procedures, and the acids related to Ia and Ib could be recovered unisomerized from their silver salts.

The acids, Ic (m.p. 221–222°) and IIc (m.p. 216–217°) were prepared by the reaction of *exo*-[4] and *endo*-bicyclo[2.2.1]-5-heptene-2-carboxylic acid,[5] respectively, with hexachlorocyclopentadiene. The acids gave the acid chlorides, Id (m.p. 100.5–101.5°) and IId (m.p. 111.5–113°), which in turn were treated with sodium peroxide to form III (m.p. *ca.* 111°, dec.) and IV (m.p. *ca.* 133°, dec.). All of the compounds gave satisfactory elemental analyses. Each peroxide decomposed largely into ester and only the *exo* bromide Ib in refluxing bromotrichloromethane. The alcohol and acid portions of each ester had the configuration of the starting acid. Infrared and isotope-dilution analyses showed that the bromide from either peroxide contained very little, if any, IIb.

The Hunsdiecker reactions of Ia and IIa in the dark in refluxing carbon tetrachloride gave bromides whose compositions as measured by infrared and isotope-dilution techniques were Ib, 69 ± 2% and IIb, 31 ± 2%. The configuration of the initial silver salt did not affect the bromide composition, nor did addition of benzoyl peroxide or *sym*-trinitrobenzene. The large amount of *endo* bromide (IIb) is striking.

The insensitivity of the composition of the bromide mixture to the configuration of the initial acid is inconsistent with any stereospecific inversion or cyclic process, while the formation of substantial amounts of *endo* bromide is inconsistent with a free-radical-chain process in which the radical V reacts with a bromine donor.[6] The data are consistent with the concept of geminate recombination of an alkyl radical and a bromine atom, formed by decomposition of the intermediate acyl hypo-

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(1) Previous paper in series: S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, accepted for publication.

(2) The authors are indebted to the Shell Development Company for partial support of this research.

(3) For pertinent references see: C. V. Wilson in R. Adams, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., N. Y., 1957, Chapter 5; R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

(4) J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

(5) K. Alder, G. Stein, M. Liebmann and E. Rolland, *Ann.*, **514**, 197 (1934).

(6) A referee has suggested that the stereochemistry of the model reaction of V with bromotrichloromethane may not be comparable to that of V with the smaller molecule bromine or with the acyl hypohalite. The conclusion that no chain reaction process is involved is based upon the assumption that these are comparable and that *exo* attack on such radicals[7] is general.

(7) S. J. Cristol and R. P. Arganbright, THIS JOURNAL, **79**, 6039 (1957).