[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Preparation and Properties of a Series of Ethereal and Unsaturated Boranes

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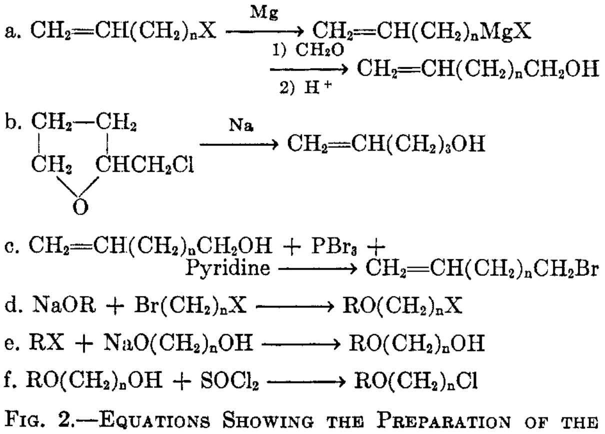
Several series of tri-alkenyl-, tris-alkyoxyalkyl-, and tris-aryloxyalkyl-boranes are reported. The ultraviolet absorption spectra of two of the tri-alkenylboranes are given and the effect of tri-*n*-butylborane on the ultraviolet absorption spectrum of α,α-diphenylethylene is described.

The chemical literature contains many references to the preparation of tri-alkylboranes,[2] but there are few reports of boranes having an additional functional group in the molecule.[3] The synthesis of two such types of boranes (unsaturated and ethereal boranes) was achieved by the reaction of an excess of the appropriate Grignard reagent with boron trifluoride-diethyl ether complex (Figure 1 and Table I). The organic halides used for the preparation of the Grignard reagents were synthesized by standard procedures summarized in Figure 2 and Table II.

a. $CH_2{=}CH(CH_2)_nX \xrightarrow{Mg} CH_2{=}CH(CH_2)_nMgX \xrightarrow{BF_3} [CH_2{=}CH(CH_2)_n]_3B$

b. $RO(CH_2)_nX \xrightarrow{Mg} RO(CH_2)_nMgX \xrightarrow{BF_3} [RO(CH_2)_n]_3B$

FIG. 1.—EQUATIONS SHOWING THE PREPARATION OF THE BORANES.



a. $CH_2{=}CH(CH_2)_nX \xrightarrow{Mg} CH_2{=}CH(CH_2)_nMgX \xrightarrow[2)\ H^+]{1)\ CH_2O} CH_2{=}CH(CH_2)_nCH_2OH$

b. $\xrightarrow{Na} CH_2{=}CH(CH_2)_3OH$

c. $CH_2{=}CH(CH_2)_nCH_2OH + PBr_3 + \text{Pyridine} \longrightarrow CH_2{=}CH(CH_2)_nCH_2Br$

d. $NaOR + Br(CH_2)_nX \longrightarrow RO(CH_2)_nX$

e. $RX + NaO(CH_2)_nOH \longrightarrow RO(CH_2)_nOH$

f. $RO(CH_2)_nOH + SOCl_2 \longrightarrow RO(CH_2)_nCl$

FIG. 2.—EQUATIONS SHOWING THE PREPARATION OF THE ORGANIC HALIDES USED AS STARTING MATERIALS.

The preparation of the Grignard reagents and the corresponding boranes from the alkenyl halides presented no difficulties; however, the formation of the Grignard reagents from the halo-ethers was subject to some limitations. The Grignard reagents cannot be prepared from β-halo-ethers,[4] and although a 64% yield of γ-phenoxypropylmagnesium chloride was reported[5] based on titration of the reaction mixture with standard acid, a more recent publication[6] indicated that γ-phenoxypropylmagnesium iodide was unstable at room temperature. Repetition of this work showed that although titration with standard acid of an aliquot of the supernatant ether solution from the reaction of γ-phenoxypropyl chloride with magnesium indicated an 87% yield of γ-phenoxypropylmagnesium chloride, the reaction mixture gave a negative Gilman test for the Grignard reagent. A second aliquot of the reaction mixture after acidification gave a 90% yield of 2,4,6-tribromophenol on treatment with bromine water, suggesting that a magnesium salt of phenol which was soluble in the ether was hydrolyzed by water to give the basic material which was titrated with the standard acid.

Unlike the γ-phenoxypropyl Grignard reagent, γ-methoxypropylmagnesium chloride is stable at the boiling point of ether.[7] Similarly, γ-benzyloxypropyl magnesium chloride could be formed and converted to γ-benzyloxybutyric acid with carbon dioxide or to the borane with boron trifluoride. Although δ-phenoxybutyl and ϵ-phenoxyamyl bromides were converted to the corresponding Grignard reagents on treatment with magnesium, 5 to 10% of the coupled products, 1,8-diphenoxyoctane and 1,10-diphenoxydecane, was isolated regardless of the presence of boron trifluoride-etherate.

All of the boranes gave indication of undergoing oxidation in the air, the tri-alkenylboranes being spontaneously flammable. The tris-phenoxyalkylboranes became cloudy from deposited boron-containing acids after an exposure to atmospheric

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(1) These results were taken in part from the thesis of Ian C. Pattison presented to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements of the Master of Science degree.

(2) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, *J. Am. Chem. Soc.*, **60**, 115 (1938); A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921); E. Krause and H. Polack, *Ber.*, **59**, 777 (1926). H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945); E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

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(4) Kharasch and Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, p. 35.

(5) H. Gilman and R. McCracken, *Rec. trav. chim.*, **46**, 463 (1927).

(6) R. Paul, *Compt. rend.*, **192**, 964 (1931).

(7) R. Letsinger and A. Schnizer, *J. Org. Chem.*, **16**, 704 (1951). N. Rabjohn and M. S. Cohen, *J. Am. Chem. Soc.*, **74**, 6290 (1952).

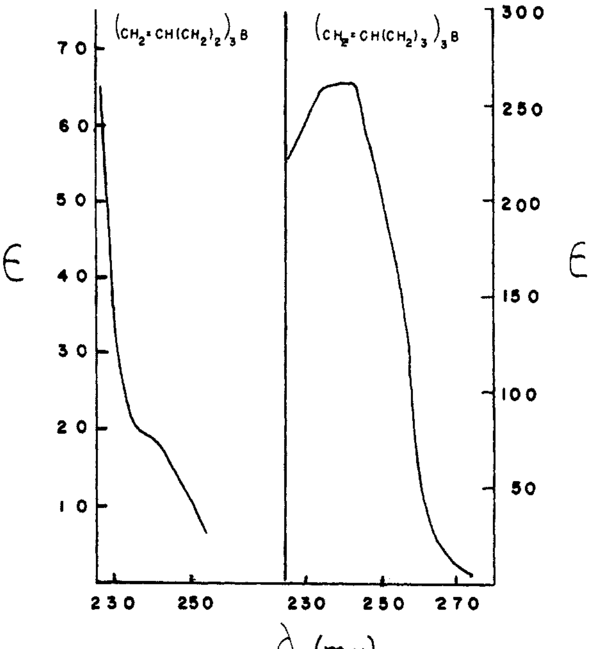


FIG. 3.—THE ULTRAVIOLET ABSORPTION SPECTRA OF TRI-3-BUTENYLBORANE AND TRI-4-PENTENYLBORANE IN 95% ETHANOL.

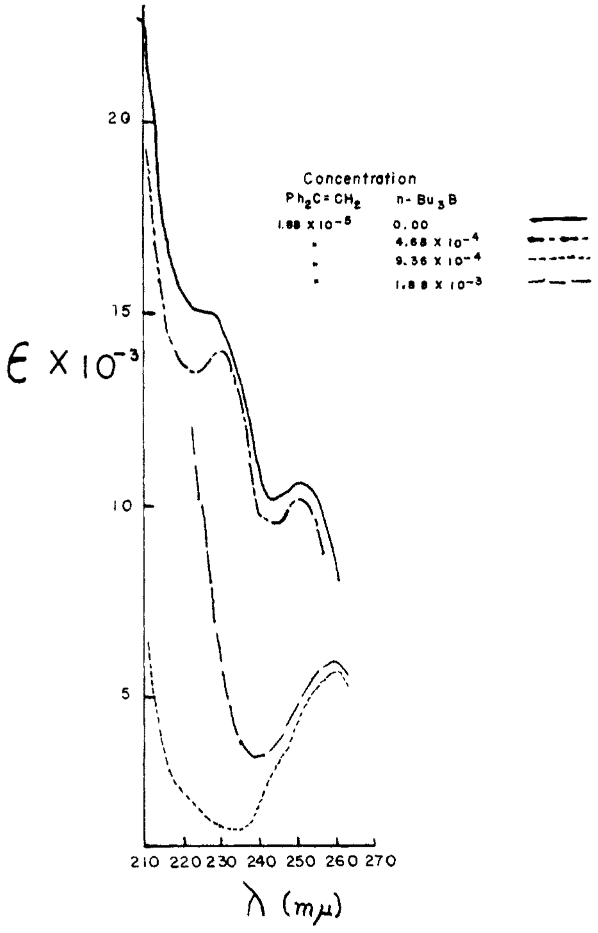
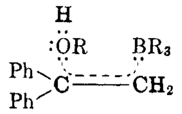


FIG. 4.—THE EFFECT OF TRI-*n*-BUTYLBORANE ON THE ULTRAVIOLET ABSORPTION SPECTRUM OF α,α-DIPHENYLETHYLENE IN 95% ETHANOL.

oxygen for several days. The greater stability of the ethereal boranes would suggest that the boron atom was coordinately bonded to the oxygen of the ether linkage.

Although the saturated tri-*n*-butylborane showed an ultraviolet absorption maximum at 205 mμ, the unsaturated tri-3-butenylborane and tri-4-pentenylborane gave respectively an inflection at 240 mμ and a definite peak at 236–242 mμ (Figure 3). To confirm this apparent interaction between the boron atom of the borane and the ethylenic bond, the ultraviolet absorption spectra of mixtures of α,α-diphenylethylene and varying amounts of tri-*n*-butylborane were determined. As the concentration of the borane was increased the inflection of the α,α-diphenylethylene at 236 mμ disappeared and the benzenoid bond at 250 mμ was decreased in intensity and shifted to 260 mμ (Figure 4). These results are consistent with the hypothesis that the coordination of the boron atom of the borane with the *pi* electrons of the ethylenic bond has destroyed the conjugated system leaving only the absorption of two substituted benzene rings. This appears to be the first definite indication of complex formation in the liquid state between the boron atom of a borane and an unsaturated hydrocarbon.[8] One plausible picture of such a complex is shown below.



The reaction of tri-3-butenylborane with bromine appeared to occur at the points of unsaturation without rupture of the boron-to-carbon bond, for the first three moles of bromine were absorbed rapidly yielding a boron-containing compound. The low and variable halogen content of this product may be caused by an inadequate analytical procedure or solvolysis of the halogen substituents during the purification by recrystallization from methanol.

EXPERIMENTAL

The microanalyses of the boranes for carbon and hydrogen were determined by Dr. Carl Tiedcke, Teaneck, N. J.

Reaction of 3-chloropropyl phenyl ether with magnesium. In a conventional 500-ml. 3-necked reaction apparatus was placed 3.00 g. of magnesium and the reaction vessel and contents were dried by heating in a stream of nitrogen. After cooling, the magnesium was covered with 25 ml. of dry ether and a solution of 3.0 ml. of 3-chloropropyl phenyl ether in 3.0 ml. of ether was added. As soon as the reaction started, the dropwise addition of 14 g. of 3-chloropropyl phenyl ether in 100 ml. of dry ether was begun. After all of the halide (17.0 g., 0.1 mole) had been added, the reaction mixture was refluxed with external heating for 2 hrs. Sufficient ether was added to make the total volume of the reaction mixture 150 ml. The Gilman test[9] for Grignard

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TABLE I

Properties of Boranes R_3B

				Analyses					
					Calc'd			Found	
R	b.p., °C.	mm.	Yield, %	C	H	B	C	H	B
$CH_2=CHCH_2CH_2-$	98–103	17	57	81.84	12.02	6.14	79.28	12.49	6.08
$CH_2=CHCH_2CH_2CH_2-$	130–133	18	76	82.56	12.47	4.96	82.67	12.60	4.90
$CH_2=CH-(CH_2)_4-$	112–123	18	70	83.06	12.78	4.16	78.40	12.95	4.82
$CH_3OCH_2CH_2CH_2-$	158–161	15	50	62.62	11.83	4.70	62.29	11.75	
$CH_3OCH_2-(CH_2)_3-$	170–180	3	27	66.18	12.22	4.05	66.13	11.94	
$CH_3OCH_2-(CH_2)_4-$	210–215	14	39	68.77	12.50	3.50	65.66	11.75	3.47
$PhOCH_2-(CH_2)_3-$[a]	295–325	5	36	78.59	8.14	2.36	78.37	8.74	2.34
$PhOCH_2-(CH_2)_4-$[b]	275–280	2	21	79.18	9.06	2.16	78.50	8.63	2.12
$PhCH_2O(CH_2)_3-$	170–180	2	30	78.59	8.14	2.40	78.84	8.22	
$PhCH_2O-(CH_2)_4-$	203–223	2	13	79.18	9.06	2.20	78.99	8.94	
$PhCH_2O-(CH_2)_4-$	225–250	4	9	79.68	9.47	2.00	81.34	10.38	2.38

[a] n_D^{25} 1.5365. [b] n_D^{25} 1.5278.

TABLE II

Preparation of Starting Halides

	Physical Constants			Literature Constants						
Compound	b.p., °C.	mm.	n_D^{25}	b.p., °C.	mm.	n_D^{20}	Ref.	Yield, %	Procedure Reference	Fig. 1
$CH_2=CHCH_2CH_2OH$	112–115	Atm.	1.4179	112–114	Atm.	1.4224	11		11, 12	a
$CH_2=CH(CH_2)_3OH$	134–139	Atm.	1.4340	134–137	Atm.	1.4308	11	51	13	b
$CH_2=CH(CH_2)_4OH$	57–58	15	1.4335					61	11	a
$CH_2=CHCH_2CH_2Br$	98–100	Atm.	1.4576	97–102	Atm.	1.4621	11	35	14	c
$CH_2=CH(CH_2)_3Br$	54–55	64	1.4620	56	75	1.4640	11	46	14	c
$CH_2=CH(CH_2)_4Br$[a]	47–51	16	1.4632					66	14	c
$MeOCH_2CH_2CH_2Cl$	110–118	Atm.	1.4123	116–118	Atm.		19	54	15	d
$MeO-(CH_2)_4Br$	68–75	35	1.4505	70–82	35		15	50	15	d
	70–82	35						62	14	f[c]
$MeO-(CH_2)_5Br$	80–86	20		183–187	Atm.		20	52	15	d
	83–95	25						48	14	f[c]
$PhOCH_2CH_2CH_2Cl$	127–129	13	1.5235	139	25		21	71	16	d
$PhO-(CH_2)_4Br$	150–161[b]	14		153–156	18		22	65	16	d
$PhO-(CH_2)_5Br$	171–175	14	1.5325	160–165	11		23	67	16	d
$PhCH_2O(CH_2)_3OH$	150–165	16		155	23		17	52	17	e
$PhCH_2O(CH_2)_4OH$	167–172	16		157	12		17	58	17	e
$PhCH_2O(CH_2)_5OH$	171–184	15		140	0.4		24	53	17	e
$PhCH_2O(CH_2)_3Cl$	135–143	16		129	16		17	80	17	f
$PhCH_2O(CH_2)_4Cl$	150–158	14		135	12		17	67	17	f
$PhCH_2O(CH_2)_5Cl$	171–175	21		86	0.1		24	60	17	f
$MeO-(CH_2)_4OH$	85–90	27		53–64	7	1.4213	18	54	18	e
$MeO-(CH_2)_5OH$	100–106	34		83–84	9	1.4244	18	44	18	e

[a] d_4^{25} 1.2017; *Anal.* Calc'd for $C_6H_{11}Br$: Br, 49.01; M_D, 37.21. Found: 48.36, 48.52, 48.36; M_D, 37.27. [b] M.p. 38–40°, lit.[22] m.p. 41°. [c] Phosphorus tribromide was used instead of thionyl chloride.

reagents was negative when applied to this solution. A 25-ml. aliquot of this solution was titrated with standard hydrochloric acid and was found to contain 0.0145 equivalent of base. A second 25-ml. aliquot, after acidification, was treated with bromine water yielding 5.13 g. of solid, m.p. 86–90°, which was shown to be 2,4,6-tribromophenol, lit. m.p. 95°.[10] This amount of 2,4,6-tribromophenol represents 0.0152 equivalent of phenol in the original aliquot. Thus an 87% yield was obtained, based on the titration with acid, or a 90% yield was obtained, based on the yield of 2,4,6-tribromophenol.

Reaction of 3-chloropropyl benzyl ether with magnesium. In a 500-ml. Grignard set-up was placed 1.20 g. of magnesium and the reaction flask and contents were dried by heating in an atmosphere of nitrogen. A solution of 2.00 g. of 3-chloropropyl benzyl ether in 20 ml. of ether was added after the flask had cooled. A few drops of methyl iodide

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were added to start the reaction, and 4.00 g. of the ether in 80 ml. of ether were added dropwise at such a rate as to maintain refluxing of the ether. After the addition was complete the reaction mixture was refluxed for 1 hr. by external heating. The solution was cooled and poured very slowly into a slurry of Dry Ice and ether. The Dry Ice-ether mixture was allowed to warm to room temperature and then 50 ml. of 10% hydrochloric acid was added with stirring. The ether layer was separated and extracted with three 25-ml. portions of 10% sodium hydroxide. On acidification of the basic extracts an oil separated and was extracted into ether. After drying, this ether solution was heated to remove the solvent, and an oily residue of 2.57 g. (40.7%) of γ-benzyloxybutyric acid remained. Since the oil failed to crystallize, it was distilled giving 1.58 g. of pure γ-benzyloxybutyric acid, b.p. 188–189° at 10 mm.; n_D^{25} 1.5098; d_4^{25} 1.0107; and 0.66 g. of impure γ-benzyloxybutyric acid, b.p. 185–188° at 10 mm.

Anal. Calc'd for $C_{11}H_{14}O_3$: C, 68.03; H, 7.27; Neut. equiv., 194.2. Found: C, 68.03; H, 7.38; Neut. equiv., 194.6.

General procedure for the preparation of boranes (*see Table II*). In a 500-ml. or 1 l. 3-necked flask fitted by standard-taper joints with condenser, mercury-sealed stirrer, and dropping-funnel, magnesium was placed in slight excess of a molar ratio of 1 to the amount of halide used. The system was heated and flushed well with "prepurified" nitrogen which had been passed through two pyrogallol traps. On cooling anhydrous ether was added with a sufficient amount of the halide to start the Grignard reaction. After the reaction had started the remainder of the halide was added in ether at such a rate as to maintain gentle reflux. To the Grignard reagent was added freshly distilled boron trifluoride-etherate in one-third the molar amount of the halide. The addition of the boron trifluoride usually caused an exothermic reaction which maintained reflux during the addition. After the reaction mixture cooled, it was refluxed for 1 to 3 hours, cooled, and water was added until no further reaction was evident. Dilute hydrochloric acid was added, avoiding an excess, to dissolve the magnesium hydroxide, and the reaction mixture was transferred under nitrogen to a separatory-funnel where the layers were separated. The ether layer was washed with water, 5% sodium bicarbonate, or dilute base, and finally with water. The ether layer was allowed to stand overnight over a drying agent and then was fractionally distilled under nitrogen at reduced pressure.

The yields and constants for these products are shown in Table II.

The distillation of the products from the reactions of 4-phenoxybutyl- and 5-phenoxypentyl-magnesium halides with boron trifluoride-etherate gave a liquid and solid which co-distilled. On treatment of this mixture with low-boiling petroleum ether (30–60°) the borane, the liquid, dissolved leaving a 10% yield of 1,8-diphenoxyoctane, m.p. 85–86°, lit.[25] m.p. 83–84°, in the one case and a 6% yield of 1,10-diphenoxydecane, m.p. 90–91°, lit.[25] m.p. 85°, in the other. The borane was recovered from the petroleum ether solution.

The reaction of bromine with tri-3-butenylborane. To a cooled solution of 0.52 g. (0.0030 mole) of tri-3-butenylborane in 15 ml. of carbon tetrachloride was added dropwise a solution of 1.42 g. (0.0089 mole) of bromine in 10 ml. of carbon tetrachloride. Because of the rapid decolorization of this bromine solution, a small excess (0.075 g.) of bromine was added. This excess was decolorized slowly with the evolution of hydrogen bromide. The solvent was removed by distillation under reduced pressure, and the remaining oil crystallized on addition of methanol. The solid appeared to melt at about room temperature, 25°, and gave the green-colored flame test characteristic of organoboron compounds. After two recrystallizations from methanol, the solid was analyzed for bromine by heating the sample under reflux with sodium methoxide in methanol and titration of the bromide ion by the Volhard method.

Anal. Calc'd for $C_{12}H_{21}BBr_6$: Br, 73.14. Found: Br, 46.37, 45.47.

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