and reduction of α-iodo ketones, α-iodomalonic esters and related compounds.[23]

Reductions with $PtHCl[P(C_2H_5)_3]_2$ (I) and $IrH_2Cl[P(C_2H_5)_2(C_6H_5)]_3$ (II).[24]—The cations used were diphenylmethyl (A), 4-methyldiphenylmethyl (B), 4,4′-dimethyldiphenylmethyl (C), triphenylmethyl (D) and 4,4′-dimethoxydiphenylmethyl (E). The respective $pK_R{}^+$ values are −13.3, −11.6, −10.4, −6.63 and −5.71. The tests were conducted by adding 10 mg. of I or II to 5 ml. of a 10^{-5} molar solution of the cation.

Hydride I immediately reduced A, required a minute to reduce B, required five minutes to reduce C and required thirty minutes to reduce E. The more highly hindered D required several days for reduction. All tests were at 25°; A-C were in 82% H_2SO_4 and D and E were in 62% acid. The limiting value for reduction is about −5 for $pK_R{}^+$. The slowness of the reactions near the limiting $pK_R{}^+$ value inhibited a more precise evaluation. A further limitation was the lack of diarylmethyl cations with $pK_R{}^+$ around −5. The much more stable xanthyl cation ($pK_R{}^+$ −0.84) was not reduced as expected.

Hydride II decomposed slowly in 82% H_2SO_4 producing an orange gum and a brown solution. Despite this complication, the reduction of A in thirty minutes could be clearly observed; B-E were either very slow or failed to reduce.

In 96% H_2SO_4, I and II immediately evolved hydrogen and this reaction took precedence over the reduction of A.

Experimental

In the HBr reductions, the decolorization of the carbonium ions were so dramatic that simple visual observations were sufficient to detect quantitative reduction. Addition of 10 mg. of finely powdered NaBr to 10 ml. of 10^{-4} molar solutions of the carbonium ions caused complete decolorization in the cases indicated in Table I. Although Br_2 is produced in this reaction, its extinction coefficients in the visible region are insignificant relative to carbonium ions. However, if large amounts of NaBr are added, Br_2 is produced in large enough amounts by direct sulfuric acid oxidation to obscure the disappearance of the carbonium ions.

Even with the HI reductions, it is possible to observe virtually complete decolorization after several seconds if the amount of added KI is kept small, is finely ground, and is added with vigorous shaking.

The formation of carbonium ions by Br_2 oxidation was determined completely by spectrophotometric measurements using a Beckman DU spectrophotometer. The absorption spectra of Br_2 and the carbonium ions were sufficiently distinct in the four cases studied.

The products recovered from HBr and HI reductions were identified by comparison of m.p. and infrared spectra with authentic samples.

Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 494.

[23] R. W. West, *J. Chem. Soc.*, **119**, 359 (1921); **121**, 2196 (1922); **125**, 710 (1924); **127**, 748 (1925); J. V. Baches, R. W. West and M. A. Whitely, *ibid.*, **119**, 360, 378 (1921); K. Meyer, *Ann.*, **380**, 212 (1911); M. Ehrenstein and M. Dunnenberger, *J. Org. Chem.*, **21**, 774 (1956); K. Balnović and V. Thaller, *ibid.*, **21**, 127 (1956); R. B. Wagner and J. M. Tome, *J. Am. Chem. Soc.*, **72**, 3477 (1950); M. L. Wolfrom and R. L. Brown, *ibid.*, **65**, 1516 (1943).

[24] We are indebted to Dr. Bernard L. Shaw of the University of Leeds for samples of these two transition metal hydrides and to Dr. Joseph Chatt of Imperial Chemical Industries Ltd. for discussions of these possibilities.

[CONTRIBUTION FROM THE EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

The Carbonylation of Organoboranes. I. The Carbonylation of Trialkylboranes. A Novel Synthesis of Trialkylcarbinols[1]

BY MELVILLE E. D. HILLMAN[2]

RECEIVED JUNE 28, 1962

Reactions of carbon monoxide with trialkylboranes have been discovered which gave a variety of novel products, depending on reaction temperature and solvent. Hexaalkyl-2,5-diboradioxanes and trialkylcarbinylboronic acids or anhydrides were obtained in near-quantitative yields. A reaction mechanism involving three boron-to-carbon alkyl migrations is proposed. Oxidation or hydrolysis of the intermediates gave the corresponding di- and trialkylcarbinols and dialkyl ketones in near theoretical yields.

Introduction

Although extensive research has lately been directed at the preparation of organoboranes,[3] very little has been reported on attempts to uncover new reactions of organoboranes.[4] Such studies seemed desirable in view of the extreme reactivity of organoboranes toward molecular oxygen. Although attempts to use organoboranes as "Grignard-type reagents" by reaction with carbon dioxide were unsuccessful, carbon monoxide reacted exothermally with trialkylboranes to give products in which novel rearrangements of the alkyl groups from boron to carbon had occurred.

Results and Discussion

When trialkylboranes (I) were carbonylated in ethers, hydrocarbons or in the absence of solvent, a mixture of products was obtained. When water or another hydroxylic solvent was used as the reaction medium, single products were obtained. Carbonylation of trialkylboranes at temperatures between 25° and 75° in the presence of excess water gave excellent yields of 2,3,3,5,6,6-hexaalkyl-2,5-dibora-1,4-dioxanes (II); whereas

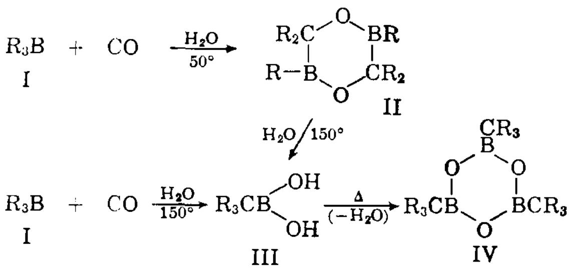
[1] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962; Abstracts of Papers, p. 9-Q.

[2] Exploratory Chemicals Section, California Research Corporation, Richmond, Calif.

[3] Some examples are: H. C. Brown, *Tetrahedron*, **12**, 117 (1961); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961); M. F. Hawthorne, *ibid.*, **83**, 2541 (1961); and E. L. Muetterties, *ibid.*, **82**, 4163 (1960).

[4] Recent review articles are: H. C. Brown, in "Organometallic Chemistry, ed. H. Zeiss, Reinhold Publishing Corp., New York, N. Y., 1960, pp. 150–193; H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; W. Gerrard, "The Organic Chemistry of Boron, Academic Press, Inc., New York, N. Y., 1961.

the same reaction at temperatures between 140° and 175° produced only the trialkylcarbinyl boronic acids (III). The boronic acids spontaneously dehydrated on vacuum distillation to give the corresponding boronic anhydrides (boroxines) (IV).[5] The diboradioxanes (II) were readily converted quantitatively into the trialkylcarbinylboronic acids (III) by heating with water at 150°. In the absence of water, hexaethyldiboradioxane did not isomerize to the boronic anhydride at 200°.



Basic peroxide oxidation of the boronic anhydrides resulted in quantitative yields of the corresponding trialkylcarbinols (V). Peroxide oxidation of compound II produced dialkylcarbinols (VI), traces of dialkyl ketone and alkanol. Alkaline hydrolysis of compound II gave the pure dialkylcarbinol VI.

$$IV + H_2O_2 \xrightarrow{NaOH} \underset{V}{3R_3COH} + 3B(OH)_3$$

$$II + H_2O_2 \xrightarrow{NaOH} \underset{VI}{R_2CHOH} + ROH + R_2CO$$

$$II + H_2O \xrightarrow{NaOH} \underset{VI}{R_2CHOH}$$

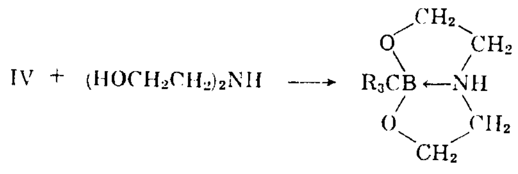
Because of the ease and high yields of these reactions, it is an excellent way to obtain trialkylcarbinols. The complete scheme has been demonstrated for tri-*n*-butylcarbinol (96% over-all yield from tri-*n*-butylboron).

$$6CH_3CH_2CH{=}CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2CH_2CH_2)_3B$$

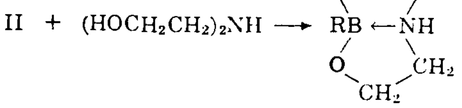
$$3(CH_3CH_2CH_2CH_2)_3B + 3CO \xrightarrow[150°]{H_2O} [(CH_3CH_2CH_2CH_2)_3CBO]_3$$

$$[(CH_3CH_2CH_2CH_2)_3CBO]_3 \xrightarrow[NaOH]{H_2O_2} 3(CH_3CH_2CH_2CH_2)_3COH$$

Further evidence for the structures of compounds II and IV was obtained by reaction with diethanolamine.[6] When the boronic anhydrides (IV) were refluxed with diethanolamine, benzene and ethanol, cyclic esters of the trialkylcarbinylboronic acids (VII), were formed as stable crystalline derivatives. The same reaction with the hexaalkyldiboradioxanes resulted in the cyclic esters of the alkylboronic acids (VIII). This reaction showed that the carbon–boron bond in the diboradioxane intermediate was unusually sensitive to hydrolysis.



VII

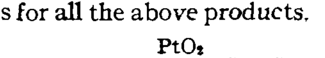


VIII

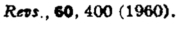
It may well be that all compounds having B–C–O bonding will be generally susceptible to hydrolysis.

Infrared and nuclear magnetic resonance spectra further established the structures of the organoboron intermediates. In the proton n.m.r. spectrum of the triethylborane, the methyl and methylene hydrogens are not significantly shifted apart; the spectrum is a broad, highly complex series of peaks centered at $\delta(CH_3)_4Si = 0.94$. The proton n.m.r. spectrum of triethylcarbinylboronic anhydride (IV, R = C_2H_5), however, exhibits a typical A_3B_2 spectrum with $V/\delta \cong 0.1$–0.2[7] analogous to that of triethylcarbinol. The ratio of methyl to methylene hydrogens is 3.2/2.0, in good agreement with the figure (3/2) calculated for a structure with all ethyl groups bonded to tertiary carbon, none to boron. 2,3,3,5,6,6-Hexaethyl-2,5-diboradioxane (II, R = C_2H_5) exhibits a similar A_3B_2 spectrum. In this case, however, the ratio of "methyl" to "methylene" is 2.88/1, in good agreement with the figure 2.75/1 (= 11/4) calculated on the assumption that methylene hydrogens of ethyl groups bonded to boron appear in the higher field "methyl" absorption. Thus II (R = C_2H_5) has nine methyl hydrogens plus two from the methylene group bonded directly to boron (a total of 11) and four hydrogens from methylene bonded to tertiary carbon.

Although no solid derivatives could be prepared from the tertiary alcohols obtained by oxidation of the boronic acids (III) or anhydrides, triethylcarbinol obtained by this process was dehydrated to give a quantitative yield of 3-ethyl-2-pentene (IX) which was hydrogenated with a platinum catalyst to 3-ethylpentane (X). The infrared and analytical data agreed with the structures for all the above products.



$$(C_2H_5)_3COH \xrightarrow[\Delta]{I_2} \underset{IX\quad C_2H_5}{C_2H_5C{=}CHCH_3}$$



$$IX + H_2 \xrightarrow{PtO_2} \underset{X\quad C_2H_5}{C_2H_5CHC_2H_5}$$

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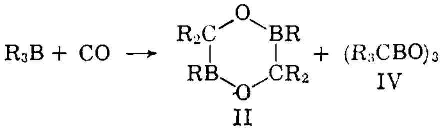
[5] After these studies were completed, patents were published which described the trialkylboron carbonyls analogous to the known borane carbonyl, $H_3B\cdot CO$. Compounds of composition $[R_nB\cdot CO]_{4-n}$, where *n* = 1, 2, 3 and 4 are reported: *Cf.* W. Reppe and A. Magin, German Patent 1,007,130, February 25, 1960, and French Patent 1,233,848, October 12, 1960.

[6] R. L. Letsinger and I. Skoog, *J. Am. Chem. Soc.*, **77**, 2491 (1955).

[7] L. M. Jackman, "Applications of N.M.R. Spectroscopy in Organic Chemistry, Pergamon Press, New York, N. Y., 1959, p. 96; P. L. Corio, *Chem. Revs.*, **60**, 400 (1960).

TABLE I

CARBONYLATION OF TRIALKYLBORANES



R	Solvent	Max. press., atm.	Max. temp., °C.	Product Yields, % II	IV	Other
C_2H_5–	H_2O	700	52	95		
C_2H_5–	H_2O	500	76	89		
C_2H_5–	H_2O	1	50	90		[a]
C_2H_5–	H_2O	950	150		92	
C_2H_5–	CH_3CH_2OH	750	80	95		
C_2H_5–	CH_3CH_2OH	950	150		89	9[b]
C_2H_5–	Acetone–H_2O (80%)	750	40	95		
C_2H_5–	Phenol–H_2O (75%)	650	150		83	6[c]
n-C_4H_9–	H_2O	725	80	84		
n-C_4H_9–	H_2O	700	150		85	
n-C_4H_9–	H_2O	700	150			96[d]
iso-C_4H_9–	H_2O	500	75	81		
n-C_4H_{13}–	H_2O	900	50	94		
n-C_6H_{13}–	H_2O	900	150		96	
n-C_8H_{17}–	H_2O	900	50	89		
n-C_8H_{17}–	H_2O	900	150		68	
C_2H_5–	Ether	900	50	72	15	
C_2H_5–	Ether	600	75	74	13	
C_2H_5–	T.H.F.	800	155		60	
C_2H_5–	T.H.F.	1	29			38[e]
C_2H_5–	*n*-Pentane	700	35		61	
C_2H_5–	None	230	75			38[e]
n-C_4H_9–	Ether	1000	75		78	
n-C_4H_9–	Ether	975	35		62	
C_2H_5–	Dioxane	700	50	95		
C_2H_5–	Glyme	650	50	96		
C_2H_5–	Triethyl orthoformate	650	50	93		

[a] 74% recovery of unreacted triethylboron. [b] A 9% yield of diethyl triethylcarbinylboronate was obtained. [c] A 6% yield of diphenyl triethylcarbinylboronate was obtained. [d] After basic peroxide oxidation an over-all yield of 96% of tri-*n*-butylcarbinol was obtained. [e] Over-all yield of triethylcarbinol after peroxide oxidation.

TABLE II

2,3,3,5,6,6-HEXAALKYL-2,5-DIBORADIOXANES (II)

R	Formula	B.p., °C.	Mm.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Boron, % Calcd.	Found	Mol. wt.[a] Calcd.	Found
C_2H_5–	$C_{14}H_{30}B_2O_2$	114	10[b]	66.72	66.80	12.00	12.01	8.59	8.69	252	251
					66.42		12.04		8.48		253
n-C_4H_9–	$C_{26}H_{54}B_2O_2$	154	0.7	74.29	73.72	12.95	12.91	5.15	5.26	420	425
					73.59		12.68				
iso-C_4H_9–	$C_{26}H_{54}B_2O_2$	125	10[c]	74.29	74.32	12.95	13.04	5.15	5.22	420	436
					74.52		13.14		5.15		433
n-C_4H_{13}–	$C_{38}H_{78}B_2O_2$	[d]		77.54	76.95	13.35	13.45	3.68	4.17	589	527
					77.29		13.75				
n-C_4H_{17}–	$C_{50}H_{102}B_2O_2$	[d]		79.33	79.25	13.58	13.75	2.96	3.15	757	591
					78.94		13.65		3.16		586

[a] Mol. wt. determinations by freezing point depression in benzene. [b] A paraffin-like waxy solid, freezing point approximately 42°. [c] M.p. 143°. [d] Volatile material was distilled off at 110° (0.5 mm.); the pot residue was a clear colorless liquid and was analyzed without further purification.

Table I contains a summary of the reaction conditions and yields of some of the carbonylation reactions carried out under this study. The reaction conditions were maintained until the carbon monoxide uptake had ceased (usually in 1 to 2 hours). Although the reaction was usually carried out under a carbon monoxide pressure of 500–900 atmospheres, a good yield of the hexaethyldiboradioxane (90%) was obtained by passing a stream of carbon monoxide through a mixture of triethylborane and water for 24 hours; however, the conversion was only 26%. When a similar reaction was run in ether instead of water, the only isolated product was triethylcarbinylboronic anhydride.

In general, the best and reproducible yields of diboradioxanes were obtained by running the reactions in water or highly polar solvents (dioxane, triethylorthoformate or glyme (1,2-dimethoxy-

TABLE III

TRIALKYLCARBINYLBORONIC ANHYDRIDES (IV)

R	Formula	B.p., °C.	B.p., Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Boron, % Calcd.	Boron, % Found	Mol. wt.[a] Calcd.	Mol. wt.[a] Found
C_2H_5–	$C_{21}H_{45}B_3O_3$	135	0.5	66.72	66.83	12.00	11.92	8.59	8.71	363	361
					66.78		12.01		8.64		367
n-C_4H_9–	$C_{39}H_{81}B_3O_3$	210	0.02	74.29	73.91	12.95	12.96	5.15	5.55	631	659
					73.63				5.51		658
n-C_6H_{13}–	$C_{57}H_{11}B_3O_3$	[b]		77.54	77.36	13.35	13.22	3.68	3.85	883	869
											837
n-C_8H_{17}–	$C_{75}H_{153}B_3O_3$	[b]		79.33	79.35	13.58	13.77	2.96	3.20	1135	1086
					79.04		13.71		3.01		1032

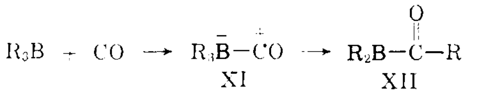
[a] Mol. wt. determinations by freezing point depression in benzene. [b] Volatile impurities were removed by distillation at 180° (0.8 mm.); the pot residue was a clear colorless liquid and was analyzed without further purification.

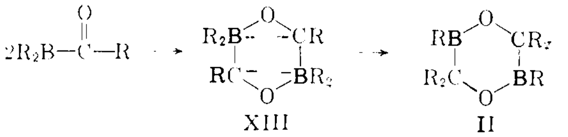
methane)) near room temperature. The best yields of boronic anhydrides were obtained by running the reactions in water at about 150°.

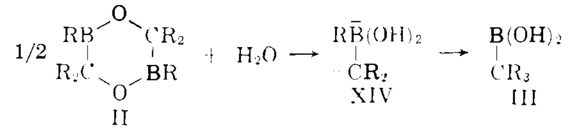
When ethers or hydrocarbons were used as solvents, the results were erratic; lower yields and mixtures were usually obtained.

Mechanism

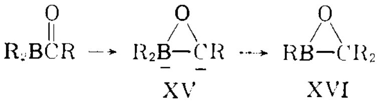
The proposed mechanism involves three migrations, in which the alkyl group migrates with its bonding electrons from negative boron to positively charged carbon. Although the known borane-carbonyl is apparently stable to rearrangement, the corresponding trialkylborane-carbonyl (XI) could not be isolated in this investigation. The postulated intermediate XII after one alkyl migration could not be detected in the reaction products; and it is proposed that this intermediate dimerizes to XIII, which then rearranges to II. The hexaalkyldiboradioxane (II) was stable in water at 80°, but at 140° it was completely isomerized to the boronic acid III.

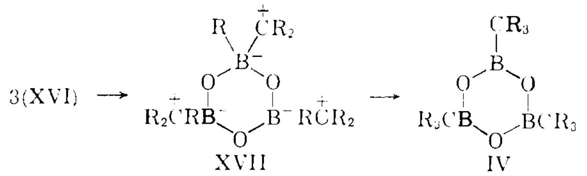




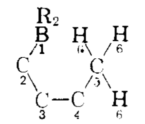


In the absence of hydroxylic solvents, a second mechanism may occur since the hexaalkyldiboradioxanes were not isomerized to the anhydrides at 200° and since changes in reaction temperature did not consistently alter the ratio of products formed. One possible mechanism could involve a three-membered ring intermediate (XVI), which trimerizes to XVII with C–O bond cleavage, followed by the last alkyl migration. The hexaalkyldiboradioxane intermediate could arise through dimerization of either XII or XVI.





Although a quantitative kinetic investigation was not undertaken, the rate of carbonylation for triethylborane was observed to be much faster than the rate for tri-n-butylborane. However, when larger groups, such as n-hexyl and n-octyl, were used there was no appreciable decrease in rate over that observed for the n-butyl system. This could be explained by Newman's "rule of six."[8] The "six-number" is zero for triethylborane and nine for tri-n-butyl-, tri-n-hexyl-, and tri-n-octyl-boranes. The shielding effect of the atoms in the "six-position" is



This observation apparently extends the "rule of six" to include reactions of systems not containing a double bond.

Experimental

N.m.r. spectra were obtained with a Varian high resolution spectrometer using a V-4311 r.f. unit operating at 56.4 Mc./s. Solutions were about 20% by volume in carbon tetrachloride.

$$\delta_{(CH_3)_4Si} \equiv \frac{\text{freq. }(CH_3)_4Si - \text{freq. sample}}{56.4}$$

Integrated areas were obtained from appropriate curves using a planimeter.

Trialkylboranes.—Triethyl- and tri-n-butylborane were obtained from Callery Chemical Co. and were used without further purification. The higher alkylboranes were prepared by modification of literature procedures.[3] The preparation of tri-n-hexylborane is described below as an example of this procedure.

Partially decomposed diborane of unknown composition was passed through a Dry Ice trap into a flask containing 1-hexene (84 g., 1.0 mole, Phillips Petroleum Co.) and anhydrous diethyl ether (200 ml). The exhaust gases were bubbled through an acetone trap. After passing diborane through the flask for 3 hours, 1-hexene (101 g.) was added dropwise with external cooling (very exothermic). The solvent and excess 1-hexene were removed by distillation, and the residue was vacuum distilled until the pot temperature reached 220° (1.5 mm.). The pot residue (134.7 g.) of

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(8) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950); M. S. Newman in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 206.

tri-*n*-hexylborane was a clear, colorless liquid and was analyzed without further purification.

Anal. Calcd. for $C_{18}H_{39}B$: C, 81.18; H, 14.76; B, 4.06. Found: C, 80.71; H, 14.82; B, 4.06, 4.11.

2,3,3,5,6,6-Hexaethyl-2,5-diboradioxane.—A stainless steel-lined shaker tube (325-ml. capacity) was charged with water (70-ml.) and triethylborane (50 g.). The bomb was gradually pressurized[9] with carbon monoxide to 200 atmospheres, and an exothermic reaction (temperature rise 25° to 37°) resulted. The pressure of carbon monoxide was gradually increased to 700 atmospheres, and the temperature was increased to 50°. The bomb was agitated for 1 hour in a pendulum shaker under these conditions. After cooling, the layers were separated under nitrogen, and the water layer was washed twice with ether. The combined organic layers were washed with water then with saturated NaCl solution, dried with $MgSO_4$, and concentrated. Vacuum distillation of the residue gave hexaethyldiboradioxane as a waxy white solid, b.p. 110° to 114° (10 mm.), 61.1 g., 95%. The analytical data are recorded in Table II.

The reaction in organic solvents is illustrated by the following example. The shaker tube was charged with dioxane (100 ml.), triethylborane (50.0 g.) and carbon monoxide (700 atm.). The bomb was heated at 50° for 1 hour, then cooled, discharged, and rinsed with ether. The resulting solution was concentrated and vacuum distilled to give hexaethyldiboradioxane, b.p. 72° to 80° (0.5 mm.), 61.2 g., 95%.

2,3,3,5,6,6-Hexaisobutyl-2,5-diboradioxane.—The shaker tube was charged with triisobutylborane (56.5 g., 0.31 mole) and water (75 ml.). Carbon monoxide was gradually introduced to a pressure of 500 atmospheres. The bomb was then heated at 75° for 4 hours. A maximum pressure of 770 atmospheres was obtained. The product was extracted with ether, dried, and vacuum distilled twice to give hexaisobutyldiboradioxane as a white crystalline solid, b.p. 123° to 128° (10.3 mm.), 52.6 g., 81%. The product was recrystallized twice from aqueous ethanol to give white plates, m.p. 143°. The analytical data are recorded in Table II.

2,3,3,5,6,6-Hexa-*n*-octyl-2,5-diboradioxane.—The bomb was charged with water (75 ml.), tri-*n*-octylborane (57.3 g., 0.1635 mole) and carbon monoxide (900 atm.). The bomb was agitated for 90 minutes at 25° to 30° then for an additional 90 minutes at 50°. The product was ether extracted, dried and concentrated; then all volatile material was removed by heating under vacuum (100°/0.5 mm). The residue was a clear colorless oil assumed to be hexa-*n*-octyldiboradioxane (54.9 g., 89%). The analytical data and the results of other reactions leading to diboradioxane intermediates are outlined in Tables I and II.

Triethylcarbinylboronic Anhydride (Tris - triethylcarbinylboroxine).—The shaker tube was charged with water (75 ml.) and triethylborane (61.5 g., 0.63 mole). Carbon monoxide was introduced gradually to a pressure of 700 atmospheres, and the temperature was then increased gradually to 150° (maximum pressure 860 atm.). After agitation for 2 hours the contents of the bomb were cooled, and the resulting layers were separated. The water layer was washed with ether, and the combined organic layers were washed with saturated sodium chloride solution, dried with calcium sulfate, and concentrated. Vacuum distillation resulted in severe bumping and cloudiness; the first fraction, b.p. 52° to 72° (10 mm.), 12.4 g., was mostly water. The next fraction, b.p. 125° to 145° (0.6 mm.), 72.7 g., 91%, was triethylcarbinylboronic anhydride. The analytical data are recorded in Table III.

Tri-*n*-butylcarbinylboronic Anhydride.—The shaker tube bomb was charged with water (75 ml.) and tri-*n*-butylborane (115 g., 0.632 mole). The bomb was charged with carbon monoxide to 700 atmospheres then heated at 50° for 25 minutes. The temperature was then increased to 150° and maintained for 2 hours. The maximum pressure obtained was 950 atmospheres. The product was extracted with ether, dried, and refluxed with toluene to remove water of dehydration with an esterification tube. Vacuum distillation gave tri-*n*-butylcarbinylboronic anhydride, b.p. 170° to 230° (20 mμ), 111.6 g., 84%.

A combination of product from two runs (same reaction conditions as above) starting with a total of 236.1 g. of tri-*n*-butylborane was oxidized directly with a 75% excess of hydrogen peroxide and 6 *N* sodium hydroxide. Vacuum distillation of the resulting product gave tri-*n*-butylcarbinol (5-butylnonanol-5), b.p. 80° to 95° (10.5 mm.), 216.5 g., 96%.

Tri-*n*-hexylcarbinylboronic Anhydride.—The shaker tube was charged with water (75 ml.), tri-*n*-hexylborane (59.5 g., 0.223 mole) and carbon monoxide (900 atm.). The tube was heated at 50° for 1 hour and at 150° for 2 hours. The product was worked up in the usual manner, and all volatile materials were distilled off by heating to 150° (0.6 mm.). The residue was a clear, colorless liquid assumed to be tri-*n*-hexylcarbinylboronic anhydride (65.6 g., 96%).

Isomerization of 2,3,3,5,6,6-Hexaethyldiboradioxane in Water.—A mixture of hexaethyldiboradioxane (195.1 g.) and water (150 ml.) was heated in the bomb at 140° for 1 hour, then cooled and extracted with ether. The ether layers were combined, dried, concentrated, and vacuum distilled to give triethylcarbinylboronic anhydride as a clear, colorless oil, b.p. 135° to 143° (0.6 mm.), 177.2 g., 91%.

Basic Hydrolysis of 2,3,3,5,6,6-Hexaethyldiboradioxane.—A mixture of hexaethyldiboradioxane (31.8 g.) and 6 *N* sodium hydroxide (100 ml.) was refluxed for 1 hour then steam distilled. The water layer of the distillate was extracted three times with ether; and the combined organic layers were dried ($MgSO_4$), concentrated, and distilled to give 3-pentanol as a clear, colorless liquid, b.p. 112° to 115° (16.7 g., 75%). The α-naphthylurethan derivative melted at 95° to 96°, and there was no depression in melting point when it was mixed with an authentic sample (lit.[10] 95°). The infrared spectrum of the product was identical with that of a commercial sample.

Peroxide Oxidation of Triethylcarbinylboronic Anhydride.—Aqueous sodium hydroxide (52 ml. of 6 *N*, 20% excess) was added slowly under nitrogen to triethylcarbinylboronic anhydride (32.1 g., 0.55 mole) with mechanical stirring followed by dropwise addition of 30% aqueous hydrogen peroxide (31 ml., 20% excess). During the peroxide addition the temperature increased from 25° to 70°. The mixture was heated under reflux (2 hours), cooled, and extracted 3 times with ether. The combined ether layers were dried with magnesium sulfate, concentrated, and distilled to give triethylcarbinol as a clear, colorless oil having a strong camphoric odor, b.p. 140° to 145° (25.8 g., 99%).

Peroxide Oxidation of Tri-*n*-hexylcarbinylboronic Anhydride.—Aqueous (30%) hydrogen peroxide (28 ml., 75% excess) was added slowly to a mixture of tri-*n*-hexylcarbinylboronic anhydride (46.4 g.) and 6 *N* sodium hydroxide (46 ml., 75% excess) with external cooling. The mixture was refluxed for 2 hours, cooled, and extracted three times with ether. The combined ether layers were dried with magnesium sulfate, filtered, concentrated, and distilled to give tri-*n*-hexylcarbinol as a clear, colorless oil, b.p. 121° to 123° (0.2 mm.), 12.3 g., 43%, and a pot residue of the starting material (16.6 g.). There appeared to be some dehydration of the tertiary alcohol to give the corresponding olefin during the distillation.

Anal. Calcd. for $C_{19}H_{40}O$: C, 80.21; H, 14.17; mol. wt., 285. Found: C, 81.29, 81.42; H, 14.35, 14.44; mol. wt., 303.

Reaction of Hexaethyldiboradioxane with Diethanolamine.—A mixture of hexaethyldiboradioxane (21.5 g.), diethanolamine (17.9 g., 0.171 mole), ethanol (200 ml.) and benzene (80 ml.) was refluxed under nitrogen so that water liberated during the reaction was collected in an esterification tube. Excess solvent was removed by distillation, and the residual solution was allowed to cool and then was filtered to give the diethanolamine ester of ethylboronic acid as small white plates (19.2 g., 59%). The product was recrystallized from benzene then from acetone; m.p. 165° to 166°.

Anal. Calcd. for $C_6H_{14}BNO_2$: C, 50.39; H, 9.87; N, 9.79; B, 7.57; mol. wt., 143. Found: C, 50.32, 50.81; H, 9.99, 10.33; N, 10.23, 10.11; B, 7.44; mol. wt., 150, 158.

Reaction of Triethylcarbinylboronic Anhydride with Diethanolamine.—A sample of triethylcarbinylboronic anhydride was allowed to react under identical conditions to

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[9] In one experiment the carbon monoxide was introduced quickly to 200 atmospheres, and the resulting exothermic reaction resulted in a temperature increase from 25° to 185°.

[10] A. J. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 264.

the above reaction to give the ethanolamine ester of triethylcarbinylboronic acid as small white plates, m.p. 131° to 133°.

Anal. Calcd. for $C_{11}H_{24}NBO_2$: C, 61.99; H, 11.35; N, 6.57; B, 5.08; mol. wt., 213. Found: C, 62.13, 62.18; H, 11.49, 11.60; N, 6.52, 6.45; B, 4.96; mol. wt., 217, 209.

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2-Bora- and 2-Thia-1,3-diazaazulenes

BY H. E. HOLMQUIST AND R. E. BENSON

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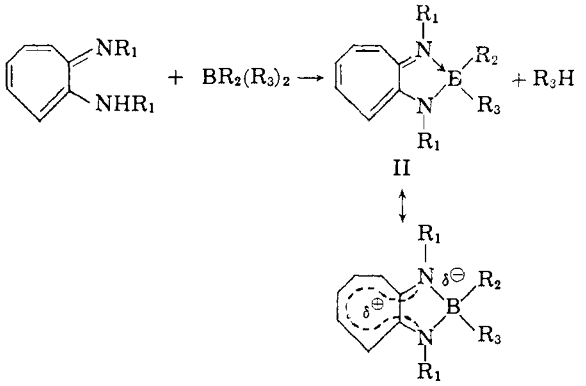
Reaction of 1-amino-7-imino-1,3,5-cycloheptatrienes with selected boron esters and halides has given chelated derivatives that are regarded as examples of the previously unknown 2-bora-1,3-diazaazulenes. This five-membered ring system is unusually stable to hydrolysis for a compound containing boron–nitrogen bonding. Aryl and alkoxyl substituents on boron are hydrolytically cleaved before the boron–nitrogen bond is ruptured. Condensation of the parent aminoimine with sulfur oxytetrafluoride has given 2-fluoro-2-oxo-2-thia-1,3-diazaazulene.

The 1-amino-7-imino-1,3,5-cycloheptatrienes (I) are non-classical aromatic compounds[1] readily accessible from the reaction of tetrafluorocycloheptadienes with primary amines. These compounds are bidentates and form chelate derivatives with metallic ions.[1,2] We have now found that the aminoimines I react readily with a variety of boron derivatives to give chelated boron compounds II in which the fourth valence of the boron atom is satisfied by a coördinate bond from the imino-nitrogen atom. These are appropriately regarded as derivatives of the previously unknown 2-bora-1,3-diazaazulene, the first completely conjugated system containing a boradiazole ring.

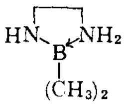


Ia, R_1 = H, CH_3, p-$CH_3OC_6H_4$
b, R_2 = F, OCH_3, C_6H_5, OH
c, R_3 = F, OH, OCH_3, OC_2H_5, C_4H_9

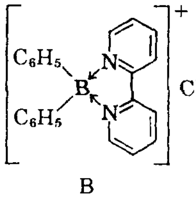
Hydrolytic Stability.—Evidence for appreciable electron delocalization in II was found in hydrolysis studies. Thus, the five-membered ring is stable to neutral, acidic and alkaline conditions, although the aryl and alkoxyl groups attached to the boron atom are replaced by hydroxyl groups.

The stabilization of boron esters toward hydrolysis through complex formation with amines has been observed previously. Thus, the hydrolytic stability of esters of ethanolamine with diaraneborinic acids,[3] diethanolamine with araneboronic acids,[4] and triisopropanolamine with boric acid[5] has been attributed to a transannular coördinate bond from the nitrogen atom to the boron atom. Compound II appears to be a special example of coördinate bonding of nitrogen to boron.

A number of 2,1,3-boradiazolines have been described in the literature. Goubeau and Zappel[6] found that A was obtained as one of the reaction products of ethylenediamine and trimethylborane. Later, several benzo-2,1,3-boradiazolines[7] were synthesized by condensation of *o*-phenylenediamines with various boron acids, esters and halides and are reported to be hydrolytically unstable. A further example of boron bonding to two nitrogen atoms in a five-membered ring is furnished by B.[8]



A



B

Although comparable results are not available, the greatest stability for a boron–nitrogen system appears to lie in the borazarenes of Dewar, in which the borazine ring contains tetracoördinate boron as a part of a conjugated bi- or tricyclic system, for example, C.[9]

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[1] W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

[2] The nickel chelates are paramagnetic and give large contact shifts in n.m.r. These studies have permitted the determination of electron spin densities in a variety of substituents located on the nitrogen atoms and on the seven-membered ring; see, for example, R. E. Benson, D. R. Eaton, A. D. Josey and W. D. Phillips, *ibid.*, **83**, 3714 (1961).

[3] R. L. Letsinger and N. Remes, *ibid.*, **77**, 2389 (1955); R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955).

[4] O. C. Musgrave and T. O. Park, *Chemistry & Industry*, 1552 (1955).

[5] H. Steinberg and D. L. Hunter, *J. Am. Chem. Soc.*, **82**, 853 (1960).

[6] J. Goubeau and A. Zappel, *Z. anorg. allgem. Chem.*, **279**, 38 (1955).

[7] (a) M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3076 (1958); (b) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958); (c) E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959); (d) L. F. Hohnstedt and A. M. Pellicciotto, Abstracts of 137th American Chemical Society Meeting, 1960, p. 7-O; P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[8] J. M. Davidson and C. M. French, *Chemistry & Industry*, 750 (1959).

[9] See M. J. S. Dewar and P. M. Maitlis, *Tetrahedron*, **15**, 35 (1961), and preceding papers.