The Carbonylation of Organoboranes. II. The Carbonylation of Trialkylboranes in the Presence of Glycols[1,2]

By M. E. D. Hillman[3]

The carbonylation of trialkylboranes in the presence of glycols gave cyclic esters of trialkylcarbinylboronic acids having 5–7 atoms in the ring. The use of 1,5- or 1,6-diols gave rise to polymeric materials. The compounds prepared had unusual hydrolytic and oxidative stability.

Results and Discussion

When the lower trialkylboranes (I) were carbonylated in the presence of water, readily distillable trialkylcarbinylboronic anhydrides (boroximes) (III) were obtained in good yields.[4] However, with larger alkyl groups, the trimeric, high molecular weight products

$$R_3B + CO \xrightarrow[150°]{H_2O} R_3CB \begin{matrix} OH \\ \diagdown \\ OH \end{matrix} \xrightarrow{\Delta}$$
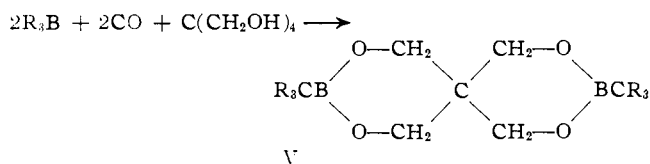
I   II   III
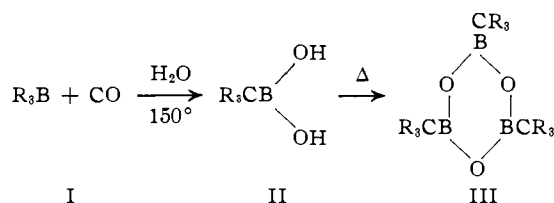
could not be vacuum distilled. Attempts to find monomeric derivatives of the boronic acids (II) led to the present discovery. For example, 2-trialkylcarbinyl-2-bora-1,3-dioxolanes (IV) were prepared in excellent yield by running the carbonylation reaction

$$R_3B + HOCH_2CH_2OH + CO \longrightarrow R_3CB \begin{matrix} O—CH_2 \\ | \\ O—CH_2 \end{matrix}$$

IV
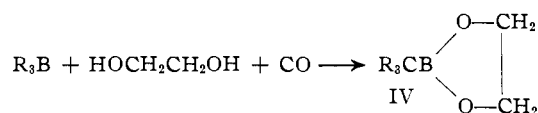
in the presence of excess ethylene glycol. This product was also prepared by esterifying the boronic anhydride (III) with ethylene glycol. Corresponding products were obtained by running the carbonylation reaction in 1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,3-butanediol or 1,5-pentanediol. The product from the latter reaction partially polymerized on distillation. The product from the reaction of 1,6-hexanediol had the appearance and properties of a low molecular weight polymer. The cyclic boronic ester from pinacol was obtained by the esterification procedure.

A novel spiro compound (V) was prepared by running the carbonylation of triethylboron in the presence of pentaerythritol.

$$2R_3B + 2CO + C(CH_2OH)_4 \longrightarrow$$

V

All of the cyclic boronic esters were stable to air and water and were soluble in all common organic solvents including hydrocarbons but were insoluble in water. The lower members were distilled at atmospheric pressure without detectable decomposition or air oxidation. The product from triethylborane and ethylene glycol (IV, R = C_2H_5) was steam distilled with no indication of hydrolysis. Oxidation of the cyclic esters with basic peroxide gave the corresponding trialkylcarbinols in good yields.

When the carbonylation of triethylboron was carried out in the presence of polyvinylalcohol, approximately 85% of the hydroxyl groups was esterified, resulting in a water-insoluble, hydrolytically stable polymer (VI) which was soluble in common organic solvents.

$$R_3B + CO + \left[CHCH_2CH—CH_2 \right]_n \longrightarrow$$

VI
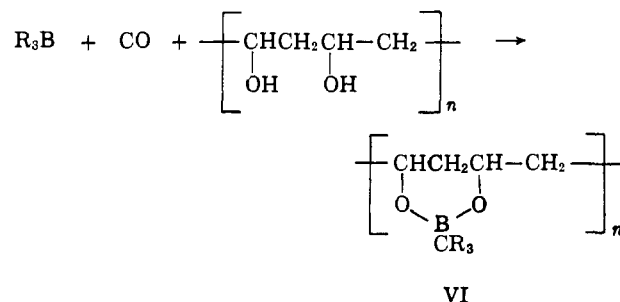
The polymer could be cast into transparent colorless films and drawn into fibers.

Table I contains a summary of the reaction conditions, yields and analyses of some of the carbonylation reactions carried out during this investigation. The reactions were all run for about 1 hour at 25–50° then at 150° for 2 hours. Some representative examples are described in detail in the Experimental section.

Mechanism.—The mechanism of the carbonylation in water and non-hydroxylic solvents has already been discussed in detail.[1] The first part of the reaction path may be identical with the reaction when carried out in water.

$$2R_3B + 2CO \longrightarrow 2R_3\bar{B}—\overset{+}{C}O \longrightarrow 2R_2B—\overset{O}{\overset{\|}{C}}—R \longrightarrow$$

VI

(1) Paper I, M. E. D. Hillman, J. Am. Chem. Soc., 84, 4715 (1962).
(2) Presented at the Pacific Southwest Regional Meeting of the American Chemical Society, Claremont, Calif., December 1, 1962.
(3) Exploratory Chemicals Section, California Research Corporation, Richmond, Calif.
(4) M. E. D. Hillman, Abstracts of the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962; Abstracts, p. 9-Q.

TABLE I

Borane	Polyol	Yield, %	B.p. °C	mm.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Boron, % Calcd.	Found
Triethyl	Ethylene glycol	94^a	50	0.5	$C_9H_{19}BO_2$	63.56	64.17	11.26	11.60	6.36	6.69
Triethyl	1,3-Propanediol	95	56	.65	$C_{10}H_{21}BO_2$	65.24	65.17	11.49	11.52	5.88	5.93
							65.45		11.47		5.93
Triethyl	1,4-Butanediol	49	68	.5	$C_{11}H_{23}BO_2$	66.69	66.68	11.70	11.82	5.46	5.82
							66.98		11.86		6.02
Triethyl	2,3-Butanediol	90	50	.5	$C_{11}H_{23}BO_2$	66.69	66.69	11.70	11.81	5.46	5.67
							66.51		11.69		5.81
Triethyl	1,3-Butanediol	90	67	.5	$C_{11}H_{23}BO_2$	66.69	66.61	11.70	11.85	5.46	5.64
							66.49		11.71		5.42
Triethyl	Pinacol	16^b	51	.2	$C_{13}H_{27}BO_2$	69.03	68.94	12.03	12.22	4.78	4.51
							69.13		12.03		4.48
Triethyl	Pentaerythritol	49	76–76.8^f		$C_{19}H_{38}B_2O_4$	64.81	64.68	10.88	11.08	6.15	5.68
							64.47		10.90		5.67
Triethyl	1,5-Pentanediol	55^c	150	.5^c	$C_{12}H_{25}BO_2$	67.94	68.51	11.88	11.96	5.10	4.85
Triethyl	Diethylene glycol	92	125	.35	$C_{11}H_{23}BO_3$	61.70	61.26	10.83	11.28	5.05	4.95
							61.40		11.10		4.69
Triethyl	Polyvinyl alcohol	^{d}			$[C_{11}H_{21}BO_2]_n$	67.37	65.36	10.80	11.02	5.52	4.54
							65.66		11.06		4.55
Tri-n-butyl	Ethylene glycol	59	96	.6	$C_{15}H_{31}BO_2$	70.86	70.40	12.29	12.40	4.26	4.22
							70.37		12.40		4.46
Tri-n-butyl	1,3-Propanediol	42	110	.14	$C_{16}H_{33}BO_2$	71.64	71.52	12.40	12.54	4.03	4.01
							71.37		12.47		4.23
Tri-n-butyl	Diethylene glycol	79	140	.5	$C_{17}H_{35}BO_3$	68.45	68.05	11.83	11.96	3.63	3.53
Tri-i-butyl	Ethylene glycol	65^e	90	.7	$C_{15}H_{31}BO_2$	70.86	70.89	12.29	12.34	4.26	4.67
							71.07		12.53		4.72
Tri-n-hexyl	Ethylene glycol	53	140	.2	$C_{21}H_{43}BO_2$	74.54	74.08	12.81	12.91	3.20	3.51
							73.90		13.07		3.72

^{a} A 94% yield was also obtained by the esterification of triethylcarbinylboronic anhydride. ^{b} By direct esterification. ^{c} A 20% pot residue of clear yellow polymer was also obtained; redistillation resulted in more of the polymeric material. ^{d} A quantitative yield of a foamy elastic solid was obtained which had analytical data corresponding to 85% esterification of the hydroxyl groups and which was soluble in organic solvents and insoluble in water. ^{e} A 32% yield of 2,3,3,5,6,6-hexaethyl-2,5-dibora-1,4-dioxane, m.p. 141–142, was also obtained. Total yield = 97%. The same solid was obtained previously[1] in the carbonylation of triisobutylborane in water at 75°. ^{f} M.p.

$VI + 2HOCH_2CH_2OH \longrightarrow$

[reaction scheme showing boron intermediate structures]
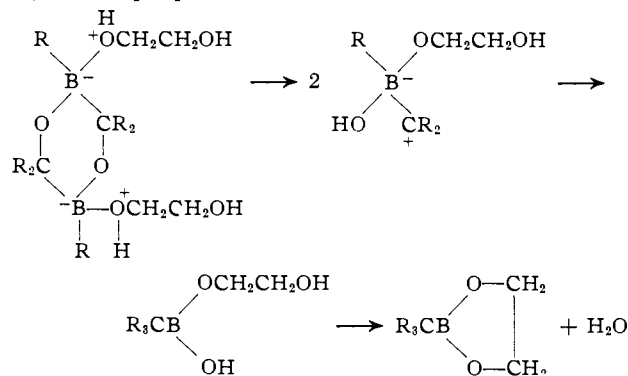
An alternate and perhaps preferable mechanism involves the direct reaction of the dialkylacylborane with the glycol followed by rearrangement.[5]

[reaction scheme]

$$R_2B-\overset{O}{\overset{\|}{C}}-R + HOCH_2CH_2OH \longrightarrow R_2\overset{+}{\bar{B}}-\overset{OH}{\underset{OCH_2CH_2OH}{\overset{|}{C}R}}$$

$$\underset{OCH_2CH_2OH}{\overset{OH}{RB-CR_2}} \longrightarrow R\bar{B}-\overset{+}{C}R_2 + H_2O \longrightarrow R_3CB \begin{smallmatrix} O-CH_2 \\ | \\ O-CH_2 \end{smallmatrix}$$
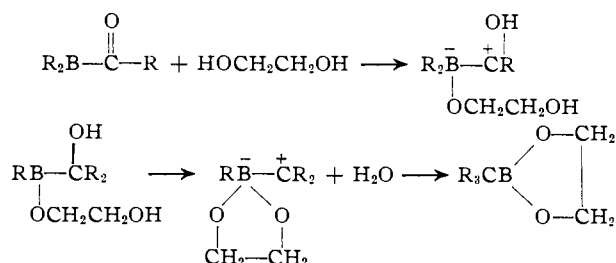
(5) The term acylborane is used here to designate the RCOB linkage. This term, however, has also been used to designate the RCOOB linkage by H. C. Brown and W. Korytnyk, *J. Am. Chem. Soc.*, **82**, 3866 (1960), and H. C. Brown and B. C. Subba Rao, *ibid.*, **82**, 681 (1960). Preferred nomenclature for the RCOOB linkage is acyl borate [*cf.* M. F. Lappert, *Chem. Rev.*, **56**, 959 (1956)] or acyloxyborane [*cf.* 1957 Report of the Commission on the Nomenclature of Inorganic Chemistry, *J. Am. Chem. Soc.* **82**, 5523 (1960)].

Experimental

A typical example of the general procedure is described below.

2-Triethylcarbinyl-2-bora-1,3-dioxolane.—A stainless steel lined shaker tube (325 ml.) was flushed with nitrogen, then charged with ethylene glycol (75 ml.) and triethylborane (53.0 g., 0.54 mole). Carbon monoxide was gradually introduced to a pressure of 650 atm. The bomb was heated at 50° for 1 hour and at 150° for 2 hours. The maximum pressure reached was 810 atm. The bomb was cooled, discharged, and rinsed with ether; and the resulting layers were separated. The glycol layer was extracted twice with ether; the combined ether layers were washed with water and saturated sodium chloride solution and dried with calcium sulfate. Vacuum distillation gave the title compound as a clear colorless mobile liquid, b.p. 50–52° (0.5 mm.) (86.6 g., 94.3%). The analyses are recorded in Table I. Subsequent runs gave yields of 92 and 95%. In the latter case, the distillation was carried out at atmospheric pressure with no decomposition; b.p. 195–196°. When this compound was exposed to the air in an open beaker for 48 hours, no noticeable change occurred in the infrared spectrum. This compound could be washed repeatedly with water with no noticeable hydrolysis occurring. A sample of the product was steam distilled by heating with an equal volume of water to give a 96% recovery of unreacted product.

The ethylene glycol ester of triethylcarbinylboronic acid was also prepared by refluxing a mixture of triethylcarbinylboronic anhydride, ethylene glycol and toluene and collecting the water formed in an esterification tube (94% yield).

2-Triethylcarbinyl-2-bora-1,3-dioxapane.—The title compound was prepared from 1,4-butanediol (100 ml.) and triethylborane (50 g.) in the usual manner. Vacuum distillation gave 2-triethylcarbinyl-2-bora-1,3-dioxapane as a clear colorless oil, b.p. 66–70°(0.5 mm.) (49.3 g., 49%). A second fraction, b.p. 120–125°(0.6 mm.), was characterized by its infrared spectrum[1] as triethylcarbinylboronic anhydride (21.4 g., 34%) (total yield, 83%).

The Esterification of Triethylcarbinylboronic Anhydride with Pinacol.—A mixture of triethylcarbinylboronic anhydride (18.7 g., 0.148 mole), pinacol (17.5 g., 0.148 mole) and benzene (200 ml.) was refluxed overnight so that the water of esterification was collected in an esterification tube. The resulting solution was concentrated; and the residue was vacuum distilled to give the pinacol ester of triethylcarbinylboronic acid as a

clear colorless oil, b.p. 50–52°(0.2 mm.)(5.0 g., 16%). Pinacol (3.5 g., 19%) was also recovered.

The Carbonylation of Triethylborane in Pentaerythritol.—The bomb was charged with pentaerythritol (39.0 g., 0.287 mole), ethanol (100 ml.) and triethylborane (60.0 g., 0.612 mole). The temperature was maintained at 50° for 30 minutes at a maximum carbon monoxide pressure of 670 atm. The temperature was then maintained at 150° for 2 hours at a maximum pressure of 890 atm. The bomb was cooled and washed with ether, and the resulting solution was concentrated. The solid residue was recrystallized twice from ethanol to give the spiro bicyclic pentaerythritol ester of triethylcarbinylboronic acid as white plates, m.p. 76–76.8° (49.3 g., 49%).

The Peroxide Oxidation of the Ethylene Glycol Ester of Triethylcarbinylboronic Acid.—A mixture of the ethylene glycol ester of triethylcarbinylboronic acid (70.1 g.), 6 N aqueous sodium hydroxide (84 ml., 30% excess) and 30% hydrogen peroxide (66 ml., 60% excess)[6] was refluxed for 2 hours, cooled, and extracted with ether. The combined ether layers were dried, concentrated, and distilled to give triethylcarbinol as a clear colorless liquid, b.p. 140–142° (39.1 g., 82%).

(6) The hydrogen peroxide should be added dropwise to a mixture of the boron compound and aqueous sodium hydroxide. The temperature should be kept below 50° during the addition, then the well stirred mixture brought slowly to reflux.

Kinetics of Autoxidation of Trialkylphosphines

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The kinetics of the autoxidation of tributylphosphines in o-dichlorobenzene have been studied by oxygen consumption measurements. The data indicate that the reaction involves the concurrent autoxidation of intermediate phosphinite esters. Tributyl phosphite was found to undergo autoxidation at a rate slower than that of tributylphosphine by a factor of at least 1.5. The data reveal that the reaction requires free radical initiation, which in this study was supplied by azobisisobutyronitrile. The autoxidation is a relatively long chain process with a very small activation energy.

Introduction

A recent investigation by Buckler has elucidated many of the important features of trialkylphosphine autoxidation.[3] For example, tributylphosphine in hexane was oxidized by air to a mixture of products identified as tributylphosphine oxide (42%), butyl dibutylphosphonate (49%), dibutyl butylphosphinate (6%) and tributyl phosphate (3%). A mechanism for the reaction was suggested on the basis of a detailed study of the products resulting from different reaction conditions. We wish to report the results of a kinetic study of the azobisisobutyronitrile (AIBN) initiated autoxidation of tributylphosphine, tributyl phosphite and triphenylphosphine in o-dichlorobenzene. Our data are compatible with the previously suggested mechanism and in addition provide some other facts regarding the reaction.

Results

Three experiments at 50.6° with o-dichlorobenzene as solvent showed that the total oxygen uptake for tributylphosphine was constantly 1.55 gram atoms of oxygen per mole of phosphine to within less than 0.5%. Isolation of the products corresponding to these conditions disclosed that two major products, tributylphosphine oxide and butyl dibutylphosphonate, are formed, in agreement with the work of Buckler.[3] The kinetics of this autoxidation were studied at temperatures between 38.0° and 60.0° by following oxygen consumption with time. The solvent used in this study, o-dichlorobenzene, was chosen because its low vapor pressure and its relatively inert behavior toward autoxidation reactions make it suitable for kinetic studies of this type. The action of AIBN as a reliable free radical initiator is well known.[4] The effect on the rate of initial substrate concentration, initiator concentration, oxygen pressure and the concentration of two inhibitors was studied. The dependency of the pseudo-first-order rate constant at 50.6° on initiator concentration is shown in Fig. 1. Two features of the reaction are immediately apparent from this plot. The zero

intercept suggests that the reaction requires radical initiation. In practice such initiation could be provided by the presence of trace amounts of impurities, leading to the well documented observation that trialkylphosphines are spontaneously oxidized by air. The second feature is the first-order dependence on the added initiator, which is usually found in radical chain processes involving unimolecular termination.[5]

Variation of oxygen pressure above the reaction solutions showed a curious effect. In the region from 740 mm. to about 200 mm., the observed pseudo-first-order rate constant was inversely proportional to the pressure. This effect is demonstrated in Table I, where the rate constant is shown to be constant with the constant ratio $[AIBN]/P_{O_2}$.

TABLE I

AUTOXIDATION OF TRIBUTYLPHOSPHINE

$[AIBN]/P_{O_2}$ = constant = 8.44×10^{-5} mole/l. × mm., T = 49.0°, $[(C_4H_9)_3P]_0 = 4.00 \times 10^{-2}$

$[AIBN] \times 10^2$	$P_{O_2}{}^a$	$k \times 10^4$, sec.$^{-1}$
6.25	740	5.51
5.00	592	5.18
3.75	444	5.25
2.50	296	4.96

a All pressures reported are corrected for vapor pressure of solvent.

The reaction is first order in tributylphosphine. At 50.6° with $[AIBN] = 9.08 \times 10^{-3}$ and initial concentrations of substrate ranging from 3.65×10^{-2} to 16.4×10^{-2} molar, eight runs disclosed that the pseudo-first-order rate constant showed no variable trends. With the oxygen pressure equal to 740 mm., this constant was 1.38×10^{-4} sec.$^{-1}$. The mean deviation was less than 10% of this constant.

The results of these experiments may be summarized by a kinetic equation in the form

$$- \frac{dO_2}{dt} = \frac{k[AIBN][(C_4H_9)_3P]}{p_{O_2}}$$

It should be mentioned that all kinetic runs were made under conditions which ensured that the reaction was kinetically controlled rather than diffusion controlled, throughout the entire duration of the experiment.

(1) From the M.S. Thesis of M. B. Floyd, 1961.

(2) Alfred P. Sloan Foundation Fellow.

(3) S. A. Buckler, J. Am. Chem. Soc., 84, 3093 (1962).

(4) (a) F. M. Lewis and M. S. Matheson, ibid., 71, 747 (1949); (b) C. G. Overberger, M. T. O'Shaughnessy and M. Shalit, ibid., 71, 2661 (1949); (c) M. Talat-Erben and S. Bywater, ibid., 77, 3712 (1955).

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 418.