

sodium O,S-diethyl phosphorothioate, 14.4 g., 33%, m.p. 213–214°.

Anal. Calcd. for C₄H₁₀O₃SPNa: C, 25.00; H, 5.25. Found: C, 25.43; H, 5.56.

(2).—Repetition of the above experiment using 4.44 g. (0.193 g.-atom) of sodium, 24 g. (0.386 mole) of ethyl mercaptan, 200 ml. of THF, 50 ml. of ethanol and 37 g. (0.187 mole) of O,O,S-triethyl phosphorothioate gave a 49% yield of sodium O,S-diethyl phosphorothioate, m.p. 213–214°, which, on recrystallization from a mixture of ether and ethanol, gave a product, m.p. 214.0–214.6°.

Anal. Calcd. for C₄H₁₀O₃SPNa: C, 25.00; H, 5.25. Found: C, 24.82; H, 5.03.

An aliquot portion of the filtrate from the above reaction mixture was treated with half its volume of ethanol and distilled through a 3-foot Fenske column to yield the ethanol-ethyl sulfide azeotrope in two fractions, b.p. 64–72.8° and 72.8–78°, reported²¹ 72.6°. A portion of this distillate was oxidized with hydrogen peroxide in acetic acid to give ethyl sulfone, m.p. 69–70.3°, in an amount corresponding to 83% over-all yield. Recrystallization from heptane gave a product, m.p. 71.5–72.5°, reported²² 72°.

(3).—A similar experiment was carried out at higher temperature in diglyme using 0.413 g. (18 mg.-atoms) of sodium, 2.0 g. (32.2 mmoles) of ethyl mercaptan, 15 ml. of diglyme and 3.18 g. (16.1 mmoles) of O,O,S-triethyl phosphorothioate. The stirred reaction mixture was maintained at 54° for 4 hours, at 65° for 18 hours and, finally, at 106° for 24 hours. After cooling, 25 ml. of water and 75 ml. of ether were added, the water was extracted several times with ether, and the combined extracts, after drying over sodium sulfate, were diluted to 250 ml. with ether. A 200-ml. portion of this solution was distilled, and the product boiling below 100° was collected and diluted to 250 ml. Analyses²³ for mercaptan and for sulfide plus mercaptan, by titration with iodine and with bromine, respectively, showed a total yield of 16.6 mmoles of sulfide obtained from 16.1 mmoles of phosphorothioate ester.

(4).—The possibility of cleavage of more than one ester linkage in the phosphorothioate molecule was investigated in an experiment similar to (3), except that 2.1 equivalents of sodium mer-

captide per mole of phosphorothioate were employed in twice the volume of diglyme solution. Analysis of the reaction product in similar fashion indicated 1.2 moles of sulfide formed per mole of phosphorothioate ester.

Reaction of Sodium Ethyl Mercaptide with Triethyl Phosphate.—A suspension of sodium ethyl mercaptide was prepared from 2.5 g. (0.108 g.-atom) of sodium and 10 ml. of ethyl mercaptan in 100 ml. of diglyme. When the sodium had dissolved, a current of nitrogen was passed through the solution to remove excess mercaptan. Then triethyl phosphate (18.2 g., 0.10 mole) was added, and the solution was maintained at reflux temperature overnight. The supernatant solution was decanted from the solid residue, diluted to 120 ml. with diglyme, and a 40-ml. portion was distilled through a 6-inch Vigreux column. Titration of the distillate as described above indicated 98% yield of sulfide based on the triethyl phosphate employed.

Reaction of Sodium Ethyl Mercaptide with O,O-Diethyl S-n-Butyl Phosphorothioate.—O,O-Diethyl S-n-butyl phosphorothioate (42.9 g., 0.187 mole) was added to a solution of sodium ethyl mercaptide prepared from 4.31 g. (0.187 mole of sodium, 60 ml. of ethanol, 200 ml. of THF and 24 g. (0.39 g.-atom) of ethyl mercaptan. The mixture was stirred at room temperature for 16 hours, during which time no precipitate was observed. After filtration to remove a trace of sediment, one-fourth of the filtrate (82.5 ml.) was diluted with 20 volumes of petroleum ether. When no precipitation occurred, even after standing 2 days in a refrigerator, the solution was concentrated by evaporation until crystals began to form. The precipitate obtained (m.p. 130–138°) was recrystallized from acetone to yield sodium O-ethyl S-n-butyl phosphorothioate, 7.51 g., 73%, m.p. 170–172°, showing an infrared spectrum very similar to that of sodium O,S-diethyl phosphorothioate (P=O at 1230 cm.⁻¹).

Anal. Calcd. for C₈H₁₄O₃PSNa: C, 32.74; H, 6.41; P, 14.08; S, 14.57. Found: C, 32.85; H, 6.72; P, 14.24; S, 14.26.

The remaining three-fourths of the reaction mixture (247.5 ml.) was treated with 50 ml. of ethanol and distilled through a 4-foot Fenske column with collection of the material boiling below 100°. Titration of this distillate as described previously indicated an 81% yield of sulfide. Oxidation of the crude distillate with H₂O₂ in acetic acid gave a 59% yield of ethyl sulfone, m.p. 72–73°; reported²² 72°, and for n-butyl sulfone²⁴ 50.5°, and for n-butyl sulfone²⁵ 43.5°.

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(25) N. Grabowsky, *Ann.*, **175**, 348 (1875).

(21) I. H. Horsley, "Azeotropic Data," *Advances in Chemistry Series No. 6*, American Chemical Society, Washington, D. C., 1952, p. 62.

(22) W. Strecker and R. Spitaler, *Chem. Ber.*, **59**, 1754 (1926).

(23) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 85, 93.

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

The Carbonylation of Organoboranes. III. The Reaction of Trialkylboranes with Carbon Monoxide and Aldehydes. Synthesis of a New Class of Organoboranes^{1,2}

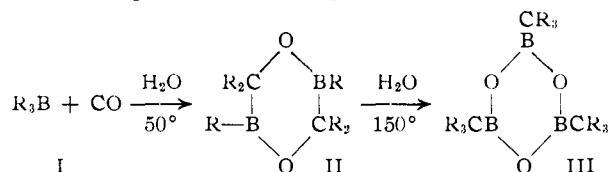
BY MELVILLE E. D. HILLMAN³

RECEIVED DECEMBER 29, 1962

A novel reaction between trialkylboranes, carbon monoxide and aldehydes gave substituted 4-bora-1,3-dioxolanes, a new class of organoboron heterocycles. A reaction mechanism involving boron to carbon alkyl migrations and a 1,3-dipolar addition is proposed. Heating at 150° with water completely converted the boradioxolanes to trialkylcarbonylboronic acids which dehydrated to the anhydrides on distillation.

Introduction

The reaction of trialkylboranes (I) with carbon monoxide in hydroxylic solvents has recently been shown⁴ to produce hexaalkyl-2,5-dibora-1,4-dioxanes



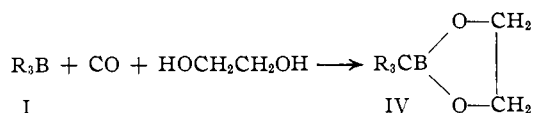
(1) Part II of this series: M. E. D. Hillman, *J. Am. Chem. Soc.*, **85**, 982 (1963).

(2) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963; Abstracts of Papers, p. 7-M.

(3) Present address: Exploratory Chemicals Section, California Research Corporation, Richmond, Calif.

(4) Melville E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 9-Q.

(II) or trialkylcarbonylboronic anhydrides (boroxines) (III) depending upon reaction temperature. The low molecular weight products (II, III, R = C₂H₅–C₄H₉) were readily distillable, but the higher alkyl products (II, III, R = C₆H₁₃–C₈H₁₇) could not be distilled with conventional laboratory apparatus. A procedure¹ was found to prepare directly readily distillable monomeric derivatives of the boronic anhydrides by conducting the carbonylation reaction in the presence of glycols. For example, the reaction of triethylborane with carbon monoxide and ethylene glycol produced a near quantitative yield of 2-triethylcarbonyl-1,3-dioxolane (IV).¹



Attempts to prepare monomeric derivatives of the

TABLE I

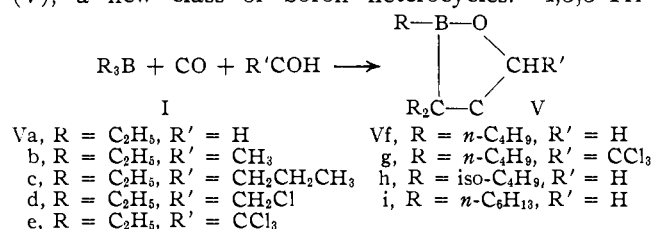
Borane	Aldehyde	Yield, %		°C.	B.p. ^a mm.	Formula	Carbon, %		Hydrogen, %		Boron, %	
		a	b				Calcd.	Found ^c	Calcd.	Found	Calcd.	Found
Triethyl	37% formaldehyde	48	48	68	22	C ₈ H ₁₇ BO ₂						
Tri- <i>n</i> -butyl	37% formaldehyde	38	49	80	0.5	C ₁₄ H ₂₉ BO ₂	70.00	69.52	12.17	12.24	4.51	4.18
								69.37		12.15		4.14
								69.51		12.14		4.45
Triisobutyl	37% formaldehyde	37	60	70	0.6	C ₁₄ H ₂₉ BO ₂	70.00	69.74	12.17	12.28	4.51	4.37
								69.51		12.14		4.45
Triethyl	Chloral hydrate	62		100	1.2	C ₉ H ₁₅ BO ₂ Cl ₃	39.53	39.65	5.90	5.87	3.96	3.81
								39.38		5.90		3.72
Tri- <i>n</i> -hexyl	37% formaldehyde	21	68	180	1.5	C ₂₀ H ₄₁ BO ₂	74.06	74.17	12.74	12.86	3.34	3.23
								74.26		12.98		3.29
Tri- <i>n</i> -butyl	Chloral hydrate	69		110	0.1	C ₁₅ H ₂₈ BO ₂ Cl ₃	50.38	50.45	7.89	7.88	3.03	3.21
												3.37 ^d
Triethyl	40% chloroacetaldehyde	92		60	0.2	C ₉ H ₁₅ BO ₂ Cl	52.85	52.56	8.87	9.04	5.29	5.04
								52.47		9.05		5.12 ^e
Triethyl	<i>n</i> -Butyraldehyde	75		55	0.5	C ₁₁ H ₂₃ BO ₂	66.36	66.69	11.70	11.43	5.46	5.72
								66.56		11.52		5.61
Triethyl	Acetaldehyde	74		35	0.25	C ₉ H ₁₉ BO ₂	63.56	63.71	11.26	11.24	6.36	6.51
								63.60		11.37		6.44

^a 4-Bora-1,3-dioxolanes. ^b 2,5-Dibora-1,4-dioxanes. ^c This compound was unstable, forming a white precipitate after several hours; no analyses obtained. ^d Calcd. Cl, 29.75; found Cl, 29.95, 29.81. ^e Calcd. Cl, 17.34; found Cl, 17.28, 17.47.

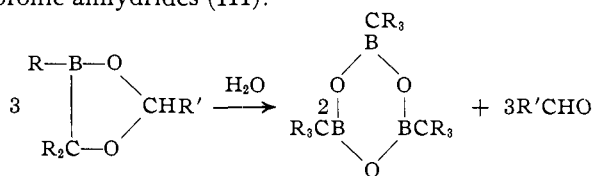
hexaalkyl-2,5-diboradioxanes (II) led to the present discovery.

Results and Discussion

The reaction of trialkylboranes with carbon monoxide and aldehydes gave substituted 4-bora-1,3-dioxolanes (V), a new class of boron heterocycles. 4,5,5-Tri-



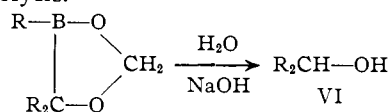
ethyl-4-bora-1,3-dioxolane (Va) was unstable, forming a white precipitate and an odor of formaldehyde after several hours. All of the other derivatives prepared were stable for long periods under a nitrogen atmosphere and were stable to water at ordinary temperatures. At 150° in the presence of water, the boradioxolane derivatives (V) were converted to the corresponding boronic anhydrides (III).⁵



Attempts to prepare the boradioxolanes by refluxing the hexaalkyl-2,5-diboradioxanes with an aldehyde were unsuccessful. This evidence suggests a 1,3-dipolar addition mechanism for the formation of the boradioxolane derivatives during the carbonylation reaction.

Although benzaldehyde appeared to undergo the reaction, there probably were undesirable side reactions because the high boiling liquid could not be readily purified and accurate analytical data were not obtained.

Evidence for the structure of 4,5,5-triethyl-4-bora-1,3-dioxolane (Va) was obtained by the isolation and characterization of 3-pentanol (VI, R = C₂H₅) after basic hydrolysis.

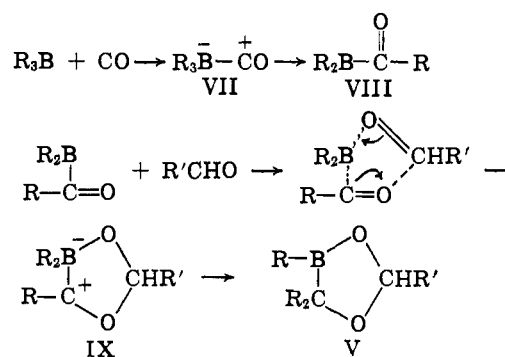


(5) The boronic acids, R₃CB(OH)₂, which form dehydrate to the anhydrides on distillation.

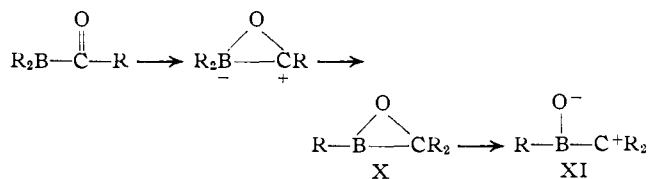
Table I contains a summary of the reactions investigated and the product analyses. Although the reactions listed were run at 50° for 1 hour with a carbon monoxide pressure of 500–700 atmosphere, essentially equivalent results were obtained by using about 100 atmosphere of carbon monoxide pressure for 4–6 hours. The aldehydes could be present as pure aldehyde, the hydrate or as aqueous solutions. In fact, the best yield (92%) was obtained from the reaction of triethylborane with carbon monoxide and 40% aqueous chloroacetaldehyde. However, aqueous formaldehyde produced mixtures of the boradioxolanes and the diboradioxanes (Table I). No attempt was made to maximize yields or optimize reaction conditions.

Mechanism

A possible mechanism is outlined. The trialkylborane carbonyls⁶ (VII) and the dialkyl acylboranes



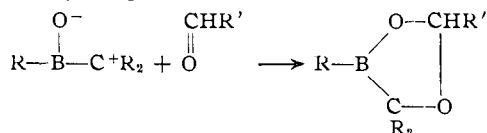
(VIII) could not be detected in the reaction mixtures. It is then assumed that the dialkylacylborane VIII undergoes a 1,3-dipolar addition reaction with the aldehyde⁷ to give an unstable charged intermediate (IX) which rearranges to the 4-bora-1,3-dioxolane (V).



(6) Reppe and Magnin report the preparation of trialkylborane carbonyls analogous to the known borane carbonyl H₃B·CO; cf. German Patent 1,007,130, February 25, 1960, and French Patent 1,233,848, October 12, 1960.

(7) The author thanks Professor R. Huisgen for first suggesting the 1,3-dipolar addition mechanism; private communication, April, 1961.

A second possible route could involve rearrangement of a second alkyl group before the reaction with the aldehyde. The intermediate XI could react with the aldehyde by a 1,3-dipolar addition or the intermediate X by a four-center reaction. These latter mechanisms seem highly improbable since the intermediates X



and XI are probably present as the dimeric hexaalkyl-2,5-diboradioxane which did not react with an aldehyde under similar conditions.

The mechanism of the formation of the hexaalkyl-2,5-diboradioxanes was discussed in a preliminary paper.⁴

Experimental

Trialkylboranes.—Triethyl- and tri-*n*-butylborane were obtained from Callery Chemical Co. and were used without further purification. The other alkylboranes were prepared by a procedure described in a previous paper.⁴

4,5,5-Triethyl-4-bora-1,3-dioxolane (Va).—A stainless steel-lined shaker tube (325-ml. capacity) was flushed with nitrogen and charged with aqueous formaldehyde (100 g. of 37%), triethylborane (54.6 g., 0.557 mole) and carbon monoxide (introduced gradually to 700 atmosphere maximum pressure) and heated at 50° for 1 hour. The bomb was agitated in a pendulum shaker under these conditions. After cooling, the layers were separated under nitrogen and the aqueous layer was washed twice with ether. The combined organic layers were washed with water, dried with magnesium sulfate, concentrated, and vacuum distilled to give presumably 4,5,5-triethyl-4-bora-1,3-dioxolane as a clear colorless liquid, b.p. 50° (0.2 mm.) (40.5 g., 48%). This compound deposited a white precipitate on standing under an atmosphere of dry nitrogen so chemical analyses were not possible.

4,5,5-Triisobutyl-4-bora-1,3-dioxolane (Vh).—The bomb was flushed with nitrogen, charged with aqueous formaldehyde (100 ml. of 37%), triisobutylborane (79.0 g., 0.433 mole) and carbon monoxide (700 atmosphere). The bomb was heated at 50° for 1 hour then cooled and washed with ether. The aqueous layer was extracted with ether, and the combined ether layers were washed with water, saturated sodium chloride, and then dried

with magnesium sulfate. Vacuum distillation gave a clear colorless liquid, b.p. 75–85° (0.65 mm.) (54.7 g., 60%, total yield 97%). This solid was recrystallized from ethanol (m.p. 142.4–142.7°) and was shown to be 2,3,3,5,6,6-hexaisobutyl-2,5-dibora-1,4-dioxane, identical (infrared spectrum and mixed m.p.) to the solid obtained by the carbonylation in water⁴ and in ethylene glycol.¹

Anal. Calcd. for C₁₈H₂₇BO: C, 74.29; H, 12.95; B, 5.15. Found: C, 74.16, 73.96; H, 12.78, 12.85; B, 5.01, 5.09.

The liquid from above was redistilled to give 4,5,5-triethyl-4-boradioxolane as a colorless liquid b.p. 68–70° (0.6 mm.) (33.0 g., 86% recovery). For analyses, see Table I.

4,5,5-Triethyl-2-chloromethyl-4-bora-1,3-dioxolane (Vd).—The bomb was flushed with nitrogen and charged with aqueous chloroacetaldehyde (150 ml. of 40%), triethylborane (50.0 g., 0.51 mole) and carbon monoxide (slowly to 500 atmosphere). The bomb was heated at 50° for 1 hour then cooled and extracted with ether. The product was worked up in the usual manner and vacuum distilled to give 4,5,5-triethyl-2-chloromethyl-4-bora-1,3-dioxolane (Vd) as a clear colorless liquid, b.p. 57–65° (0.2 mm.) (96.0 g., 92%). Redistillation gave a constant boiling fraction, b.p. 60° (0.2 mm.) (88% recovery).

4,5,5-Tri-*n*-butyl-2-trichloromethyl-4-bora-1,3-dioxolane (Vg).—The bomb was flushed with nitrogen and charged with chloral hydrate (100 g., 0.6 mole), ethanol (50 ml.), tri-*n*-butylborane (91 g., 0.5 mole) and carbon monoxide (600 atmosphere). The bomb was shaken and heated at 50° for 1 hour then cooled and extracted with ether. The mixture was concentrated then vacuum distilled to give 4,5,5-tri-*n*-butyl-2-trichloromethyl-4-bora-1,3-dioxolane (Vg) as a clear colorless liquid, b.p. 110° (0.1 mm.) (116.5 g., 69%).

4,5,5-Triethyl-2-methyl-4-bora-1,3-dioxolane (Vb).—The bomb was charged with acetaldehyde (75 g., 1.7 moles) and triethylboron (98 g., 1.0 mole). Carbon monoxide was introduced gradually in 20-atmosphere increments (very exothermic) to a maximum pressure of 200 atmosphere. The bomb was shaken for 1 hour at a temperature of 35–55° (no external heat was applied). The contents of the bomb were concentrated and vacuum distilled to give the title compound as a clear colorless mobile liquid, b.p. 35° (0.25 mm.) (135.0 g., 74%). For analyses and a summary of other compounds prepared see Table I.

The Attempted Reaction of 2,3,3,5,6,6-Hexaethyl-2,5-dibora-1,4-dioxane with *n*-Butyraldehyde.—A solution of *n*-butyraldehyde (36 g., 0.5 mole) and 2,3,3,5,6,6-hexaethyl-2,5-diboradioxane (63 g., 0.5 mole) was refluxed for 1.5 hours (pot temperature 90–94°). Vacuum distillation gave *n*-butyraldehyde (30.2 g., 84% recovery) and hexaethyl-2,5-diboradioxane, b.p. 68–70° (0.6 mm.) (60.4 g., 96% recovery). No 4,5,5-triethyl-2-*n*-propyl-4-boradioxolane was detected in the reaction product.

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The S_N Mechanism in Aromatic Compounds. Part XXVII.¹ A Quantitative Approach to Aromatic Nucleophilic Substitution

By J. MILLER

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Energy calculations are made for a number of anion-dipole aromatic nucleophilic substitutions utilizing the concept of an intermediate complex. Recorded data, wherever available, for bond energies, electron affinities and solvation energies are used together with an allowance for electronic reorganization, to calculate energies of initial and final states and an intermediate complex. In a consistent way these are related to transition states and activation energies. The results, which are shown to be in accord with experiment, cover several important systems including methanolysis of aryl halides, aryl halide exchange, the formation of stable intermediates, and the change in relationship of reactivity of fluoro— and other halogeno—compounds with change in reagent. Solvent effects are also discussed. A clearer understanding of the factors which influence nucleophilic strength emerges and this is discussed also. The principles involved should permit wider applications than are considered in the present paper.

In this paper energy calculations are made for some aromatic nucleophilic substitutions involving reactions of anionic reagents with neutral substrates, utilizing the concept of a cyclohexadienide intermediate complex.^{2,3} Meisenheimer,⁴ among early workers, demon-

strated the formation of such compounds, and later workers have confirmed and extended this.^{5–8}

It has been commonly, though not quite universally, accepted practice to extrapolate to less activated systems for which there is much supporting evidence.^{1,9–12}

(1) (a) Part XXXVI: *J. Am. Chem. Soc.*, **83**, 117 (1961). (b) A brief report of this work has been made at the Australian & New Zealand Association for the Advancement of Science Congress held in Sydney, Australia, in August, 1962.

(2) (a) J. Miller, *Rev. Pure & Applied Chem.* (Australia), **1**, 171 (1951); (b) B. A. Bolto and J. Miller, *Australian J. Chem.*, **9**, 304 (1956).

(3) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1952).

(4) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(5) O. L. Brady and H. V. Horton, *J. Chem. Soc.*, **127**, 2230 (1925).

(6) J. Miller, *J. Am. Chem. Soc.*, **77**, 180 (1955).

(7) J. B. Ainscough and E. F. Caidin, *J. Chem. Soc.*, 2528 (1956).

(8) R. C. Farmer, *ibid.*, 3425, 3430 (1959).

(9) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953).

(10) N. Muller, L. W. Pickett and R. S. Mulliken, *ibid.*, **76**, 4770 (1954).

(11) E. J. Corey and C. K. Sauers, *ibid.*, **79**, 248 (1957).

(12) J. F. Bunnett and J. J. Randall, *ibid.*, **80**, 6020 (1958).