

TABLE I

REACTION OF SODIUM ETHYL MERCAPTIDE WITH PHOSPHORUS ESTERS							
Phosphorus compound	Equiv. NaSEt	Time, hr.	Temp., °C.	Solvent ^a	Product identified ^b	Yield, ^c %	
EtSPO(OEt) ₂	1.0	13	25	THF-EtOH	Et ₂ SO	83	
					EtSP(OEt)O ₂ Na	49	
EtSPO(OEt) ₂	1.1	24	106	Diglyme	Sulfide	103	
EtSPO(OEt) ₂	2.1	24	106	Diglyme	Sulfide	120	
<i>n</i> -BuSPO(OEt) ₂	1.0	16	25	THF-EtOH	Sulfide	81	
					Et ₂ SO	59	
					BuSP(OEt)O ₂ Na	73	
(EtO) ₃ PO	1.1	16	160	Diglyme	Sulfide	98	
PhSPO(OEt) ₂	1.0	24	40-60	EtOH-EtSH	PhSP(OEt)O ₂ Q	High	
EtPO(OEt) ₂	1.0	24	40-60	EtOH-EtSH	EtP(OEt)O ₂ Q	High	

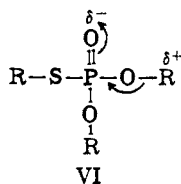
^a THF = tetrahydrofuran, diglyme = diethyleneglycol dimethyl ether. ^b Sulfide determined by bromine titration of thioether-solvent distillate (corrected for mercaptan content); sulfones isolated and crystallized following oxidation of the distillate with H₂O₂; Q = *S-p*-chlorobenzylthiuronium group (*cf.* ref. 8). ^c Yield based on phosphorus compound; >100% signifies more than one alkoxy group cleaved.

could be detected. From this one example, it appears that the reaction of unsymmetrical disulfides with sodium diethyl phosphonate follows the same pattern as that observed¹ for triethyl phosphite; namely, the displacement of the more stable mercaptide anion.

As discussed in detail by Foss⁵ and by Parker and Kharasch,⁶ the reaction of organic disulfides with nucleophilic reagents appears to be a reversible process (eq. 3) in which the equilibrium generally lies rather



far to the left, so that for the reaction to proceed it is often necessary to add a trapping agent to remove the mercaptide as it is formed. In the present reaction of disulfides with sodium diethyl phosphonate, the reaction proceeds to completion with great rapidity, so that no trapping of the mercaptide is necessary. Although there is a back reaction of mercaptide with phosphorothioate, this relatively slow process is not the reverse of the forward reaction. Rather it is attack of mercaptide at an alkoxy linkage, which, because of the ability of phosphorus to expand its outer valency shell, apparently is the most electrophilic center in the molecule (VI).



As was pointed out earlier, this interaction between sodium ethyl mercaptide and O,O,S-triethyl phosphorothioate, either as a secondary process in the reaction of sodium diethyl phosphonate with diethyl sulfide or when the phosphorothioate ester is treated directly with sodium mercaptide prepared from ethyl mercaptan (Table I), leads to the formation of sodium O,S-diethyl phosphorothioate (IIIa) rather than sodium O,O-diethyl phosphorothioate, (EtO)₂POSNa, a compound previously prepared by Foss⁷ by treatment of sodium diethyl phosphonate with sulfur. The two isomeric salts are readily distinguished by their melting points, infrared spectra, *S-p*-chlorobenzylthiuronium derivatives⁸ and the fact that IIIa but not the O,O-diethyl compound forms a precipitate with silver nitrate. Treatment of O,O-diethyl *S-n*-butyl phosphorothioate with sodium ethyl mercaptide gives the analogous salt and diethyl sulfide rather than ethyl *n*-butyl sulfide (Table I). The results indicate that the carbon-oxygen

bond is considerably more susceptible to nucleophilic attack than is the carbon-sulfur linkage. The same conclusion was reached by Lecocq and Todd,⁹ who observed that lithium chloride in boiling ethoxyethanol readily converts diphenyl *n*-propyl phosphate to lithium diphenyl phosphate and propyl chloride, whereas O,O-diphenyl *S*-ethyl phosphorothioate is inert to lithium chloride under similar conditions.

Although alkoxy linkages in phosphorothioate esters appear to be more susceptible to cleavage by nucleophilic reagents than are simple thioether linkages, appropriate substitution of the group attached to sulfur can increase the lability of the carbon-sulfur bond. The isolation of β -acetamidoethyl sulfide (V) from the prolonged reaction of sodium diethyl phosphonate with β -acetamidoethyl disulfide (Ib) shows that the presence of the acetamido group enhances the susceptibility of the carbon-sulfur bond to attack by the mercaptide. Similarly, the unique course of the reaction of acyl disulfides with triethyl phosphite to give an acyl sulfide and O,O,O-triethyl phosphorothioate¹ indicates that, in the phosphonium intermediate, an acyl-sulfur bond is cleaved in preference to an ethoxy linkage.

The ability of sodium ethyl mercaptide to cleave phosphorothioate esters, even at room temperature, suggested the general utility of mercaptides for the dealkylation of pentavalent phosphorus esters. From the results of experiments summarized in Table I, it is evident that sodium ethyl mercaptide is an effective reagent for the monodealkylation of phosphate, phosphonate and phosphorothioate esters, especially at elevated temperature. With excess mercaptide, a second ester linkage is not readily cleaved. Warming with sodium ethyl mercaptide in a mixture of ethyl mercaptide and ethanol was found to be an excellent means of converting such esters to their monobasic salts for identification through their *S-p*-chlorobenzylthiuronium derivatives.⁸

Experimental

Methods and Materials.—All reactions of disulfides with sodium diethyl phosphonate were carried out under an atmosphere of nitrogen. Commercial tetrahydrofuran (THF) was distilled from calcium hydride and stored under nitrogen over calcium hydride. Diethyl phosphonate (Victor) and ethyl disulfide (Eastman Kodak Co.) were redistilled before use. Diethyleneglycol dimethyl ether (Ansul 141), hereafter referred to as diglyme, was freed of its amine-like odor by shaking it with a weakly acidic ion-exchange resin (Amberlite IR-120), followed by distillation from calcium hydride.

Ethyl phenyl disulfide, b.p. 77° (1 mm.), *n*_D²⁰ 1.5978, reported¹⁰ b.p. 126° (15 mm.), was synthesized in 52% yield from the reaction of benzenesulfonyl chloride¹¹ with ethyl mercaptan. Attempted preparation of this disulfide from ethanesulfonyl

(5) O. Foss in "Organic Sulfur Compounds," Vol. I, Pergamon Press, London, 1959.

(6) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

(7) O. Foss, *Acta Chem. Scand.*, **1**, 8 (1947).

(8) R. G. Harvey and E. V. Jensen, *J. Org. Chem.*, **28**, 470 (1963).

(9) J. Lecocq and A. R. Todd, *J. Chem. Soc.*, 2831 (1954).

(10) H. Britzinger and M. Langheck, *Chem. Ber.*, **86**, 557 (1953).

(11) W. E. Truce, H. E. Hill and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2760 (1956).

chloride and thiophenol as described previously¹⁰ led to only products of disproportionation, ethyl disulfide and phenyl disulfide.

Anal. Calcd. for $C_8H_{10}S_2$: C, 56.43; H, 5.92; S, 37.67. Found: C, 55.57; H, 5.74; S, 37.53.

β -Acetamidoethyl mercaptan (N-acetylcysteamine), prepared from ethylenimine and thioacetic acid,¹² was oxidized with excess 30% hydrogen peroxide and the product was recrystallized from acetone to yield β -acetamidoethyl disulfide, m.p. 91.5–92°, reported¹² 87°.

O,O-Diethyl S-butyl phosphorothioate, b.p. 92.5° (3 mm.), n_D^{25} 1.4566, was prepared from *n*-butyl bromide and sodium O,O-diethyl phosphorothioate by the method described^{13,14} for analogous phosphorothioate esters. The infrared spectrum of this ester showed a strong P=O absorption at 1256 cm^{-1} and corresponded closely to that of $EtSPO(OEt)_2$.

Sodium diethyl phosphonate was prepared by the reaction of sodium hydride with diethyl phosphonate as previously described.¹⁵ The reagent used in the reactions with ethyl disulfide and β -acetamidoethyl disulfide was prepared from du Pont sodium hydride as previously recommended.¹⁵ When the du Pont product became unavailable, it was found that an oil dispersion of sodium hydride, supplied by the Anderson Chemical Co. or by K & K Laboratories, Inc., is quite satisfactory and offers the distinct advantage that it does not require a dry-box for handling. The 2 *N* solution of sodium diethyl phosphonate used in the reaction with ethyl phenyl disulfide was prepared in the following manner.

A 44.5-g. amount of a 54% dispersion of sodium hydride in oil was suspended in 100 ml. of dry ether in an atmosphere of dry nitrogen. After stirring, the solid was allowed to settle and the supernatant solution removed by pipet. This washing process was repeated three more times using 50-ml. portions of dry ether. Then 200 ml. of dry THF was added, the flask immersed in an ice-water-bath and diethyl phosphonate (138 g., 1.00 mole) added slowly over the course of 3.5 hours. The mixture was stirred at room temperature for an additional hour and then diluted to 500 ml. with THF. During the reaction, a nearly quantitative amount of hydrogen was evolved. Analysis of the resulting sodium diethyl phosphonate solution was carried out by allowing an aliquot portion to react with excess ethyl iodide followed by partition of the products between pentane and water and titration of the aqueous phase for iodide by the Volhard method. The liberation of 2.07 meq. of iodide per ml. of phosphonate solution indicated a sodium diethyl phosphonate concentration close to that expected (2.00 *N*).

Reaction of Sodium Diethyl Phosphonate with Ethyl Disulfide.

(1) **Rapid Work-up.**—A solution of sodium diethyl phosphonate (0.106 mole) in 100 ml. of THF was added over a period of 10 minutes to a rapidly stirred solution of 12.9 g. (0.106 mole) of ethyl disulfide in 100 ml. of THF held at 0°. As the two solutions came in contact, a practically instantaneous precipitation of white solid occurred. After an additional 5 minutes of stirring, the solution was filtered through a sintered glass funnel under a positive pressure of nitrogen to effect rapid filtration. Distillation of the filtrate gave 15.5 g., 74%, of O,O,S-triethyl phosphorothioate, b.p. 103–107° (7 mm.), n_D^{25} 1.4532; reported b.p. 120° (16 mm.),¹⁶ n_D^{25} 1.4540.¹⁷ The infrared spectrum of this product showed characteristic P=O absorption at 1256 cm^{-1} , and the substance slowly formed a copious white precipitate when treated with aqueous or alcoholic silver nitrate.

Anal. Calcd. for $C_8H_{15}O_3SP$: C, 36.35; H, 7.63; P, 15.66. Found: C, 36.55; H, 7.75; P, 15.34.

Attempts to characterize the original precipitate (11.6 g.) obtained in this experiment were not successful, but a similar product obtained from a subsequent experiment was identified as sodium ethyl mercaptide by treatment of the precipitate with 2,4-dinitrochlorobenzene to yield 2,4-dinitrophenyl ethyl sulfide, m.p. 113–114°, reported¹⁸ 115°.

(2) **Delayed Work-up.**—A solution of sodium diethyl phosphonate (0.08 mole) in 200 ml. of THF was added during a period of 1 hour to a rapidly stirred solution of 9.76 g. (0.08 mole) of ethyl disulfide in 100 ml. of THF at ambient temperature. The reaction mixture was allowed to stand at room temperature for 21 hours and then filtered. The solid product was recrystallized twice from THF and once from chloroform to yield sodium O,S-diethyl phosphorothioate, 9.42 g., 70%, m.p. 213–214°.

(12) R. Kuhn and G. Quadbeck, *Chem. Ber.*, **84**, 844 (1951).

(13) C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957).

(14) M. I. Kabachnik and T. A. Mastryukova, *Zhur. Obshchei Khim.*, **25**, 1924 (1955).

(15) R. G. Harvey, T. C. Myers, H. I. Jacobson and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2612 (1957).

(16) P. S. Pishchikmuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

(17) H. I. Jacobson, R. G. Harvey and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955).

(18) R. W. Bost, J. O. Turner and R. D. Norton, *ibid.*, **54**, 1985 (1932).

Anal. Calcd. for $C_4H_{10}O_3SPNa$: C, 25.00; H, 5.25. Found: C, 24.57; H, 5.41.

This product, showing strong infrared absorption at 1228 cm^{-1} presumably due to P=O, formed a precipitate immediately when treated with aqueous silver nitrate. It is clearly different from the isomeric sodium O,O-diethyl phosphorothioate (m.p. 199–201°, reported⁷ 181°; Found: C, 25.03; H, 5.24), synthesized by the reaction of sulfur with sodium diethyl phosphonate.⁷ The latter isomer shows no absorption bands between 1180 and 1350 cm^{-1} and gives no precipitate with silver nitrate.

Reaction of Sodium Diethyl Phosphonate with β -Acetamidoethyl Disulfide. (1) **Rapid Work-up.**—A solution of sodium diethyl phosphonate in THF (10.4 mmoles in 7.1 ml.) was added rapidly to 23 ml. of a solution of 2.44 g. (10.4 mmoles) of β -acetamidoethyl disulfide in THF contained in a centrifuge bottle. Immediately after the addition, the precipitate was stirred with a glass rod and the mixture centrifuged for 3 minutes at 2000 r.p.m. The supernatant solution was removed and the residue washed with a small amount of THF. The supernatant solutions and washings from this and three other replicate reaction mixtures were pooled and evaporated at reduced pressure to give 5.65 g. of an oil. Molecular distillation of 2.86 g. of this oil gave O,O-diethyl S- β -acetamidoethyl phosphorothioate, 2.35 g., 44%, n_D^{25} 1.4860.

Anal. Calcd. for $C_8H_{15}O_4NPS$: C, 37.65; H, 7.11; N, 5.49; P, 12.15. Found: C, 38.18; H, 7.09; N, 5.06, 5.26; P, 11.33.

(2) **Delayed Work-up.**—A solution of sodium diethyl phosphonate in THF (46.5 mmoles in 192 ml.) was added during a period of 20 minutes to a stirred solution of β -acetamidoethyl disulfide (11.0 g., 46.5 mmoles) in 100 ml. of THF at ambient temperature. A gummy white precipitate formed in the reaction mixture which was stirred with some difficulty for 4 hours longer and then allowed to stand for 6 days with occasional agitation. The supernatant solution was decanted from the amorphous white precipitate and evaporated to leave 6.98 g. of an oil containing white solid which was collected on a filter. The filtrate was diluted with a small amount of THF to yield additional solid which was combined with the first portion to yield β -acetamidoethyl sulfide, 1.29 g., 14%, m.p. 94–98°, recrystallized from acetone to yield the analytical sample, m.p. 101–102°.

Anal. Calcd. for $C_8H_{15}O_2N_2S$: C, 47.03; H, 7.90; N, 13.72; S, 15.69. Found: C, 47.46; H, 7.93; N, 13.53; S, 15.32.

Attempts to isolate additional products either from the amorphous white precipitate of the original reaction mixture or from the THF-soluble oil, proved unsuccessful.

Reaction of Sodium Diethyl Phosphonate with Ethyl Phenyl Disulfide.—The reaction of sodium diethyl phosphonate with ethyl phenyl disulfide was carried out as rapidly as possible in order to minimize the secondary reaction of mercaptide with the phosphorothioate ester. Fifty ml. (0.10 mole) of a 2 *N* sodium diethyl phosphonate solution in THF was added during 8 minutes to a rapidly stirred solution of 17.0 g. (0.10 mole) of ethyl phenyl disulfide in 125 ml. of THF, at a temperature maintained below 40°. Immediately after addition was complete, 6 ml. of glacial acetic acid was added to quench further reaction. The solvent was removed by distillation, and the residual product was partitioned between water and pentane. The organic layer, after drying over magnesium sulfate, was evaporated at reduced pressure, and the residue was distilled through a 6-inch Vigreux column. The first product obtained was thiophenol, 7.11 g., 65%, b.p. 80° (40 mm.), n_D^{25} 1.5820; reported b.p. 86° (50 mm.),¹⁹ n_D^{25} 1.5879,²⁰ identified by reaction with 2,4-dinitrochlorobenzene to yield 2,4-dinitrophenyl phenyl sulfide, m.p. 120–121°, reported¹⁸ 121°. Further distillation yielded O,O,S-triethyl phosphorothioate, 14.02 g., 71%, b.p. 80° (0.5 mm.), n_D^{25} 1.4568, showing an infrared spectrum identical with that of the authentic material.

Anal. Calcd. for $C_{12}H_{18}N_2SO_4$: C, 52.18; H, 2.92; N, 10.14; S, 11.61. Found: C, 52.27; H, 2.88; N, 10.26; S, 11.87.

The identity of O,O,S-triethylphosphorothioate was confirmed further by conversion to its mono *S-p*-chlorobenzylthiuronium derivative,⁸ m.p. 151–152°, not depressed by mixing with the derivative of an authentic sample of this ester.

Reaction of Sodium Mercaptide with O,O,S-Triethyl Phosphorothioate. (1)—A solution of sodium ethoxide, prepared by the reaction of sodium (5.3 g., 0.23 g.-atom) with excess ethanol (50 ml.) in 200 ml. of THF, was treated with ethyl mercaptan (14.6 g., 0.23 mole) to yield a suspension of sodium ethyl mercaptide. To this stirred suspension O,O,S-triethyl phosphorothioate (45.5 g., 0.23 mole) was added slowly, whereupon the reaction flask warmed spontaneously to about 35°, and the mercaptide dissolved. After 20 minutes, a thick white precipitate began to form. The reaction mixture was stirred for an additional 12 hours and then chilled and filtered to yield white needles of

(19) E. Bourgeois, *Rec. trav. chim.*, **18**, 426 (1899).

(20) F. Taboury, *Ann. chim. phys.*, [8] **15**, 5 (1908).

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°.

(24) H. Gilman and N. J. Beaher, *J. Am. Chem. Soc.*, **47**, 1449 (1925).

(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}

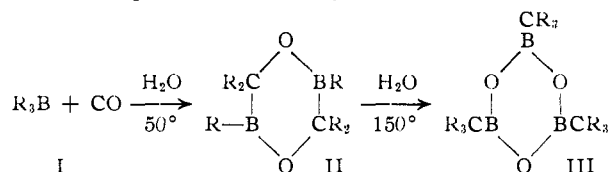
BY MELVILLE E. D. HILLMAN³

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



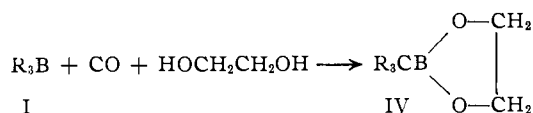
(1) Part II of this series: M. E. D. Hillman, *J. Am. Chem. Soc.*, **85**, 982 (1963).

(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-1,2-bora-1,3-dioxolane (IV).¹



Attempts to prepare monomeric derivatives of the