

medium for making a pure dimethylgermanium oxide because it has been shown that it does not affect the methyl groups. Accordingly, 7.63 g. of pure distilled  $(\text{CH}_3)_2\text{GeS}$  was refluxed with 20 ml. of water and 0.5 ml. of concentrated sulfuric acid for seven hours, or until there no longer was a rapid evolution of hydrogen sulfide. A solution of barium hydroxide then was added dropwise until the solution was just alkaline to phenolphthalein, and the barium sulfate was filtered off.<sup>13</sup> The clear filtrate was evaporated under reduced pressure to a sirup. The remaining water was distilled off, along with some volatile dimethylgermanium oxide or hydroxide, in the range 100 to 105°, and then the boiling point rose rapidly to over 200° and a polymer of dimethylgermanium oxide distilled. The empirical composition was shown to correspond to  $(\text{CH}_3)_2\text{GeO}$ .

*Anal.* Calcd.: C, 20.24; H, 5.10; Ge, 61.2. Found: C, 20.34, 20.52; H, 5.25, 5.16; Ge, 60.96, 60.28.

The dimethylgermanium oxide so prepared melts at 133.4°<sup>14</sup> and boils at 211°. It does not dissolve readily in water, benzene or cyclohexane. It dissolves in alcohol, and upon addition of water is not precipitated but reverts to the water-soluble form encountered during the preparation. Cryoscopic determinations of the molecular weight of

(13) The weight of dried barium sulfate was slightly under the weight expected from the amount of sulfuric acid originally used, showing that there was no oxidation of sulfide to sulfate during the hydrolysis.

(14) Melted samples solidify to a glassy phase which then melts at about 125°.

the solid in cyclohexane were inconclusive, probably because of the very limited solubility of the substance. Camphor was found to be a good solvent, however, and determinations of molecular weight (found, 491; calcd. for  $(\text{CH}_3)_2\text{GeO}$ , 118.7) indicate that the substance is a tetramer.<sup>15</sup> However, upon repeated melting of the camphor solutions in sealed tubes the depression of the freezing point was found to increase in a way that suggests an (as yet unknown) alteration of the polymeric state of the oxide.

### Summary

1. The hydrolysis of dimethylgermanium dichloride is shown to be reversible to an extent which makes impractical the preparation of dimethylgermanium oxide by the techniques used for preparing silicones.

2. Dimethylgermanium sulfide (m. p. 55.5°, b. p. 302°) has been prepared.

3. Dimethylgermanium oxide has been obtained in a crystalline polymeric form (m. p. 133.4°, b. p. 211°) by hydrolysis of the sulfide.

(15) Probably cyclic, see related tetramer of  $(\text{C}_6\text{H}_5)_2\text{GeO}$  in Morgan and Drew, ref. 4.

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## Alcoholysis of Ethyl Phosphate. The Preparation of Mixed Ethyl Butyl Phosphates

BY WALTER H. C. RUEGGEBERG AND JACOB CHERNACK

Examples of the alcoholysis of esters derived from inorganic acids are not nearly so plentiful in the chemical literature as are those of the organic acid esters. Recently, the alcoholysis of alkyl silicates was studied by Peppard, Brown and Johnson,<sup>1</sup> who found that in some cases the alcoholysis of silicates proceeded without the addition of catalysts to yield mixed silicic acid esters, while, in other instances, hydrogen chloride or silicon tetrachloride was needed to catalyze the reaction. A similar transalkylation reaction between butyl silicate and ethyl silicate under the catalytic influence of aluminum chloride or the alkoxides of aluminum, antimony or magnesium was also found by these same authors<sup>2</sup> to produce mixed alkyl silicates.

Morel and Friedel<sup>3</sup> have shown that under the influence of sodium ethylate, a mixture of ethanol and phenyl phosphate will yield mixed ethyl phenyl phosphates as well as phenetole. The latter property of alkylation is an interesting feature in this reaction and has been extended by

Noller and Dutton.<sup>4</sup> Toy<sup>5</sup> has found that methyl alkyl ethers can be prepared by refluxing a mixture of trimethyl phosphate and alcohols whose boiling points are greater than 160°. The residue products in this reaction are described by Toy to be alkali soluble mixtures of alkyl acid phosphates.

The reaction between *n*-butanol and ethyl phosphate was studied in this Laboratory with the view of obtaining diethyl *n*-butyl and ethyl di-*n*-butyl phosphates. It was observed that an equimolar mixture of ethyl phosphate and *n*-butanol would not undergo appreciable reaction even at temperatures of about 160°. In the presence of small amounts of sodium butylate, however, alcoholysis proceeded rapidly at temperatures between 90 and 120°. In Table I, it can be seen that the relative amounts of diethyl *n*-butyl phosphate and ethyl di-*n*-butyl phosphate depend upon the relative amounts of sodium butylate present in the reaction mixture and also upon the mole ratio of ethyl phosphate to *n*-butanol. Some physical properties of the mixed esters are presented in Table II.

(1) Peppard, Brown and Johnson, *THIS JOURNAL*, **68**, 73 (1946).

(2) Peppard, Brown and Johnson, *ibid.*, **68**, 77 (1946).

(3) Morel and Friedel, *Compt. rend.*, **128**, 507 (1899).

(4) Noller and Dutton, *THIS JOURNAL*, **55**, 424 (1933).

(5) Toy, *ibid.*, **66**, 409 (1944).

TABLE I  
 ALCOHOLYSIS AND ETHER FORMATION WITH ETHYL PHOSPHATE

Reagents, moles			Products, moles							Residue, g.
<i>n</i> -BuOH	Na	Et <sub>3</sub> PO <sub>4</sub>	EtOH <sup>a</sup>	Ether <sup>a,b</sup>	<i>n</i> -BuOH	Et <sub>3</sub> PO <sub>4</sub>	BuEt <sub>2</sub> PO <sub>4</sub>	Bu <sub>2</sub> EtPO <sub>4</sub>		
1.0	0.03	0.5	0.18	0.02	0.81	0.32	0.12	..	12.3	
1.0	.07	.5	.50	.06	0.51	.14	.19	0.06	24.1	
1.0	.13	.5	.55	.08	0.37	.10	.16	.08	36.9	
2.0	.13	.5	.76	.11	1.09	.04	.12	.15	..	
3.0	.13	.5	.77	.09	2.16	.02	.13	.15	43.9	
3.0	.22	.5	.90	.14	1.98	.01	.06	.12	..	

<sup>a</sup> The total ethanol-ether cut from the distillation was subjected to a separate analysis for per cent. alcohol using acetic anhydride and pyridine followed by titration for acid in the usual manner. <sup>b</sup> This is chiefly ethyl *n*-butyl ether, containing less than 2% of a material boiling between 33 and 35° which possesses the characteristics of ethyl ether.

 TABLE II  
 SOME PHYSICAL CONSTANTS OF MIXED ETHYL BUTYL PHOSPHATES

Et <sub>2</sub> BuPO <sub>4</sub> <sup>a</sup>			EtBu <sub>2</sub> PO <sub>4</sub> <sup>b</sup>			
<i>T</i> , °C.	<i>dT</i> / <i>d</i> , g./ml.	<i>n</i> <sub>D</sub>	Viscosity, centi-stokes	<i>dT</i> / <i>d</i> , g./ml.	<i>n</i> <sub>D</sub>	Viscosity, centi-stokes
9.8	.....	.....	2.73	.....	.....	3.76
10.0	1.0380	1.4170	..	1.0112	1.4215	..
20.0	....	1.4131	..	....	1.4182	..
24.7	....	....	1.97	....	....	..
25.0	1.0243	....	..	0.9984	....	2.54
30.0	....	1.4091	..	....	1.4148	..
35.0	1.0151	....	1.61	0.9897	....	2.05

<sup>a</sup> Surface tension at 27.0° = 28.8 dynes/cm.; parachor, calcd. 480.7; found 476.3. <sup>b</sup> Surface tension at 29.2° = 28.0 dynes/cm.; parachor, calcd. 560.7; found 553.4.

In addition to the products of alcoholysis, there were obtained other products which proved to be ethers of which ethyl *n*-butyl ether predominated.

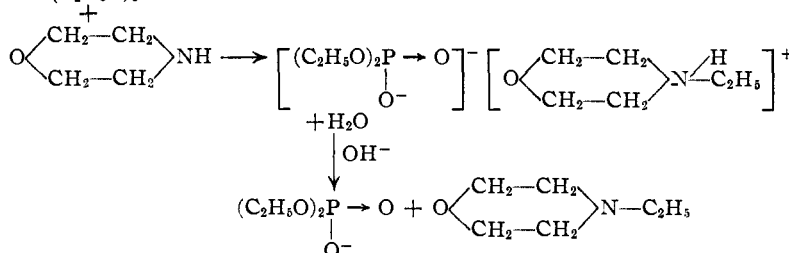
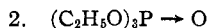
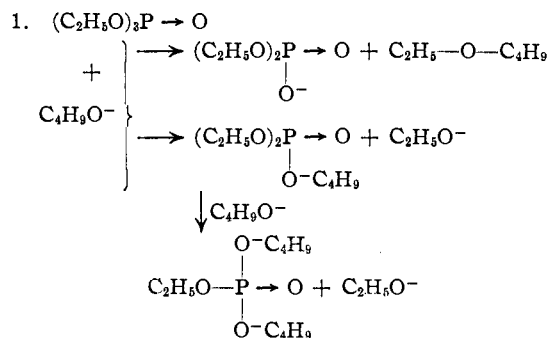
The mole ratio of ether to mixed butyl esters formed (calculated as difference between moles butanol in products and residue and moles butanol originally used) is about 1 to 7. This indicates that sodium butylate acts catalytically in the alcoholysis but is destroyed through ether formation.

The alkylation of butylate ion by ethyl phosphate is in many respects similar to the alkylation of aromatic amines studied by Billman, Radike and Mundy.<sup>6</sup> In order to establish the similarity between the alkylation of amines and of butylate ion, the reaction of an equimolar mixture of morpholine and ethyl phosphate was investigated. It was found that upon heating an oily, non-volatile substance, presumably an ammonium salt, was formed which upon hydrolysis with aqueous caustic yielded pure *N*-ethylmorpholine. Although amidation of the phosphoric acid ester, similar to alcoholysis, was not detected, this reaction may be of value in the de-alkylation of phosphoric acid esters.<sup>7</sup>

(6) Billman, Radike and Mundy, *THIS JOURNAL*, **64**, 2977 (1942).

(7) Similar work is being considered at Cambridge University, England, and was learned by one of us (WHCR) through a personal communication with Prof. A. R. Todd of Cambridge.

These reactions may be summarized by the equations



It is obvious from reaction 1, above, that small amounts of diethyl as well as dibutyl ether are to be expected through further reaction of the ethylate and butylate ions on the phosphates, and indeed these substances are found.

### Experimental

**Alcoholysis of Ethyl Phosphate.**—*n*-Butanol, clean metallic sodium and ethyl phosphate were placed in the kettle of an all-glass, fifteen-plate column still in the order indicated. The amounts of reagents used in each particular run are given in Table I. Ethyl phosphate was not added to the other components until all of the sodium had dissolved in the butanol. The complete reaction mixture was heated by means of a Glas-Col heating mantle. Boiling of the reagents occurred when the kettle temperature reached about 115°. The still head was set to constant reflux until boiling and the reflux rate became steady. Then, a low boiling fraction (about 0.5 g., *n*<sub>D</sub><sup>20</sup> 1.3655, probably diethyl ether) was removed. The fraction boiling from 36 to 93° was collected and found to be a mixture of ethanol and chiefly ethyl *n*-butyl ether, containing from 75–80% ethanol as found by acetylation with acetic anhydride. The refractive index of these cuts varied between *n*<sub>D</sub><sup>20</sup> 1.365 to 1.368 and the densities, *d*<sub>4</sub><sup>20</sup>, from 0.780 to 0.788 g./ml. During the removal of this fraction, the kettle temperature rose slowly to 140°

and on occasions the temperature was allowed to climb to 160° in order to remove all of this fraction at atmospheric pressure.

The pressure was subsequently reduced to 50 to 60 mm. and *n*-butanol ( $n_D^{20}$  1.390 to 1.398) was removed. After removing unreacted ethyl phosphate at pressures varying between 3 and 10 mm. of mercury (b. p. 66–69° at 3 to 4 mm.;  $n_D^{20}$  1.404–1.4055), diethyl *n*-butyl phosphate (b. p. 82–87° at 3 to 4 mm.) and ethyl di-*n*-butyl phosphate (b. p. 95–96° at 3 to 4 mm.) were fractionated out of the reaction mixture.

*Anal.* Calcd. for  $C_8H_{19}PO_4$ : P, 14.7;  $M_R$  51.1.<sup>8</sup> Found: P, 14.9;  $M_R$  51.5. Calcd. for  $C_{10}H_{23}PO_4$ : P, 13.0;  $M_R$  60.5. Found: P, 13.2;  $M_R$  59.8.<sup>8</sup>

The material balances in all runs including residues amounted to 97 to 99%.

**Isolation of Ethyl *n*-Butyl Ether.**—Fifty grams of the ethanol-ether fraction (b. p. 36–93°) was added to 180 ml. of water. The upper layer, amounting to 8.9 g., was separated, dried over activated silica gel and distilled. The main fraction boiled at 90–93° and was found to have the following constants:  $d_4^{20}$ , 0.752;  $n_D^{20}$  1.3818;  $M_R$  calcd., 31.6; found, 31.6.

*Anal.* Calcd. for  $C_6H_{14}O$ : C, 70.5; H, 13.8. Found: C, 70.6; H, 13.9.

Treatment of the ether with hydriodic acid yielded ethyl and *n*-butyl iodides.

**Alkylation of Morpholine.**—An equimolar mixture of morpholine and ethyl phosphate was charged to a round-bottomed flask equipped with a water-cooled reflux condenser. The mixture was heated by means of a Glas-Col mantle and brought to 150° in fifteen to twenty minutes. At this temperature, vigorous refluxing took place due to heat of reaction, and the mixture changed from a water white to a reddish brown color. If too well insulated, the reaction temperature may rise to 190°. It was found, however, that by maintaining the reaction temperature between 157 and 159° good results can be obtained. The product was poured into 500 ml. of water and heated with

(8) The molecular refractivities were calculated from that of ethyl phosphate by adding the proper value for the required number of methylene groups to that molecule.

10% excess (44 g.) of sodium hydroxide. The basic aqueous solution was charged to a still and the amine distilled with water as an azeotrope over the range 95–99.8°. The azeotropic distillate was saturated with potassium carbonate whereupon the amine was salted out. After separating from the aqueous layer, the amine was dried over sodium sulfate, filtered and distilled; b. p. 137–138°,  $d_4^{20}$  0.919,  $n_D^{20}$  1.4418; yield 70%.

*Anal.* Calcd. for  $C_6H_{13}NO$ : C, 62.2; H, 11.4; N, 12.2. Found: C, 62.3; H, 11.5; N, 11.9.

All physical constants given for known compounds agree satisfactorily with those previously published.

**Acknowledgment.**—The authors are indebted to Messrs. N. Beitsch, S. Sass and B. Zeffert of this Laboratory for having performed the necessary analytical and physical determinations.

### Summary

Sodium butylate behaves catalytically on a mixture of *n*-butanol and ethyl phosphate yielding diethyl *n*-butyl phosphate and ethyl di-*n*-butyl phosphate. This alcoholysis is accompanied by a side reaction which causes the alkylation of the butylate ion to ethyl *n*-butyl ether.

This behavior indicates that ethyl phosphate under the conditions employed behaves both as a true ester undergoing alcoholysis and as an alkylating agent. The degree to which each of the products of reaction is produced depends upon the concentration of sodium butylate as well as upon the mole ratio of *n*-butanol to ethyl phosphate.

The alkylation of morpholine to *N*-ethylmorpholine by means of ethyl phosphate is also described.

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[CONTRIBUTION FROM THE ESSO LABORATORIES, CHEMICAL DIVISION, STANDARD OIL DEVELOPMENT COMPANY]

## Study of the Reaction of Buna Rubbers with Aliphatic Mercaptans<sup>1</sup>

BY G. E. SERNIUK, F. W. BANES AND M. W. SWANEY

### Introduction

The relative proportion of 1,4- versus 1,2-addition of diene units and the elucidation of the partial structure of polymers and copolymers of butadiene have been investigated by various chemical and physical methods such as ozonolysis,<sup>2–5</sup> perbenzoic acid oxidation,<sup>6,7</sup> potassium permanganate oxidation,<sup>6</sup> and infrared absorption.<sup>8</sup> The

(1) This paper was presented before the Division of Rubber Chemistry at the American Chemical Society Meeting in Chicago, 1946.

(2) Hill, Lewis and Simonsen, *Trans. Faraday Soc.*, **35**, 1067 (1939).

(3) Yakubchik, Vasiliev and Zhabina, *Rubber Chem. and Tech.*, **18**, 780 (1945).

(4) Alekseeva and Belitzkaya, *ibid.*, **15**, 693 (1942).

(5) Rabjohn, Bryan, Inskoop, Johnson and Lawson, *THIS JOURNAL*, **69**, 314 (1947).

(6) Weidlein, Jr., *Chem. Eng. News*, **34**, 772 (1946).

(7) Kolthoff, Lee and Mairs, *J. Polymer Science*, **2**, 220 (1947).

(8) Rasmussen and Brattain, private communication.

work presented in this paper was undertaken in an attempt to obtain further information regarding the structure of butadiene polymers and copolymers by studying the reaction of these polymers with aliphatic mercaptans.

The reaction of mercaptans with unsaturated compounds including natural and synthetic rubbers is not new. Posner,<sup>9</sup> Gunnar, Axberg and Holmberg,<sup>10</sup> Hoag and Eichwald,<sup>11</sup> Kharasch, Read and Mayo,<sup>12</sup> Jones and Reid,<sup>13</sup> Cunneen,<sup>14</sup> and others have treated mercaptans with various types of unsaturated compounds. Holmberg<sup>15</sup> treated natural pale crepe rubber with thiogly-

(9) Posner, *Ber.*, **38**, 646 (1905).

(10) Gunnar, Axberg and Holmberg, *ibid.*, **66B**, 1193 (1933).

(11) Hoag and Eichwald, *Rec. trav. chim.*, **58**, 481 (1939).

(12) Kharasch, Read and Mayo, *Chem. and Ind.*, **57**, 752 (1938).

(13) Jones and Reid, *THIS JOURNAL*, **60**, 2452 (1938).

(14) Cunneen, *J. Chem. Soc.*, **36**, 134 (1947).

(15) Holmberg, *Ber.*, **65**, 1349 (1932).