The following preparations are typical of the general procedure used to prepare the alkyl v-triazoles.

4-*n*-Propyl-v-triazole.—Four soda type bottles (capacity about 180 ml.) each containing 16 ml. (0.16 mole) of pentyne-1 and 50 ml. of benzene solution containing 18.5 g. of hydrazoic acid per 100 ml. (0.22 mole) were capped and heated at 95–100° for 48 hours. The bottles were cooled, opened, the contents filtered and the filter washed with benzene. The filtrate was evaporated to low volume on a steam-bath, then distilled under vacuum to yield 22.5 g. (31%) of crude 4-*n*-propyl-v-triazole, boiling at 120–130° (14 mm.). The crude triazole was purified by extracting with two 5-ml. portions of water followed by drying the non-aqueous phase over magnesium sulfate and finally redistillation under vacuum, boiling point 122–124° (13 mm.).

4-*n*-Butyl-v-triazole.—Two tubes each containing 10 g. of hexyne-1 (0.12 mole) and 50 ml. of benzene containing 14.7 g. of hydrazoic acid per 100 ml. (0.16 mole) were sealed and heated at 132–135° for 29 hours. The tubes were cooled, opened, the contents filtered, and the filter washed with benzene. The filtrate was evaporated to low volume on a steam-bath and distilled under vacuum to yield 17 g. of crude 4-*n*-butyl-v-triazole (56%) boiling at 83–85° at 1 mm. The crude material was purified by redistillation, boiling at 96–97° (12 mm.). On cooling to −40° the substance formed a glass, but did not crystallize.

The neutralization equivalent was determined according to the procedure of Fritz and Lisicki[16] which involves titration with sodium methylate in benzene–methanol using thymol blue as an indicator. The triazole was dissolved in pyridine. Neutralization equivalent: calcd. 125.2, found 127.

In the preparation of 4-*n*-butyl-v-triazole, as well as in all other reactions in which hydrazoic acid was heated at temperatures above 90° for prolonged periods, a small amount of white crystals formed at the top of the sealed tubes during the course of the reaction. The tubes were held in an upright position during heating; the crystals appeared to have sublimed from the reaction mixture, the level of which was about 25 cm. below the top of the tube. Crystals were isolated from one experiment and were found to be soluble in water and insoluble in ethyl acetate. The crystals melted at 150–155° with sublimation. With sodium hydroxide solution, ammonia was liberated. Addition of silver nitrate to a solution of the crystals produced a white precipitate, insoluble in dilute nitric acid. These properties indicated the material to be ammonium azide.

4-*n*-Decyl-v-triazole.—Four tubes each charged with 20 g. (0.12 mole) of dodecyne-1 and 50 ml. of benzene containing 14 g. of hydrazoic acid per 100 ml. were sealed and heated at 107–115° for 40 hours. The tubes were cooled and opened; the contents were filtered and the filter washed with ethanol. The filtrate was reduced to low volume by evaporation on a steam-bath, then distilled under vacuum to yield 30 g. of crude 4-*n*-decyl-v-triazole (29%) boiling at 148–149° at 0.6 mm. pressure, as well as 30 g. of unchanged dodecyne-1. The crude triazole which solidified in the condensing flask was recrystallized twice from heptane, washed with a small amount of petroleum ether, and dried under vacuum at 40–50° overnight. The pure triazole melted at 58.5–59°.

4-Phenyl-v-triazole.—Three combustion tubes, each containing 14.7 g. of phenylacetylene (0.144 mole) and 50 ml. of 14.2% hydrazoic acid in benzene (0.165 mole HN_3) were sealed and heated in a bath for 40 hours at 110–115°. Some crystals were present in the tubes on first removing them from the heating bath. After cooling to room temperature nearly the entire contents appeared to crystallize. The solid was collected on a filter and washed with benzene. After twice recrystallizing from benzene using decoloring charcoal during the first crystallization 30 g. of product melting at 148.4° was obtained. The yield was 48% of the theoretical amount.

Oxidation of 4-*n*-Amyl-v-triazole.—To a mixture of 1.9 g. of 4-*n*-amyl-v-triazole in 20 ml. of water and 5.6 ml. of concentrated sulfuric acid was added portionwise 7 g. of potassium permanganate keeping the temperature at 60–70°. After all the permanganate had been added, the mixture was heated 30 minutes on a steam-bath, and allowed to stand at room temperature for 48 hours. The mixture was cooled in ice and the white solid which had precipitated was filtered and recrystallized from a small amount of water. The 4-carboxy-v-triazole so obtained melted at 213°. The melting point recorded in the literature[3] for this compound is 213–215°.

Anal. Calcd. for $C_3H_3N_3O_2$: C, 31.83; H, 2.67. Found: C, 31.7; H, 2.3.

The absorption spectra were determined in 95% ethanol solution with a Model DU Beckman quartz spectrophotometer.

The authors wish to express their appreciation to Dr. Paul D. Sternglanz and staff for the analytical and ultraviolet absorption spectra data and to Mr. D. James Kay for the bacteriological tests reported here.

SOUTH NORWALK, CONN.

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[16] J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, THE LUBRIZOL CORPORATION]

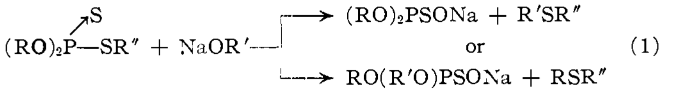
Chemistry of the Aliphatic Esters of Phosphorothioic Acids.[1] III. Alkoxide Cleavage of O,O,S-Trialkyl Phosphorodithioates[2]

BY W. E. BACON AND W. M. LESUER

RECEIVED JULY 21, 1953

A convenient sulfide synthesis based on the alkoxide cleavage of O,O,S-trialkyl phosphorodithioates is described. The addition of O,O-dialkyl hydrogen phosphorodithioates to unsymmetrical olefins exhibits a peroxide effect. The structures of the O,O,S-trialkyl phosphorodithioates formed in this addition reaction were proven by alkoxide cleavage and subsequent identification of the sulfides obtained.

The alkoxide cleavage reaction of O,O-diethyl-S-(2-octyl) phosphorodithioate with sodium ethoxide and ethanol to yield ethyl 2-octyl sulfide and sodium O,O-diethyl phosphorothioate has been reported.[2] The present work has extended this reaction to similar phosphorodithioates as a method for the determination of the structure of O,O,S-trialkyl phosphorodithioates, and as a convenient method for the preparation of certain sulfides. Table I lists the starting triesters and the sulfides obtained. The sulfides were identified by conversion to sulfones or sulfilimines for comparison with synthetic samples. In all cases we have compared the infrared absorption spectra of the sulfides with authentic samples.



$$(RO)_2\overset{\nearrow S}{P}\text{—SR}'' + NaOR' \longrightarrow \begin{cases} (RO)_2PSONa + R'SR'' \\ \text{or} \\ RO(R'O)PSONa + RSR'' \end{cases} \qquad (1)$$

The O,O,S-trialkyl phosphorodithioates were

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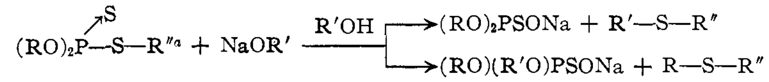
[1] The nomenclature of organic phosphorus compounds used throughout this paper has been outlined in *Chem. Eng. News*, **30**, 4515 (1952).

[2] For preceding article in this series see G. R. Norman, W. M. LeSuer and T. W. Mastin, THIS JOURNAL, **74**, 161 (1952).

TABLE I



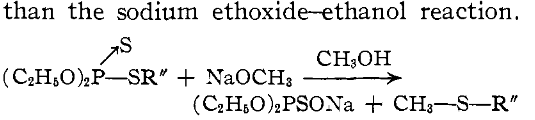
$$(RO)_2\overset{\nearrow S}{P}-S-R''^{a} + NaOR' \xrightarrow{R'OH} \begin{cases} (RO)_2PSONa + R'-S-R'' \\ (RO)(R'O)PSONa + R-S-R'' \end{cases}$$

	R	R″	R′	R–S–R″ or R′–S–R″	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	S, % Calcd.	S, % Found
1	C_2H_5	i-C_3H_7	CH_3	CH_3–S–i-C_3H_7	14[i]	81–82	...	1.4390	35.50	35.70
2	C_2H_5	C_2H_5	C_2H_5	C_2H_5–S–C_2H_5[c]	...	90	...	....	...	...
3	C_2H_5	n-Octyl[b]	CH_3	CH_3–S–n-Octyl[d]	38	87–88	10	1.4580	20.00	19.85
4	C_2H_5	n-Octyl[b]	C_2H_5	C_2H_5–S–n-Octyl[e]	60	103	11	1.4570	18.39	17.86
5	C_2H_5	2-Octyl	CH_3	CH_3–S–2-Octyl[f]	65[i]	80–82	10	1.4561	20.00	19.59
6	C_2H_5	2-Octyl	C_2H_5	C_2H_5–S–2-Octyl	61	66–69	2.5	1.4563	18.39	18.47
7	C_2H_5	2-Octyl	n-C_4H_9	C_2H_5–S–2-Octyl	43	87–89	8	1.4562	18.39	18.20
				n-C_4H_9–S–2-Octyl	20	113	8	1.4590	15.85	15.60
8	C_2H_5	–$CH(CH_3)C_6H_5$	CH_3	CH_3–S–$CH(CH_3)C_6H_5$[g]	69[k]	70	4	1.5497	21.05	20.59
9	C_2H_5	$CH_2CH_2C_6H_5$	CH_3	CH_3–S–$CH_2CH_2C_6H_5$[h]	61	80–83	4	1.5513	21.05	20.85
10	C_2H_5	–$CH_2CH_2C_6H_5$[m]	C_2H_5	C_2H_5–S–$CH_2CH_2C_6H_5$[o]	59	92–94	3	1.5420	19.26	19.60
11	C_2H_5	–$CH(CH_3)C_6H_5$	C_2H_5	C_2H_5–S–$CH(CH_3)C_6H_5$	55	73–74	3	1.5397	19.26	19.10
12	C_2H_5	–$CH(CH_3)C_6H_5$	n-C_4H_9	C_2H_5–S–$CH(CH_3)C_6H_5$	46	79–81	3.4	1.5398	19.26	19.06
				n-C_4H_9–S–$CH(CH_3)C_6H_5$	26	69–71	0.25	1.5272	16.48	16.63
13	C_2H_5	c-Hexyl	CH_3	CH_3–S–c-Hexyl	34	69–72	19	1.4942	24.60	24.60
14	C_2H_5	c-Hexyl	C_2H_5	C_2H_5–S–c-Hexyl[n]	43	68–70	10	1.4908	22.21	21.95
15	n-C_4H_9	c-Hexyl	C_2H_5	C_2H_5–S–c-Hexyl	31	70–74	10	1.4904	22.21	21.86
				n-C_4H_9–S–c-Hexyl	13	101–103	10	1.4864	18.60	18.60
16	n-C_4H_9	2-Octyl	n-C_4H_9	n-C_4H_9–S–2-Octyl	61	114–116	8	1.4590	15.85	15.68
17	2-Ethylhexyl	2-Octyl	n-C_3H_7	n-C_3H_7–S–2-Octyl	47	111	15	1.4573	17.05	17.10
18	C_6H_5	2-Octyl	C_2H_5	C_2H_5–S–2-Octyl	37	85–90	9	1.4560	18.39	17.90

[a] Unless otherwise noted, the O,O,S-trialkyl phosphorodithioates were prepared by the addition of crude O,O-dialkyl hydrogen phosphorodithioates to olefins. [b] Triester prepared by $(C_2H_5O)_2\overset{\nearrow S}{P}SNa + n\text{-OctylBr} \rightarrow n\text{-Octyl}-S-\overset{\nearrow S}{P}-(OC_2H_5)_2 + NaBr$.[2] [c] Converted to sulfone, m.p. 69°. [d] Sulfilimine, m.p. 89–90°. [e] Sulfone, m.p. 89°. [f] Sulfilimine, m.p. 108–109°. [g] Sulfone, m p. 83–84°. [h] Sulfone, m.p. 85–86°. [i] 25% sodium salt was isolated, m.p. 190–191°. [j] 63% sodium salt was isolated. [k] 78% sodium salt was isolated. [m] Triester prepared from sodium salt and β-bromoethylbenzene.[2] [n] Sulfone, m.p. 35°. [o] Sulfone, m.p. 74–75°; sulfilimine, m.p. 113–114°.

prepared by two methods[2]: (a) the alkylation of sodium O,O-dialkyl phosphorodithioates with an alkyl bromide, and (b) the addition of O,O-dialkyl hydrogen phosphorodithioates to olefins. With unsymmetrically substituted olefins the latter method may yield either of two isomeric S-alkyl phosphorodithioates. The addition exhibits the peroxide effect, which will be discussed later in this paper.

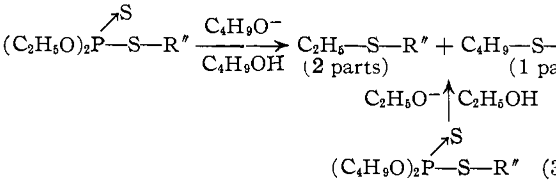
The cleavage of O,O-diethyl-S-alkyl phosphorodithioate with sodium methoxide and methanol gave the corresponding methyl alkyl sulfide and sodium O,O-diethyl phosphorothioate. This cleavage reaction is unique in that no ethyl alkyl sulfide was produced. Sodium methoxide is the only alkoxide that yields one sulfide without altering the O,O-dialkyl groups initially present, when the latter are different from the RO– group of the sodium alkoxide. The sodium methoxide–methanol cleavage reaction gave a higher yield of sulfide than the sodium ethoxide–ethanol reaction. The



$$(C_2H_5O)_2\overset{\nearrow S}{P}-SR'' + NaOCH_3 \xrightarrow{CH_3OH} (C_2H_5O)_2PSONa + CH_3-S-R'' \quad (2)$$

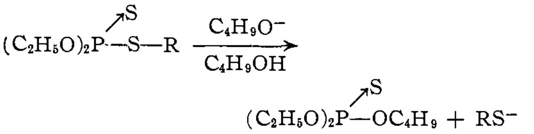
yields of n-butyl alkyl sulfides from the reaction of O,O-(di-n-butyl)-S-alkyl phosphorodithioate with sodium n-butoxide and n-butanol were similar to the yields of ethyl alkyl sulfides obtained from the reaction of O,O-diethyl-S-alkyl phosphorodithioate with sodium ethoxide and ethanol. The latter two reactions could yield only one sulfide and one sodium O,O-dialkyl phosphorothioate since R = R′ (see reaction 1).

The reaction of sodium n-butoxide and n-butanol with O,O-diethyl-S-alkyl phosphorodithioate produced a mixture of the corresponding ethyl alkyl sulfide and n-butyl alkyl sulfide in which the ratio of the former to the latter was approximately 2:1. This ratio was not changed when O,O-(di-n-butyl)-S-alkyl phosphorodithioate reacted with sodium ethoxide and ethanol.

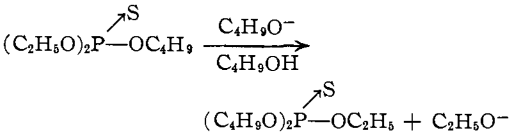


$$\begin{array}{l} (C_2H_5O)_2\overset{\nearrow S}{P}-S-R'' \xrightarrow[C_4H_9OH]{C_4H_9O^-} \underset{(2\ \text{parts})}{C_2H_5-S-R''} + \underset{(1\ \text{part})}{C_4H_9-S-R''} \\ \qquad\qquad\qquad\qquad\qquad\qquad C_2H_5O^- \uparrow C_2H_5OH \\ \qquad\qquad\qquad\qquad\qquad\qquad (C_4H_9O)_2\overset{\nearrow S}{P}-S-R'' \end{array} \quad (3)$$

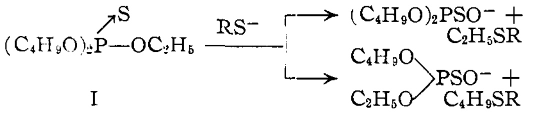
The formation of the two sulfides in approximately the same ratio in both reactions can be explained by assuming that both proceed through the same intermediate, di-n-butyl ethyl phosphorothionate (I). The ester interchange of n-butyl diethyl phosphorothionate (reaction 5) with sodium



$$(C_2H_5O)_2\overset{\nearrow S}{P}-S-R \xrightarrow[C_4H_9OH]{C_4H_9O^-} (C_2H_5O)_2\overset{\nearrow S}{P}-OC_4H_9 + RS^- \quad (4)$$



$$(C_2H_5O)_2\overset{\nearrow S}{P}-OC_4H_9 \xrightarrow[C_4H_9OH]{C_4H_9O^-} (C_4H_9O)_2\overset{\nearrow S}{P}-OC_2H_5 + C_2H_5O^- \quad (5)$$

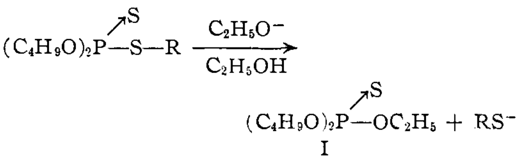


$$(C_4H_9O)_2\overset{\nearrow S}{P}-OC_2H_5 \xrightarrow{RS^-} \begin{cases} (C_4H_9O)_2PSO^- + C_2H_5SR \\ (C_4H_9O)(C_2H_5O)PSO^- + C_4H_9SR \end{cases} \quad (6)$$

I

n-butoxide and *n*-butanol yielding I is similar to the previously reported reaction of triethyl phosphate with sodium *n*-butoxide and *n*-butanol.[3] Separation of the mixture of sodium salts obtained in reaction 6 has not been accomplished.

In the reaction of di-*n*-butyl ethyl phosphorothionate (I) with sodium ethoxide and ethanol, ester interchange would not be expected to take place and sulfide formation would again occur according to reaction 6. The cleavage of an ethyl group from di-*n*-butyl ethyl phosphorothionate



$$(C_4H_9O)_2\overset{\nearrow S}{P}-S-R \xrightarrow[C_2H_5OH]{C_2H_5O^-} (C_4H_9O)_2\overset{\nearrow S}{P}-OC_2H_5 + RS^- \quad (7)$$

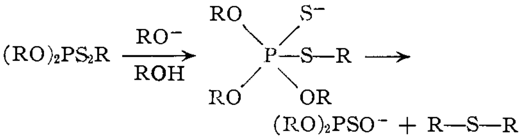
I

(I) must therefore occur more rapidly than the butyl group and thus a higher proportion of the corresponding ethyl sulfide is obtained. In the case of diethyl methyl phosphorothionate, the cleavage of the methyl group is so rapid that only the corresponding methyl sulfide is obtained.

A cleavage reaction of O,O-diphenyl-S-(2-octyl) phosphorodithioate with sodium ethoxide and ethanol gave in addition to ethyl 2-octyl sulfide, a 55% yield of phenol. No phenetole was isolated. Pishchimuka[4] reported the reaction of triphenyl phosphorothionate with sodium ethoxide and ethanol to yield phenetole and sodium O,O-diethyl phosphorothioate. The initial reaction probably involves the ester interchange of the phenoxy group with the ethoxy group, followed by the alkylation of the phenoxide ion with triethyl phosphorothionate yielding phenetole.

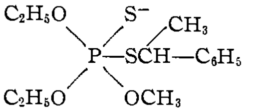
The low molecular weight phosphorodithioates undergo the alkoxide cleavage reaction; however, the isolation of the sulfides is complicated by the formation of azeotropic mixtures of alcohols with sulfides. The cleavage of O,O,S-triethyl phosphorodithioate with sodium ethoxide and ethanol produced diethyl sulfide and sodium O,O-diethyl phosphorothioate. The diethyl sulfide was converted to the sulfone m.p. 69°. The low yield of diethyl sulfide is due to azeotrope formation with ethanol.[5] Attempts to isolate methyl *t*-butyl sulfide from the reaction of O,O-diethyl-S-(*t*-butyl) phosphorodithioate with sodium methoxide and methanol were unsuccessful; however, a 77% yield of sodium O,O-diethyl phosphorothioate was isolated. Isobutylene was isolated and characterized as the α,β-dibromide. Under cleavage conditions, methyl *t*-butyl sulfide could be expected to yield isobutylene.

It has been postulated that the alkoxide cleavage reaction proceeds through a quasi-phosphonium structure which decomposes spontaneously or on heating to yield the sulfide and the sodium O,O-dialkyl phosphorothioate.[6]



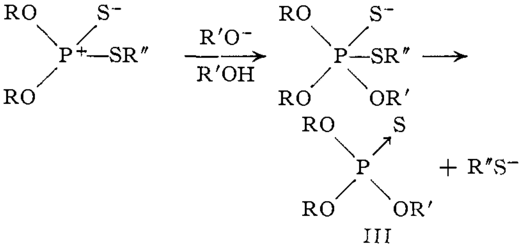
$$(RO)_2PS_2R \xrightarrow[ROH]{RO^-} (RO)_2\overset{S^-}{P}(OR)-S-R \longrightarrow (RO)_2PSO^- + R-S-R \quad (8)$$

In the reaction of O,O-diethyl-S-(α-phenethyl) phosphorodithioate with sodium methoxide and methanol a 20% yield of dimethyl ether was isolated in addition to methyl α-phenethyl sulfide and sodium O,O-diethyl phosphorothioate. If this reaction proceeded by the decomposition of the quasi-phosphonium structure (II), we would expect



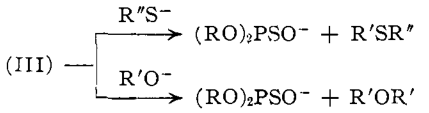
$$(C_2H_5O)_2\overset{S^-}{P}(OCH_3)-SCH(CH_3)-C_6H_5 \quad \text{II}$$

to obtain methyl ethyl ether, and not dimethyl ether. To account for the formation of dimethyl ether in this alkoxide cleavage reaction, it is probable that the reaction proceeds through the steps



$$(RO)_2\overset{S^-}{\overset{+}{P}}-SR'' \xrightarrow[R'OH]{R'O^-} (RO)_2\overset{S^-}{P}(OR')-SR'' \longrightarrow (RO)_2\overset{\nearrow S}{P}-OR' + R''S^- \quad (9)$$

III



$$(\text{III}) - \begin{cases} \xrightarrow{R''S^-} (RO)_2PSO^- + R'SR'' \\ \xrightarrow{R'O^-} (RO)_2PSO^- + R'OR' \end{cases} \quad (10)$$

$R = -C_2H_5$
$R' = -CH_3$
$R'' = -CH(CH_3)C_6H_5$

The intermediate trialkyl phosphorothionate III functions as an alkylating agent between two competing anions, the mercaptide and the alkoxide ion. The reaction of trimethyl phosphorothionate with sodium ethylmercaptide to give methyl ethyl sulfide and sodium O,O-dimethyl phosphorothioate is reported.[4] Trialkyl phosphorothionates undergo ester interchange as pointed out previously to account for the formation of two sulfides in the same reaction. Ether formation by the above mechanism would lower the yield of sulfide without substantially affecting the yield of sodium O,O-dialkyl phosphorothioate. The formation of ethyl *n*-butyl ether has been reported previously in the reaction of triethyl phosphate with sodium *n*-butoxide and *n*-butanol.[3]

Sodium O,O-diethyl phosphorothioate does not alkylate sodium mercaptides under conditions of the alkoxide cleavage reaction. It was found, however, that under strongly basic conditions sodium O,O-dialkyl phosphorothioate will function as an alkylating agent.

The Peroxide Effect.—Crude O,O-dialkyl hydrogen phosphorodithioates are obtained by the re-

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[3] W. H. C. Rueggeberg and J. Chernack, THIS JOURNAL, **70**, 1802 (1948).

[4] P. S. Pishchimuka, *J. Russ. Chem. Soc.*, **44**, 1406 (1912).

[5] L. H. Horsely, *Anal. Chem.*, **19**, 508 (1947).

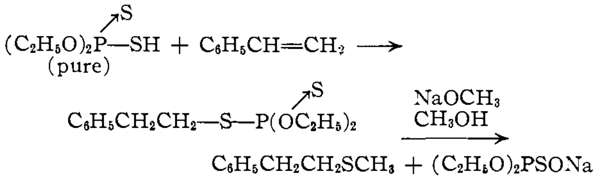
[6] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y.

action of alcohols with phosphorus pentasulfide.[7] These acids are of 80–90% purity, as determined by titration with standard alkali. Additions of crude O,O-dialkyl hydrogen phosphorodithioates to unsymmetrical olefins yield the normal addition product, *i.e.*, addition according to Markownikoff's rule.[2]

The addition of crude O,O-diethyl hydrogen phosphorodithioate, as prepared above, to commercial styrene gave a high yield of the normal addition product, O,O-diethyl-S-(α-phenethyl) phosphorodithioate. The alkoxide cleavage reaction of this triester with sodium methoxide and methanol gave methyl α-phenethyl sulfide which was readily oxidized to the sulfone (m.p. 83–84°) for identification. A mixed melting point with an authentic sample showed no depression. A high yield of the normal addition product was also obtained by the addition of crude O,O-diethyl hydrogen phosphorodithioate to commercial 1-octene. The triester, O,O-diethyl-S-(2-octyl) phosphorodithioate, subjected to the alkoxide cleavage reaction with sodium methoxide and methanol, gave methyl 2-octyl sulfide. The sulfilimine derivative[8] of this sulfide, m.p. 108–109°, showed no depression in a mixed melting point with an authentic sample.

The O,O-dialkyl hydrogen phosphorodithioates undergo many reactions suggestive of a highly acidic mercaptan. For example, they are readily oxidized to disulfides; they form salts which can be alkylated with alkyl halides to form triesters; and they add rapidly to olefins. The addition of crude O,O-dialkyl hydrogen phosphorodithioates to olefins to give high yields of the normal addition product is, however, at variance with the addition of mercaptans to olefins. Most of the addition reactions of mercaptans, thiolacetic acid and thiophenol to olefins occur contrary to the Markownikoff rule, that is, abnormal addition. Ordinary samples of olefins appear to contain enough peroxides to bring about abnormal addition.[9]

It was found that the addition of purified O,O-diethyl hydrogen phosphorodithioate to olefins is similar to the addition of mercaptans to olefins. Purified O,O-diethyl hydrogen phosphorodithioate adds readily to commercial styrene to yield only the abnormal addition product, as determined by the alkoxide cleavage reaction. The alkoxide cleavage product, methyl β-phenethyl sulfide, was oxidized to the sulfone, m.p. 85–86°. A mixed melting point with an authentic sample showed no depression of the melting point, while a mixed melting point with the sulfone from the sulfide derived from the crude acid addition product showed a 20° depression.

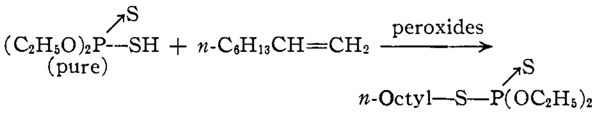


$$\underset{\text{(pure)}}{(C_2H_5O)_2}\overset{\nearrow S}{P}\text{—}SH + C_6H_5CH{=}CH_2 \longrightarrow$$

$$C_6H_5CH_2CH_2\text{—}S\text{—}\overset{\nearrow S}{P}(OC_2H_5)_2 \xrightarrow[CH_3OH]{NaOCH_3} C_6H_5CH_2CH_2SCH_3 + (C_2H_5O)_2PSONa$$

Ethanethiol is reported to add to 1-octene to yield 28% ethyl *n*-octyl sulfide and 4% ethyl 2-octyl sulfide.[10] Purified O,O-diethyl hydrogen phosphorodithioate adds to commercial 1-octene similarly to give a mixture of the normal and abnormal addition products. The sodium methoxide–methanol cleavage reaction gave 40% methyl 2-octyl sulfide and 26% methyl *n*-octyl sulfide. When this addition was repeated using peroxide-free 1-octene, only the normal addition product was obtained. These sulfides were characterized through their sulfilimine derivatives. The absence of peroxides in the 1-octene did not retard the addition of purified O,O-diethyl hydrogen phosphorodithioate. It is reported that the use of peroxide-free reagents retards or sometimes halts the addition of a mercaptan to an olefin.[11]

Since peroxide-free reagents result in the normal addition of O,O-diethyl hydrogen phosphorodithioate to 1-octene, the presence of peroxides during the addition should yield the abnormal addition product. Thiolacetic acid, for example, adds to styrene or 1-octene in the presence of ascaridole to give high yields of the abnormal addition product.[12] It was found similarly that addition of purified O,O-diethyl hydrogen phosphorodithioate to 1-octene in the presence of cumene hydroperoxide gave only the abnormal addition product. The sodium methoxide–methanol cleavage product, methyl *n*-octyl sulfide, was converted to the sulfilimine derivative,[8] m.p. 89–90°.



$$\underset{\text{(pure)}}{(C_2H_5O)_2}\overset{\nearrow S}{P}\text{—}SH + n\text{-}C_6H_{13}CH{=}CH_2 \xrightarrow{\text{peroxides}} n\text{-Octyl—}S\text{—}\overset{\nearrow S}{P}(OC_2H_5)_2$$

Crude O,O-dialkyl hydrogen phosphorodithioate, obtained from the reaction of an alcohol with P_4S_{10}, must therefore contain either a specific catalyst for the normal addition, or a reducing agent. This reducing agent could destroy the peroxides in the olefin thus allowing normal addition to occur.

An attempt was made to isolate from the crude O,O-dialkyl hydrogen phosphorodithioate a catalyst or a reducing agent which would promote normal (Markownikoff) addition when purified acid was added to a commercial sample of olefin from which peroxides had not been removed. The procedure used in purifying the crude acids was to dissolve the acid in cold sodium carbonate solution and extract the neutral organic portion. Acidification of the aqueous layer yielded the acid which was further purified by fractionation. On removal of the solvent from the neutral organic portion a liquid was obtained, which was found to be effective in promoting normal addition of the purified acid to commercial olefins. Fractionation of the neutral portion extracted from crude O,O-diethyl hydrogen phosphorodithioate led to the

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[7] T. W. Mastin, G. R. Norman and E. A. Weilmuenster, THIS JOURNAL, **67**, 1662 (1945).

[8] M. A. McCall, D. S. Tarbell and M. A. Havill, *ibid.*, **73**, 4477 (1951).

[9] V. N. Ipatieff and B. S. Friedman, *ibid.*, **61**, 71 (1939).

[10] S. O. Jones and E. E. Reid, *ibid.*, **60**, 2452 (1938).

[11] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 392 (1940).

[12] R. Brown, W. E. Jones and A. R. Pinder, *J. Chem. Soc.*, 2123 (1951).

TABLE II

THE ADDITION OF PURIFIED[a] O,O-DIETHYL HYDROGEN PHOSPHORODITHIOATE TO 1-OCTENE AND STYRENE

Olefin	Catalyst	Product	M[b]	Yield, %	Remarks
1-Octene	Cumene hydroperoxide	$(C_2H_5O)_2PSS$-*n*-Octyl	A	75	Commercial octene
1-Octene		$(C_2H_5O)_2PSS$-2-Octyl	N	87	1-Octene washed with $FeSO_4$ soln. prior to addn.
1-Octene		$(C_2H_5O)_2PSS$-*n*-Octyl	AN	26[c]	Commercial octene
		$(C_2H_5O)_2PSS$-2-Octyl		40[c]	
Styrene		$(C_2H_5O)_2PSSCH_2CH_2C_6H_5$	A	97	Commercial styrene
Styrene		$(C_2H_5O)_2PSSCH_2CH_2C_6H_5$	AN	57[c]	Styrene freshly distilled
		$(C_2H_5O)_2PSSCH(CH_3)C_6H_5$		20[c]	
Styrene	Sulfur	$(C_2H_5O)_2PSSCH_2CH_2C_6H_5$	A	89	Commercial styrene
Styrene	$(C_2H_5O)_3PS$	$(C_2H_5O)_2PSSCH_2CH_2C_6H_5$	A	76	Commercial styrene
Styrene	H_2S	$(C_2H_5O)_2PSSCH_2CH_2C_6H_5$	A	97	Commercial styrene
Styrene	P_4S_3	$(C_2H_5O)_2PSSCH(CH_3)C_6H_5$	N	85	Commercial styrene
Styrene	Ether extract	$(C_2H_5O)_2PSSCH(CH_3)C_6H_5$	N	98	Commercial styrene Ether extract obtained from crude $(C_2H_5O)_2PS_2Na$ (see Discussion)

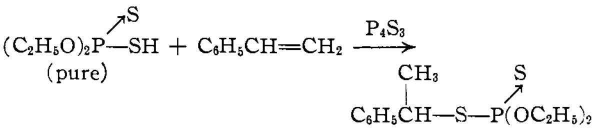
[a] Crude acids invariably add to unsymmetrical olefins to give high yields of normal addition products.[2] [b] Mode of addition: A, abnormal addition; N, normal addition; AN, mixture of addition types observed. [c] Yield based on the sulfides obtained by the alkoxide cleavage reaction.

isolation of three products. Triethyl phosphorothionate was isolated as a liquid distillate and from the crystallized distillation residue it was possible to isolate O,O,O,O-tetraethyl trithiopyrophosphate and sulfur. Hydrogen sulfide is a fourth impurity which is known to be present in the unpurified acid. Jones and Reid[10] have reported that the addition of ethyl mercaptan to propylene in the presence of sulfur yielded mainly ethyl isopropyl sulfide, the normal addition product. Sulfur showed no such effect when used as a catalyst in the addition of purified O,O-diethyl hydrogen phosphorodithioate to commercial styrene. The abnormal addition product was obtained. Similarly, saturation of the purified O,O-diethyl hydrogen phosphorodithioate with hydrogen sulfide before addition to commercial styrene did not promote normal addition. Both triethyl phosphorothionate and O,O,O,O-tetraethyl trithiopyrophosphate were found to have no effect on the addition reaction, abnormal addition products being obtained in both instances.

Further examination of the distillation residue showed the presence of both phosphorus and sulfur, and it was found that this material, crystalline in nature, reduced ammoniacal silver nitrate solution. When this material was used as a catalyst in the addition of purified O,O-diethyl hydrogen phosphorodithioate to commercial styrene the normal addition product was obtained. This behavior suggested the possibility that we were working with some reduced form of a sulfide of phosphorus. Attempts to isolate any pure sulfide of phosphorus were unsuccessful. An analysis of the phosphorus pentasulfide used in the preparation of the O,O-dialkyl hydrogen phosphorodithioates showed the presence of 0.2–2% of P_4S_3.

Phosphorus sesquisulfide does not react with alcohols, water or dilute base at room temperature.[13] It is readily oxidized and is soluble in diethyl ether, the solvent used in extracting the neutral residue from sodium O,O-diethyl phosphorodithioate. P_4S_3 could be expected therefore to be present and act as a reducing agent in the crude O,O-dialkyl hydrogen phosphorodithioates.

The addition of purified O,O-diethyl hydrogen phosphorodithioate to commercial styrene in the presence of P_4S_3 gave a high yield of the normal addition product. It is therefore probable that P_4S_3 present in the crude O,O-diethyl hydrogen phosphorodithioate is the active material which



$$\underset{\text{(pure)}}{(C_2H_5O)_2P(\nearrow S)\text{—}SH} + C_6H_5CH{=}CH_2 \xrightarrow{P_4S_3} C_6H_5\overset{CH_3}{\overset{|}{C}}H\text{—}S\text{—}P(\nearrow S)(OC_2H_5)_2$$

causes decomposition of the olefin peroxides, thus allowing normal addition to occur. Reactions concerned with the peroxide effect are summarized in Table II.

Under controlled conditions O,O-dialkyl hydrogen phosphorodithioates may be made to add to unsymmetrical olefins to yield either the normal or the abnormal addition products. Through the alkoxide cleavage reaction of various O,O,S-trialkyl phosphorodithioates an unlimited number of sulfides may be prepared. In many cases, this method is much more convenient than the present methods.

Experimental[14]

I. Methyl 2-Octyl Sulfide (from the Alkoxide Cleavage of O,O-Diethyl-S-(2-octyl) Phosphorodithioate).—Sodium methoxide was prepared by the addition of 23 g. (1.0 mole) of sodium to 300 ml. of absolute methanol. The resulting solution was heated to reflux and 149 g. (0.50 mole) of O,O-diethyl-S-(2-octyl) phosphorodithioate[15] was added dropwise over a period of 20 minutes. After complete addition of the triester the solution was heated to reflux for six hours, cooled to 30°, and blown with carbon dioxide for one hour. The reaction mixture was then steam distilled until only traces of organic material was obtained in the distillate. The volume of distillate was approximately three liters. The distillate was saturated with sodium chloride and extracted with diethyl ether. The ether layer was dried with magnesium sulfate, ether removed, and the residue fractionated *in vacuo*, yielding 52 g. (65%) of methyl 2-octyl sulfide, b.p. 80–82° (10 mm.), n^{20}_D 1.4561.

Anal. Calcd. for $C_9H_{20}S$: S, 20.00. Found: S, 19.60.

The residue from the steam distillation was evaporated on a steam-bath. The salts were extracted with 400 ml. of ethyl acetate and the insoluble sodium carbonate was re-

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(13) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y.

(14) All melting points are uncorrected.

(15) Prepared by the addition of crude O,O-diethyl hydrogen phosphorodithioate to the corresponding olefin (see reference 2).

moved by filtration. The ethyl acetate solution was evaporated to a volume of 200 ml. and cooled in an ice-bath. The solution was diluted with 1500 ml. of petroleum ether (80–110°). On standing, 60 g. (63%) of sodium O,O-diethyl phosphorothioate precipitated as fine white needles, m.p. 190–191°.

Anal. Calcd. for $C_4H_{10}O_3PSNa$: P, 16.14; Na, 12.00. Found: P, 15.80; Na, 12.20.

The sulfilimine derivative of methyl 2-octyl sulfide was prepared by treating a solution of 3.2 g. (0.02 mole) of methyl 2-octyl sulfide dissolved in 10 ml. of ethanol with a solution of 8.4 g. (0.03 mole) of chloramine T dissolved in 60 ml. of 50% ethanol–water solution. The solution was heated on the steam-bath for 20 minutes, then allowed to stand overnight. The crystals were collected, washed with diethyl ether, and recrystallized twice from dilute ethanol, m.p. 108–109°.

Anal. Calcd. for $C_{16}H_{27}NO_2S_2$: S, 19.45; N, 4.26. Found: S, 19.30; N, 4.35.

An authentic sample of methyl 2-octyl sulfide was prepared by the alkylation of 2-octanethiol with dimethyl sulfate.[16] The sulfilimine was prepared as described above, m.p. 108–109°. A mixed melting point of the two samples showed no depression.

II. Methyl α-Phenethyl Sulfide (from the Alkoxide Cleavage of O,O-Diethyl-S-(α-phenethyl) Phosphorodithioate).—The sodium methoxide–methanol cleavage of O,O-diethyl-S-(α-phenethyl) phosphorodithioate[15] was carried out using the same molar quantities and procedure described under I. Methyl α-phenethyl sulfide, 63 g., was obtained in a 69% yield, b.p. 70° (4 mm.), $n^{20}D$ 1.5497.

Anal. Calcd. for $C_9H_{12}S$: S, 21.05. Found: S, 20.70.

The residue from the steam distillation treated as described under I, gave 75 g. (78%) of sodium O,O-diethyl phosphorothioate, m.p. 190–191°.

Methyl α-phenethyl sulfone was prepared by oxidizing the sulfide with hydrogen peroxide dissolved in glacial acetic acid. The product was recrystallized from ethanol, m.p. 83–84°.

Anal. Calcd. for $C_9H_{12}O_2S$: S, 17.38. Found: S, 17.14.

An authentic sample of methyl α-phenethyl sulfide was prepared by alkylating α-phenethylthiol[17] with dimethyl sulfate. The sulfone prepared from this sulfide showed no depression in a mixed melt with the above sample obtained by alkoxide cleavage.

III. Purification of O,O-Diethyl Hydrogen Phosphorodithioate.—Crude O,O-diethyl hydrogen phosphorodithioate[7] (1000 g., 5.4 moles) was added dropwise to a solution of 318 g. (3.0 moles) of sodium carbonate in three liters of water at room temperature under an atmosphere of nitrogen. After complete addition, the product was agitated for 30 minutes and then extracted with diethyl ether to remove neutral material. The aqueous layer containing sodium O,O-diethyl phosphorodithioate was made strongly acid with concentrated hydrochloric acid and the mixture extracted with diethyl ether. The ether layer was dried with magnesium sulfate and the ether removed by distillation under nitrogen. The residue was fractionated *in vacuo* yielding 835 g. (84%) of O,O-diethyl hydrogen phosphorodithioate, b.p. 65–67° (0.8 mm.).

Anal. Calcd. for $C_4H_{11}O_2PS_2$: P, 16.65; S, 34.40; neut. equiv., 186. Found: P, 16.68; S, 33.90; neut. equiv., 185.

The ether layer containing the neutral material was dried with magnesium sulfate, the ether removed under nitrogen, and the residue fractionated *in vacuo* under nitrogen. Triethyl phosphorothionate, b.p. 62–64° (2 mm.), $n^{20}D$ 1.4509, was obtained in the distillate. This product was identified through its infrared pattern. O,O,O,O-Tetraethyl trithiopyrophosphate and sulfur were isolated from the distillation residue. The former, m.p. 41–42°, was identified through a mixed melting point with an authentic sample.[18]

IV. O,O-Diethyl-S-(β-phenethyl) Phosphorodithioate (by the Addition of Purified O,O-Diethyl Hydrogen Phosphorodithioate to Styrene).—Commercial styrene (62.5 g., 0.6 mole) was added dropwise to 83 g. (0.45 mole) of purified O,O-diethyl hydrogen phosphorodithioate in a 3-neck flask equipped with an agitator, nitrogen inlet tube, a condenser and a thermometer well. The addition was conducted at a rate such that the reaction temperature did not rise above 60°. After complete addition of the styrene, the reaction mixture was heated four hours at 70°, at which time the acidity of the reaction mixture had decreased to a substantially constant value. The product was cooled, washed with 200 ml. of 10% sodium hydroxide and extracted with 200 ml. of isopropyl ether. The ether layer was washed with water several times and dried with magnesium sulfate. The ether was removed by distillation and the residue stripped to 130° (0.5 mm.). The residue, 111 g., corresponds to an 84% yield of crude O,O-diethyl-S-(β-phenethyl) phosphorodithioate. Titration with standard alkali showed the product to be neutral.

Methyl β-Phenethyl Sulfide (by Alkoxide Cleavage of O,O-Diethyl-S-(β-phenethyl) Phosphorodithioate).—The crude triester was subjected to the sodium methoxide–methanol cleavage reaction as outlined under I. A 61% yield of methyl β-phenethyl sulfide was obtained, b.p. 80–86° (4 mm.), $n^{20}D$ 1.5513.

Anal. Calcd. for $C_9H_{12}S$: S, 21.05. Found: S, 20.85. Methyl β-phenethyl sulfone, m.p. 86°.

An authentic sample of methyl β-phenethyl sulfide was prepared by the alkylation of β-phenethylthiol[16] with dimethyl sulfate. The physical properties of this sulfide and the sulfide from the cleavage reaction were identical. A mixed melt of the two sulfones showed no depression. The infrared patterns of the two sulfides were also similar.

V. O,O-Diethyl-S-(α-phenethyl) Phosphorodithioate (by Addition of Purified O,O-Diethyl Hydrogen Phosphorodithioate to Styrene in Presence of P_4S_3).—Commercial styrene (63 g., 0.6 mole) was added dropwise to 97 g. (0.53 mole) of purified O,O-diethyl hydrogen phosphorodithioate containing 3 g. of P_4S_3. The addition was conducted at a rate such that the reaction temperature did not rise above 60°. After complete addition, the reaction was heated to 110° for eight hours. The reaction mixture was treated as outlined under IV.

The product, 130 g. (85%), was subjected to the sodium methoxide–methanol cleavage reaction as outlined under I. Methyl α-phenethyl sulfide, 42 g. (62%), was obtained, b.p. 70–72° (4 mm.), $n^{20}D$ 1.5494, methyl α-phenethyl sulfone, m.p. 83–84°.

VI. O,O-Diethyl-S-(2-octyl) Phosphorodithioate (by Addition of Purified O,O-Diethyl Hydrogen Phosphorodithioate to Peroxide-free 1-Octene).—Commercial 1-octene was washed with a 10% ferrous sulfate solution, dried with magnesium sulfate and filtered under a nitrogen atmosphere. The "peroxide-free" 1-octene (55 g., 0.49 mole) was added under nitrogen to 73 g. (0.39 mole) of purified O,O-diethyl hydrogen phosphorodithioate at such a rate to maintain the temperature below 70°. After complete addition, the reaction was heated to 70–75° for six hours or until the acidity had decreased to a substantially constant value. The product was cooled, washed with 200 ml. of 10% sodium hydroxide, extracted with isopropyl ether and washed with 200 ml. of water five times. The ether layer was dried with magnesium sulfate, the ether removed by distillation, and the residue stripped to 120° (0.5 mm.). The residue, 101 g. (87%), was the desired triester. Titration of a sample of the triester with standard alkali showed the product to be neutral.

The sodium methoxide–methanol cleavage of this crude triester gave methyl 2-octyl sulfide (68%) as outlined under I; b.p. 80–82° (10 mm.); $n^{20}D$ 1.4561.

Anal. Calcd. for $C_9H_{20}S$: S, 20.00. Found: S, 19.92. Sulfilimine derivative, m.p. 108–109°.

VII. O,O-Diethyl-S-(*n*-octyl) Phosphorodithioate (by Addition of Purified O,O-Diethyl Hydrogen Phosphorodithioate to 1-Octene in Presence of Peroxide).—The 1-octene (67 g., 0.60 mole) and cumene hydroperoxide (2 ml.) were stirred at room temperature for three hours. Purified O,O-diethyl hydrogen phosphorodithioate (93 g., 0.50 mole) was added dropwise at a rate such as to maintain the temperature at 35–40°. After complete addition, the reaction mixture was agitated for four hours, then heated at 60–70° for ten hours. The acidity of the reaction mixture had decreased to a substantially constant value. The product was cooled, washed with 200 ml. of 10% sodium hydroxide and ex-

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(16) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1081 (1935).

(17) D. Sontag, *Ann. chim.*, [II] **1**, 359 (1934).

(18) Kindly furnished by Dr. Norman Meinhardt of this Laboratory.

tracted with 200 ml. of isopropyl ether. The ether layer was washed with 200 ml. of water five times and dried with magnesium sulfate. The ether was removed and the residue stripped to 125° (2 mm.). The crude triester, 76 g., was obtained in 51% yield. Titration of a sample of the triester with standard alkali showed the product to be neutral.

The sodium methoxide–methanol cleavage reaction as outlined under I gave methyl *n*-octyl sulfide, 15 g. (38% theory), b.p. 85–88° (10 mm.), $n^{20}D$ 1.4580.

Anal. Calcd. for $C_9H_{20}S$: S, 20.00. Found: S, 19.85. Sulfilimine derivative, m.p. 89–90°.

VIII. O,O-Di-(2-ethylhexyl)-S-(2-octyl) Phosphorodithioate.—The 1-octene (392 g., 3.5 moles) was added dropwise to the crude O,O-di-(2-ethylhexyl) hydrogen phosphorodithioate[7] (1060 g., 3.0 moles) at such a rate that the temperature did not rise above 100°. After the addition was completed, the stirred solution was heated to 115–120° and maintained at this temperature until the acidity had decreased to a substantially constant value. The reaction mixture was cooled and washed with 10% sodium hydroxide solution. The organic layer was washed with water (sodium chloride was used to break the emulsion). The product was dried with magnesium sulfate and the excess olefin was removed by heating to a pot temperature of 125° (0.1 mm.). The residue, 1380 g., corresponds to a 95% yield of the triester. Titration with standard alkali showed the product to be neutral.

Anal. Calcd. for $C_{24}H_{51}O_2PS_2$: P, 6.66; S, 13.70. Found: P, 6.36; S, 14.04.

***n*-Propyl 2-Octyl Sulfide.**—The cleavage of the crude O,O-di-(2-ethylhexyl)-S-(2-octyl) phosphorodithioate with sodium *n*-propoxide and *n*-propanol was carried out as outlined under I. The *n*-propyl 2-octyl sulfide was obtained in a 47% yield, b.p. 111° (15 mm.), $n^{20}D$ 1.4573.

Anal. Calcd. for $C_{11}H_{26}S$: S, 17.05. Found: S, 17.05.

The infrared patterns of this sulfide and the synthetic sample were identical.

A small amount of 2-ethylhexanol was isolated from this reaction. This was probably formed during the prolonged period of steam distillation from the alkaline medium.

The residue after steam distillation contained two layers. The organic layer was dried by refluxing with benzene and trapping out the water. The benzene was evaporated and the residue, 55 g. (53%) of sodium O,O-di-(2-ethylhexyl) phosphorothioate, was isolated. No purification of this product was carried out.

IX. O,O-Diethyl-S-(*t*-butyl) Phosphorodithioate.—The crude O,O-diethyl hydrogen phosphorodithioate, 1028 g. (5.5 moles), was placed in the stainless steel liner of a 1-gallon Aminco shaker autoclave. The liner was cooled to −75° and 355 g. (6.3 moles) of liquefied isobutylene was added. The liner was then quickly assembled in the autoclave. The autoclave was shaken and heated to 100–115° and the reaction was maintained at this temperature for six hours. The autoclave was cooled and the excess isobutylene was vented. The crude reaction product was washed with 5% sodium hydroxide, extracted with isopropyl ether, washed with 500 ml. of water, and dried over magnesium sulfate. The solvent was removed and the product fractionated *in vacuo* under nitrogen. O,O-Diethyl-S-(*t*-butyl) phosphorodithioate, 930 g., was obtained in a 70% yield; b.p. 78–80° (0.4 mm.), $n^{20}D$ 1.5023.

Anal. Calcd. for $C_8H_{19}PO_2S_2$: S, 26.5; P, 12.8. Found: S, 26.7; P, 12.8.

The sodium methoxide–methanol cleavage of O,O-diethyl-S-(*t*-butyl) phosphorodithioate was carried out as described under I. No methyl *t*-butyl sulfide was isolated; however, isobutylene was isolated from the Dry Ice trap and characterized as the α,β-dibromide,[19] b.p. 149–150°, $n^{20}D$ 1.5118.

From the residue after steam distillation, 74 g. (77%) of sodium O,O-diethyl phosphorothioate was obtained, m.p. 190–191°.

Miscellaneous Alkoxide Cleavage Reactions.—All alkoxide cleavage reactions reported in the tables and not described in the Experimental section were carried out as reported in procedure I.

Acknowledgment.—The authors wish to thank Drs. T. W. Mastin and G. R. Norman for their helpful suggestions and continued interest during this investigation and Mr. H. Ferber who carried out the phosphorus and sulfur determinations.

[19] W. Krestinsky, *Ber.*, **55**, 2757 (1922).

CLEVELAND, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

Oxygen Analogs of Pteroic Acid

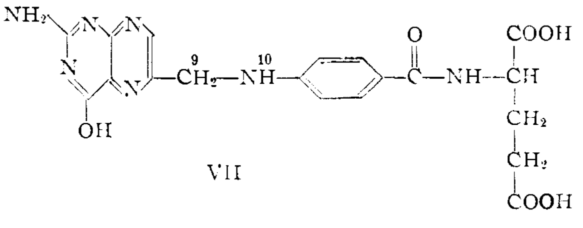
BY E. I. FAIRBURN, B. J. MAGERLEIN,[1] L. STUBBERFIELD, E. STAPERT AND D. I. WEISBLAT

RECEIVED AUGUST 31, 1953

The synthesis of four oxygen analogs of pteroic acid and pteroylglutamic acid in which the N^{10} nitrogen is replaced by oxygen is described. Data are presented showing that these compounds are folic acid antagonists.

Various analogs of pteroylglutamic acid have been reported in the literature as folic acid antagonists.[2] The chemical variations in the basic pteroylglutamic acid structure (VII) have been summarized and classified by Cosulich, *et al.*[3]

The synthesis of pteroylglutamic acid recently reported from this Laboratory[4] is admirably suited to prepare pteroic acid and pteroylglutamic acid analogs in which the N^{10} nitrogen is replaced by oxygen. The syntheses of four compounds of this type are shown in Chart I.



VII

p-Acetoxybenzoyl chloride, prepared by the method of Robertson and Robinson,[5] was condensed with diethyl L-glutamate to give diethyl *p*-acetoxybenzoyl-L-glutamate (I). Transesterification of this product with ethanol gave diethyl *p*-hydroxybenzoyl-L-glutamate (IIa) in high yield.

The alkylation of II and IIa with 2,3-oxidopropionaldehyde diethyl acetal[4] in the presence of py-

[1] Send requests for reprints to this author.

[2] J. B. Thiersch and F. S. Phillips, *Am. J. Med. Sci.*, **217**, 575 (1949); H. G. Petering, *Physiol. Rev.*, **32**, 197 (1952).

[3] D. B. Colsulich, D. R. Seeger, M. J. Fahrenbach, B. Roth, J. H. Mowat, J. M. Smith, Jr., and M. E. Hultquist, THIS JOURNAL, **73**, 2554 (1951).

[4] D. I. Weisblat, B. J. Magerlein, D. R. Myers, A. R. Hanze, E. I. Fairburn and S. T. Rolfson, *ibid.*, **75**, 5983 (1953).

[5] A. R. Robertson and R. Robinson, *J. Chem. Soc.*, 1713 (1926).