

Alkoxyethylphosphonic and Alkoxyethylphosphonothioic Derivatives

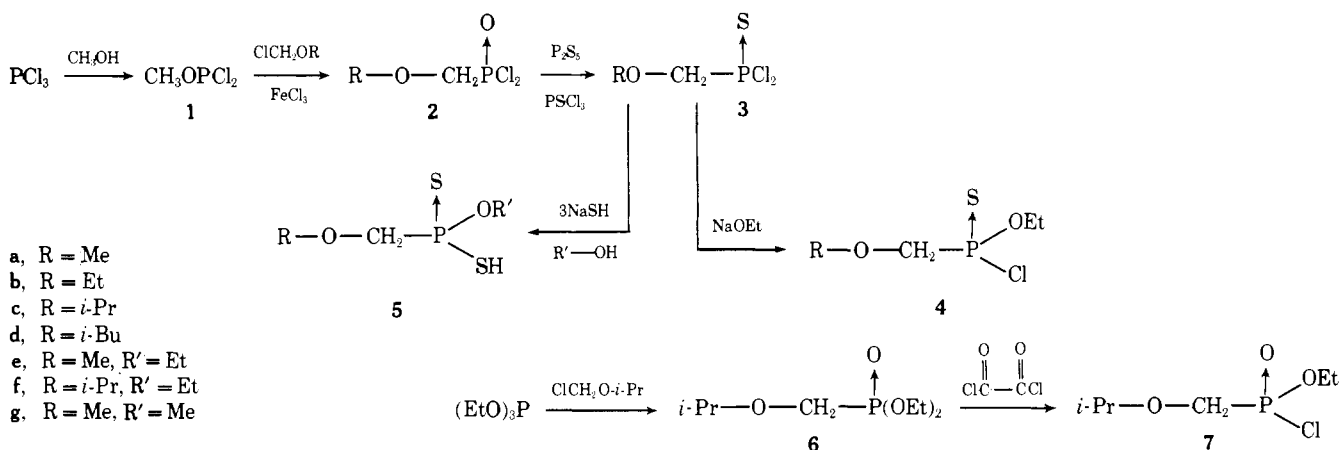
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Definitive physical properties for new compounds in the following classes: alkoxyethylphosphonothioic dichlorides, *O*-ethyl alkoxyethylphosphonochloridothioates, and alkoxyethylphosphonothiolothionic acids are reported. Improved syntheses for convenient medium scale laboratory preparations of these compounds are

described. P³¹ nuclear magnetic resonance spectra for all compounds have been obtained, and an analysis of the H¹ nmr spectra of the alkoxyethylphosphonothioic dichlorides shows the presence of a long-range ⁴J(P—H) P³¹—H¹ coupling in these materials.

The following routes were used to obtain the compounds of interest:



Methyl phosphorodichloridite 1 was obtained in high yield from the reaction of methanol with a 50% excess of phosphorus trichloride (8, 13). The resulting binary mixture of 1 (65 wt %) and phosphorus trichloride was reacted in the next step. This procedure obviated a tedious fractional distillation which unpredictably caught fire owing to the formation of a pyrophoric residue.

Moderate yields of crude alkoxyethylphosphonic dichlorides (Table I) resulted from the reaction of methyl phosphorodichloridite with chloromethyl alkyl ethers in the presence of ferric chloride catalyst (7). Short path distillations under pressures of lower than 0.2 mm (Hg) and temperatures of less than 80° were necessary to prevent extensive decomposition of the products. In the case of methoxymethylphosphonic dichloride, the *ir*, P³¹ nmr, H¹ nmr, and elemental analysis of the purified material were consistent with the structure 2a. A common method (14) used to obtain alkylphosphonic dichlorides failed to yield 2a: the reaction of dimethyl methoxymeth-

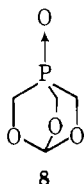
ylphosphonate with two equivalents of phosphorus pentachloride resulted in a crude mixture containing methyl methoxymethylphosphonochloridate in addition to a mixture of unidentified products.

The alkoxyethylphosphonothioic dichlorides, 3, were obtained by reactions of crude 2 with phosphorus pentasulfide (15). Drastically reduced yields of the products occurred without solvent, in this case, thiophosphoryl chloride. The products 3 were carefully purified and characterized (Table II). The P³¹ nmr resonances of 3 (a-d) are within the range of those of a number of alkylphosphonothioic dichlorides (-79.4 to -114.5 ppm) (9). It is interesting, in this respect, that chloromethylphosphonothioic dichloride has its resonance at -73 ppm (9).

The chemical shifts, splitting patterns, and relative areas of the peaks in the H¹ nmr spectra of 3 (a-d) are consistent with the structures of their respective alkoxyethyl groups (Table III). The resonance of the methylene protons (b) adjacent to the phosphorus in 3 (a-d) is found close to -4.4 ppm and exhibits ²J(P—H) of 7.0 cps. These values are comparable with the resonance of

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the closely related structures, $\text{Cl}-\text{CH}_2-\overset{\text{S}}{\uparrow}\text{PCl}_2$ at -4.3 ppm, ${}^2\text{J}(\text{P}-\text{H})$, 3.9 cps (19) and **8** (2) at -4.42 ppm, ${}^2\text{J}(\text{P}-\text{H})$ 7.4 cps.



The range of the peaks of the protons (a) (Table III) is 0.2–0.5 ppm downfield from those of the analogous protons in aliphatic ethers (22). These peaks, with the exception of that of the isopropyl derivative, **3c**, exhibit long range ${}^1\text{H}-\text{P}^{31}$ spin-spin coupling, ${}^4\text{J}(\text{P}-\text{H})$, 2–3 cps. This is analogous to the ${}^4\text{J}(\text{P}-\text{H})$ of 3 cps observed in the related structure **8** (2). In addition, the chemical shifts of protons (c) **3** (b–d) are found very close to those of the corresponding β protons in aliphatic ethers (21). Resonance of protons (d) in the isobutoxy group of **3d** occurs in the range of methyl groups of aliphatic hydrocarbons (27) consistent with this structure.

Although it has been stated that alkoxides are not suitable for the conversion of phosphonothioic dichlorides to pure *O*-alkyl phosphonochloridothioate (18), **4** (a, c, d) were prepared in a high state of purity by the reaction of sodium ethoxide with the corresponding alkoxymethylphosphonothioic dichlorides (3). The compounds **4** (a, c, d) were characterized by their analyses, ir and P^{31} nmr spectra. Purities were determined by gas chromatography (Table IV). In the P^{31} nmr spectra of **4** (a, c, d), the chemical shifts are close to the range of other reported *O*-alkyl alkylphosphonochloridothionates, (-95 to -106 ppm) (10).

The alkoxymethylphosphonothioic acids **5** (e, f, g) were obtained in variable yield by the reaction of alkoxymethylphosphonochloridothionates **3** with sodium hydrosulfide in alcohols (16) (Table V). The products **5** had P^{31} nmr chemical shifts close to those of several "in situ" *O*-alkyl methylphosphonothioic acids (-94 ppm) (11).

Diethyl isopropoxymethylphosphonate, **6** (4, 17), and ethyl isopropoxymethylphosphonochloridate, **7** (20), were prepared by standard procedures. Their structures are consistent with their elemental analyses and ir spectra.

Table I. Crude Alkoxymethylphosphonic Dichlorides

Compound	Bp, crude	$n^{25\text{D}}$	P^{31} nmr, ppm	Yield, %
2a	40–58°/0.1–0.25 mm	1.4668	–41.5	49
2b	43–61°/0.25 mm	1.4614	...	36
2c	33–62°/0.06 mm	1.4562	–42.3	42
2d	44–74°/0.5 mm	1.4557	–42.2	58

Table II. Alkoxymethylphosphonothioic Dichlorides^a

Compound	Bp	$n^{25\text{D}}$	P^{31} nmr, ppm	Yield, %
3a	83–85°/18 mm	1.5408	–81.9	44
3b	88.5–90°/14 mm	1.5261	–80.4	35
3c	87.5–94.5°/14 mm	1.5146	–83.0	40
3d	44.5–47°/0.13 mm	1.5084	–81.5	33

^a Elemental analyses (C, H, O, P, S) in agreement with theoretical values were obtained and were submitted for review.

Additional structural evidence is derived from the comparison of the P^{31} nmr chemical shifts of **2c**, **6**, **7** with those of analogous compounds (Table VI). The isopropoxy-methyl derivatives follow the general trend that progressive substitution of chloride for ethoxy on phosphorus leads to a corresponding deshielding of the phosphorus nucleus. Another conclusion from the data in Table VI is that the P^{31} nmr chemical shift of these phosphonic derivatives is related roughly to the electronegativity of the α substituent such that increasing electron withdrawal results in upfield chemical shifts. The same phenomenon has been reported for a series of phosphonates (23).

Experimental

Materials. Methanol (Matheson, synthetic) was distilled over calcium hydroxide in a dry atmosphere, bp 65–65.5°. Benzene (Matheson, purified) was dried by distillation. Phosphorus trichloride (reagent), phosphorus pentachloride (reagent) chloromethyl ether (bp 58–60°), ferric chloride (anhydrous reagent sublimed), phosphorus pentasulfide (mp 278–280°), triethyl phosphite (tech.), and oxalyl chloride (mp -10 to -8°) were obtained from the Matheson Co. and were used as received. Thiophosphoryl chloride (Stauffer Chemical Co.) was used as received. Chloromethyl isopropyl ether, bp 32–36.5°/50–67 mm, $n^{21\text{D}}$ 1.4068 (Lit., bp 36°/45 mm, $n^{20\text{D}}$ 1.4095 (5)), was synthesized by the reaction of isopropanol (Matheson, bp 82–83°) with paraformaldehyde (Matheson, 95%), and hydrogen chloride (Matheson anhydrous) (5). Anhydrous sodium hydrosulfide was prepared in situ by saturating an ethanol solution of sodium ethoxide (1.8 m) with hydrogen sulfide (Matheson, cp) at 25–40°. Dimethyl methoxymethylphosphonate, bp 46–48°/0.1 mm, $n^{23\text{D}}$ 1.4234 (Lit., bp 91°/7 mm, $n^{20\text{D}}$ 1.4242 (1)) was prepared by the reaction of chloromethyl methyl ether with trimethyl phosphite (Matheson pract.) at 51–118°.

Spectroscopy

Infrared spectra were obtained on a Perkin-Elmer Model 137B Infracord spectrophotometer. ${}^1\text{H}$ nmr spectra were recorded on a Varian A-60 nmr spectrometer. Chemical shifts were recorded in parts per million (ppm) relative to tetramethyl silane as an internal standard. ${}^{31}\text{P}$ nmr spectra were recorded with a Varian HA-100 spectrometer. Chemical shifts are reported relative to 85% phosphoric acid as an external standard. Gic analyses were performed on a Varian Aerograph Model 600-D.

Preparation of Methyl Phosphorodichloridite

Methanol (128.0 grams, 4.00 moles) was added dropwise during 1 hr under the surface of well-stirred phosphorus trichloride (824.4 grams, 5.999 moles) maintained at -3° to -7° with cooling in a dry nitrogen atmosphere. The cooling bath was removed, a dry ice condenser was added, and the stirred reaction mixture was swept with a moderate stream of dry nitrogen during 24 hr. The bottom layer of the reaction mixture (23 grams) was separated, and the top layer was distilled with stirring under nitrogen to yield a liquid, bp 55–91° (pot to 97°). A pot temperature of over 100° resulted in the formation of a yellow semisolid which decomposed exothermally with the evolution of pyrophoric vapors. The liquid contained methyl phosphorodichloridite, 453.0 grams, 86% yield, and phosphorus trichloride, 241.0 grams, 88% recovery. The P^{31} nmr spectrum had two peaks: -179 and -218 ppm (Lit., CH_3OPCl_2 , -181 ppm; PCl_3 , -219 ppm (12)).

The proportions of methyl phosphorodichloridite and phosphorus trichloride in the liquid were determined by reaction of an aliquot with excess *n*-propanol in triethylamine (6). The resulting mixture of di-*n*-propylmethyl

Table III. Proton Nmr Values of Alkoxyethylphosphonothioic Dichlorides

Structure	Peak, a ^a	Form	¹ J _{P-H} ^b	No. of protons	Peak, b ^a	Form	² J _{P-H} ^b	No. of protons	Peak, c ^a	Form	³ J _{H-H} ^b	No. of protons	Peak, d ^a	Form	³ J _{H-H} ^b	No. of protons
$\begin{array}{c} \text{S} \\ \uparrow \\ \text{CH}_3\text{-O-CH}_2\text{-PCl}_2 \\ \text{(a)} \\ \text{(b)} \end{array}$	-3.70	2	2.5	3.0	-4.43	2	7.5	2.0								
$\begin{array}{c} \text{S} \\ \uparrow \\ \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-PCl}_2 \\ \text{(c)} \\ \text{(a)} \\ \text{(b)} \end{array}$	-3.88	8	2.0 (estd)	1.9	-4.42	2	7.0	1.9	-1.23	3	7.0	3.1				
$\begin{array}{c} \text{S} \\ \uparrow \\ \text{CH}_3\text{-CH-O-CH}_2\text{-PCl}_2 \\ \text{(c)} \\ \text{(a)} \\ \text{(b)} \end{array}$	-3.98	7	<0.5	1.1	-4.35	2	6.5	2.1	-1.22	2	6.0	5.9				
$\begin{array}{c} \text{S} \\ \uparrow \\ \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-PCl}_2 \\ \text{(c)} \\ \text{(a)} \\ \text{(b)} \end{array}$	-3.60	4	2.5 (estd)	1.9	-4.40	2	7.0	1.9	-1.88	M	7.0	1.1	-0.95	2	7.0	5.9

^aValues in ppm. ^bValues in cps.

phosphite and tri-*n*-propyl phosphite was analyzed quantitatively by gas-liquid chromatography (column, 5% SE-30 on 60-80 mesh chromosorb W; 5 ft X 1/8-in. o.d.; temp, 95°, N₂ 16 psi, flame ionization detector). The di-*n*-propylmethyl phosphite and tri-*n*-propylphosphite had retention times of 2.2 and 5.2 min, respectively.

Reaction of Dimethyl Methoxymethylphosphonate with Phosphorous Pentachloride (1:2)

Approximately 10 ml of a solution of dimethyl methoxymethylphosphonate (30.8 grams, 200 mmol) in carbon tetrachloride (250 ml) was distilled and discarded. Phosphorus pentachloride (85.0 grams, 400 mmol) was added in portions during 15 min to the solution at 5-10° (ice bath cooling) in a dry atmosphere. The ice bath was removed, and the stirred reaction mixture was heated to 53° during three-quarters of an hour to yield a clear solution. There was a rapid evolution of gas. The mixture was heated at 56° for 2 hr. The volatiles were distilled to a pot temperature of 78°. The liquid residue was distilled through an 8-in. Vigreux column to yield the product, 14.0 grams, 43% yield, bp 94-97°/12 mm, *n*²⁵_D 1.4445.

Anal. Calcd for C₃H₈ClO₃P: C, 22.8; H, 5.1; Cl, 22.4; P, 19.6. Found: C, 22.7; H, 4.9; Cl, 22.8; P, 19.8.

The infrared spectrum of the product was identical with that of the product resulting from the reactants (1:1) which had a P³¹ nmr chemical shift of -36 ppm (52%) and minor peaks at -42.5 ppm (14%); -24.7 ppm (d) 11%; -15.0 ppm (18%); and -4.0 ppm (5%).

Preparation of Methoxymethylphosphonic Dichloride

Chloromethyl methyl ether (286.0 grams, 3.550 moles) was added dropwise during 1 hr and 15 min to a stirred mixture of methyl phosphorodichloridite (444.0 grams, 3.350 moles), phosphorus trichloride (243.0 grams), and ferric chloride (5.0 grams) at 28-34° in a dry nitrogen atmosphere. The reaction mixture was heated at 36-40° for 4 hr, then allowed to stand at 25° for 12 hr and heated gradually to 62° for 3 hr and 10 min. The amber-colored reaction mixture was stripped in a dry atmosphere at 50°/20 mm to yield a mobile liquid. The mixture was distilled in a short path distillation apparatus to yield a distillate, 272.0 grams, bp 40-58°/0.1-0.25 mm. The distillate was redistilled through an 8-in. Vigreux column to yield a fraction I, 6.8 grams, bp 36-38°/0.27 mm; II, 213.8 grams, bp 36-38°/0.15 mm, *n*²⁵_D 1.4668; III, 42.9 grams, bp 27.5-29°/0.15 mm, *n*²⁵_D 1.4658. The infrared spectra of II and III were identical to each other and to an authentic sample. The product (II, III), 256.6 grams (49% yield), Lit., bp 40-46°/0.1-2 mm (8, 13).

An authentic sample, bp 33-38°/0.1-0.5 mm, *n*²⁵_D 1.4679 was prepared in the same manner.

Anal. Calcd for C₂H₅Cl₂O₂P: C, 14.7; H, 3.1, P, 19.0. Found: C, 14.8; H, 3.2; P, 19.1.

The infrared spectrum of the product had peaks at 2950 cm⁻¹ (C-H), 1270 cm⁻¹ (P → O), and 1090 cm⁻¹ (C-O-C). The proton nmr had peaks at -3.62 ppm (d), ⁴J_{P-H} 3.0 cps (3.2), -4.38 ppm (d), ²J_{P-H} 3.5 cps (2.0).

Isopropoxymethylphosphonic Dichloride (Crude)

Chloromethyl isopropylether (123.6 grams, 1.140 moles) was added dropwise during 1 hr and 25 min to a stirred mixture of methyl phosphorodichloridite (132.0 grams, 0.9990 mole), phosphorus trichloride (75.6 grams), and ferric chloride (1.8 grams) at 23-28° under nitrogen with intermittent water bath cooling. The mixture was heated gradually to 46° during 9 hr. The mixture was rotary evaporated at 40°/20 mm for 1 hr to yield a dark amber-colored fluid. The fluid was purged with dry nitro-

gen for one-half hour and then distilled in a short path distillation apparatus to yield the product. The infrared spectrum of the product had peaks at 3030 cm^{-1} (aliphatic C—H); 1270 cm^{-1} (P → O) and 1100 cm^{-1} (broad) (C—O—C).

Isopropoxymethylphosphonothioic Dichloride

A stirred mixture of crude isopropoxymethylphosphonic dichloride (103.3 grams, 0.5400 mole), phosphorus pentasulfide (P_4S_{10}) (26.3 grams, 0.050 mole), and thiophosphoryl chloride (186 ml) was heated nitrogen during 5 hr to 110° by means of an oil bath. The mixture was heated at 110–115° for 5 hr. The reaction mixture was cooled to room temperature and diluted with 2 × 300-ml portions of *n*-hexane to yield an insoluble solid. The mixture was filtered, and the solid was washed with hexane. The filtrate was washed quickly with water (350 ml), dried over anhydrous magnesium sulfate, filtered, and rotary evaporated at 50°/20 mm for 2 hr to yield a yellow liquid residue, 170.0 grams. The liquid was fractionated with a 12-in. Vigreux column to yield the product.

The gas chromatogram of the product (Column, SE-30; temp, 85°) had a peak at 3.8 min (area, >98%) followed by a shoulder (area <2%) at 5.2 min. The infrared spectrum of the product had peaks at 2990 cm^{-1} (aliphatic C—H) and 1090 cm^{-1} (C—O—C).

Table IV. *o*-Ethyl Alkoxyethylphosphonochloridothioates^a

Compound	Bp	n_D^{25}	P^{31} nmr, ppm	% Purity by gc	Yield, %
4a	100.5–103.5°/16 mm	1.4952	–92.9	98	79
4c	61–63°/0.1 mm	1.4825	–93.4	95	61
4d	54.5–57°/0.13 mm	1.4781	–93.0	95	65

^a Elemental analyses (C, H, O, P, S) in agreement with theoretical values were obtained and were submitted for review.

Table V. Alkoxyethylphosphonothioic Acids^a

Compound	Bp	n_D^{25}	P^{31} nmr, ppm	Yield, %
5e	72–77°/0.5 mm	1.5333	–92.9	77
5f	74–80°/0.1 mm	1.5127	–94.2	58
5g	63–66°/0.3 mm	1.5489	–96.2	35

^a Elemental analyses (C, H, O, P, S) in agreement with theoretical values were obtained and were submitted for review.

Table VI. P^{31} Nmr Chemical Shifts of Phosphonic Derivatives

Structure	δ , ppm		
	$\text{R}=(\text{Cl}-\text{CH}_2-)$ (12)	$\text{R}=(i\text{-Pr}-\text{O}-\text{CH}_2)$	$\text{R}=\text{CH}_2\text{CH}_2$ (12)
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{R}-\text{P}(\text{OEt})_2 \end{array}$	–20	–21.3	–33
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{R}-\text{P} \begin{array}{l} \nearrow \text{OEt} \\ \searrow \text{Cl} \end{array} \end{array}$...	–33.9	–45
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{R}-\text{P} \text{Cl}_2 \end{array}$	–38	–42.3	–54

Ethyl Isopropoxymethylphosphonochloridothionate

Sodium ethoxide (0.20 mole) in ethanol (100 ml) was added dropwise during 1 hr and 10 min to a stirred solution of isopropoxymethylphosphonothioic dichloride (39.9 grams, 0.190 moles) in benzene (200 ml) at 2–4° in a nitrogen atmosphere. The reaction mixture was warmed to 26° during 10 min, washed with water (3 × 250 ml), and dried over anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was rotary evaporated at 45°/20 mm to yield a colorless oil, 41.0 grams. The oil was distilled through a 12-in. Vigreux column to yield the product.

The gas chromatogram of the product (column, SE-30; temp, 110°) had a peak at 3.6 min (area, 95%) and peaks at 2.2 min (area, 1%) and 5.0 min (area, 4%). The infrared spectrum of the product had peaks 1100 cm^{-1} (C—O—C) and 1040 cm^{-1} , 970 cm^{-1} (P—O—C).

Ethyl Isopropoxymethylphosphonothiothionic Acid

Isopropoxymethylphosphonothioic dichloride (35.2 grams, 0.170 mole) was added dropwise during 30 min to a stirred solution of sodium hydrosulfide (0.51 mole) in ethanol (295 ml) at –9° to –2° (Dry Ice–acetone cooling). The reaction mixture was evaporated at 50°/20 mm for 20 min to yield a viscous opaque liquid. Water (130 ml) was added to the liquid to yield a cloudy, yellow solution which was cooled to 10° by the addition of ice. Concentrated hydrochloric acid (20 ml) was added to the stirred solution at 0–10°. The resulting mixture was extracted with methylene chloride (3 × 200 ml). The organic phase was dried with anhydrous magnesium sulfate, filtered, and the filtrate was evaporated at 40°/20 mm to yield a yellow liquid, 34.6 grams. The liquid was fractionated through a Vigreux column (8 in.) to yield the product. The infrared spectrum of the product had peaks at 3100 cm^{-1} (aliphatic C—H), 2550 cm^{-1} (S—H), 1090 cm^{-1} (C—O—C), and 1040 cm^{-1} , 960 cm^{-1} (P—O—C).

Diethyl Isopropoxymethylphosphonate

Triethyl phosphite (157.0 grams, 0.9500 mole) was added during 10 min to chloromethyl isopropyl ether (117 grams, 1.08 mole) at 21–30°. The stirred mixture was heated to 80° during 75 min. There was rapid gas evolution from the reaction mixture. The mixture was heated at 80–95° during 4 hr and 20 min, and then at 95–108° for 35 min. The gas evolution had ceased at this time. The colorless solution was rotary evaporated at 40–80°/20 mm and then fractionated through a Vigreux (12 in.) to yield the product, 154.2 grams, 77% yield, bp 62.5–64.5°/0.05 mm, n_D^{25} 1.4195.

Anal. Calcd for $\text{C}_8\text{H}_{19}\text{O}_4\text{P}$: C, 45.8; H, 9.1; P, 14.8. Found: C, 45.6; H, 9.2; P, 14.7.

The infrared spectrum of the product had peaks at 3100 cm^{-1} (aliphatic C—H), 1260 cm^{-1} (P → O), 1100 cm^{-1} (C—O—C), 1050 cm^{-1} , 970 cm^{-1} (P—O—C).

Ethyl Isopropoxymethylphosphonochloridate

Oxalyl chloride (44.5 grams, 0.350 mole) was added rapidly to stirred diethyl isopropoxymethylphosphonate (63 grams, 0.30 mole) in a dry atmosphere, cooled by a water bath. The temperature of the mixture rose from 21° to 40° with evolution of gas. The temperature of the mixture dropped to 31° during 35 min. The mixture was then heated to 75° during 40 min, then at 74–83° for 45 min. The gas evolution ceased. The solution was evaporated at 50°/20 mm to yield an amber-colored liquid. The liquid was fractionated through a Vigreux column (12 in.) to yield the product, 43.1 gram, 71% yield, bp 52–54°/0.16 mm, n_D^{25} 1.4364.

Anal. Calcd for C₆H₁₄ClO₃P: Cl, 17.7. Found: Cl, 17.6.

The infrared spectrum of the product had peaks at 2940 cm⁻¹ (aliphatic C—H), 1260 cm⁻¹ (P → O), 1100 cm⁻¹ (C—O—C), 1020 cm⁻¹, 962 cm⁻¹ (P—O—C).

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Literature Cited

- (1) Arbutov, A., Abramov, V., *Izvest. Akad. Nauk. SSSR. Otdel. Khim. Nauk.*, **1959**, p 35; *CA*, **53**, 15956 (1959).
- (2) Boros, F., Coskran, K., King, R., Verkade, J., *J. Amer. Chem. Soc.*, **88**, 1140 (1966).
- (3) Coellin, R., Schrader, G., Brit. Patent 917,085 (Jan. 30, 1963); *CA*, **59**, 5197 (1963).
- (4) Green, M., *J. Chem. Soc.*, **1963**, p 1324.
- (5) Henze, H., Duff, V., Matthews, Jr., W., Melton, J., Forman, E., *J. Amer. Chem. Soc.*, **64**, 1222 (1942).
- (6) Kosolapoff, "Organophosphorus Compounds," p 184, Wiley, New York, N.Y., 1950.
- (7) Kwiatek, J., Copenhaver, J., U.S. Patent 2,882,313 (April 14, 1959); *CA*, **53**, 16965 (1959).
- (8) Malowan, J., Martin, D., Pizzolato, P., *Inorg. Syn.*, **IV**, 63 (1953).
- (9) Mark, V., Dungan, C., Crutchfield, M., Van Wazer, J., in "Topics in Phosphorus Chemistry," M. Grayson and E. Griffith, Eds., Vol 5, pp 359-60, Interscience, New York, N.Y., 1967.
- (10) Mark, V., Dungan, C., *ibid.*, p 367.
- (11) Mark, V., Dungan, C., *ibid.*, p 372.
- (12) Mark, V., Dungan, C., *ibid.*, p 227.
- (13) Marlin, D., Pizzolato, P., *J. Amer. Chem. Soc.*, **72**, 4584 (1950).
- (14) Muller, E., Ed., "Methoden der Organischen Chemie," Vol 12 (1), p 388, G. Thieme, Stuttgart, Germany, 1963.
- (15) Muller, E., Ed., *ibid.*, p 553.
- (16) Muller, E., Ed., *ibid.*, p 583.
- (17) Muller, E., Ed., *ibid.*, p 433.
- (18) Muller, E., Ed., *ibid.*, p 560.
- (19) Nixon, J., Schmutzler, R., *Spectrochim. Acta*, **22**, 565 (1966).
- (20) Pelchowicz, Z., *J. Chem. Soc.*, **1961**, p 238.
- (21) Silverstein, R., Bassler, G., "Spectrometric Identification of Organic Compounds," 2nd ed., p 136, Wiley, New York, N.Y., 1967.
- (22) Silverstein, R., Bassler, G., *ibid.*, p 137.
- (23) Van Wazer, J., Letcher, J., in "Topics in Phosphorus Chemistry," M. Grayson and E. Griffith, Eds., Vol 5, p 197, Interscience, New York, N.Y., 1967.

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Chemical Reduction of 2,4,6-Trinitrotoluene—Initial Products

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High-purity model compounds were needed for comparison with the products formed during the biodegradation of 2,4,6-trinitrotoluene (TNT). Thus, an attempt to prepare 12 reduction products of TNT (amino, hydroxylamino, azo, and azoxy compounds) was made. Eight of these compounds were successfully prepared, two of which (4,4',6,6'-tetranitro-2,2'-azoxytoluene and 2,4'-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene) have not previously been reported in the literature. Improvements were made in the purity and method of preparation of several of the compounds previously reported in the literature.

In a study of the products from the biodegradation of 2,4,6-trinitrotoluene (TNT), it was necessary to have a series of the initial reduction products of TNT for use as model compounds. These compounds were desired in high purity so that their presence among the biodegradation products of TNT could be determined quantitatively using such methods as thin-layer chromatography, gas chromatography, and ultraviolet spectroscopy. It was thought that the initial biodegradation products of TNT might include hydroxylamino, amino, azo, and azoxy compounds. Thus, the preparation of representative compounds from each of these classes was undertaken.

Hydroxylamino compounds: 2,6-dinitro-4-hydroxylaminotoluene (I) and 4,6-dinitro-2-hydroxylaminotoluene (II). Compound I, prepared according to Elvove (3), contained a small amount of 4-amino-2,6-dinitrotoluene (IV) which was removed by column chromatography.

Attempts to prepare II by the method of McGookin et al. (5) or by the oxidation of 2-amino-4,6-dinitrotoluene (III) with *m*-chloroperoxybenzoic acid were unsuccessful. In the latter case, II was rapidly converted to the azoxy derivative under the reaction conditions and could not be isolated.

Amino compounds: 2-amino-4,6-dinitrotoluene (III), 4-amino-2,6-dinitrotoluene (IV) (1), and 2,4-diamino-6-nitrotoluene (V) (6). Attempts to prepare III by the method of McGookin et al. (5) did not yield a pure compound, but a modification of the procedure gave a yield of high-purity product. Reduction of III with alcoholic ammonium sulfide yielded 2,4-diamino-6-nitrotoluene (V), and oxidation of III with *m*-chloroperoxybenzoic acid in methylene chloride yielded 4,4',6,6'-tetranitro-2,2'-azoxytoluene (VIII).

Azo compounds: 2,2',6,6'-tetranitro-4,4'-azotoluene (VI). Compound VI was prepared by a modification of the procedure of Brand and Eisenmenger (2). (See Experimental section.)

Azoxy compounds: 2,2',6,6'-tetranitro-4,4'-azoxytoluene (VII), 4,4',6,6'-tetranitro-2,2'-azoxytoluene (VIII), 2,4'-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene