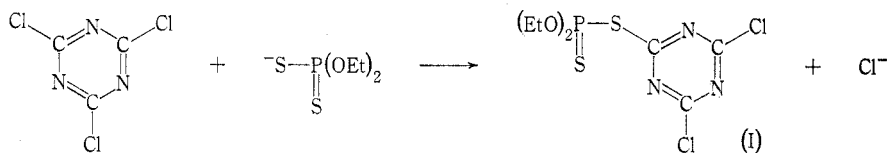


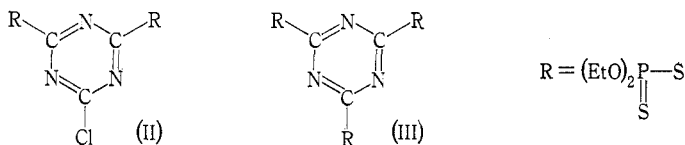
THE SYNTHESIS OF BIS-DIETHOXYPHOSPHINOTHIOYLTHIO AND OF TRIS-DIETHOXYPHOSPHINOTHIOYLTHIO DERIVATIVES OF 1,3,5-TRIAZINE*

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In recent years the synthesis of a number of derivatives of 1,3,5-triazine has been recorded and many of these compounds have been subjected to biological screening procedures as candidate herbicides or insecticides. However, despite increasing interest in the synthesis of organophosphorus compounds with insecticidal activity, little attention has been paid to the examination of derivatives of 1,3,5-triazine phosphorylated directly on the heterocyclic ring. Reaction between cyanuric chloride and potassium diethyl phosphorothioate has been reported¹ to yield tetraethyl pyrophosphorothioate as the major product, although it has recently been shown² that phosphorylated triazines may be isolated from comparable reactions between cyanuric chloride and sodium dialkylphosphorodithioates. Thus, cyanuric chloride reacts with one molar proportion of sodium diethyl phosphorodithioate in acetone to give 2,4-dichloro-6-diethoxyphosphinothioylthio-1,3,5-triazine (I).



We have now examined the products of reaction between cyanuric chloride and two as well as three molar proportions of potassium diethyl phosphorodithioate. When these reactions are carried out in acetone at ice temperature phosphorylated triazines of structure (II) and (III) may be isolated as crystalline solids. However,



in the presence of a large excess of diethyl phosphorodithioate anion, tetraethyl pyrophosphorotrithioate becomes the major phosphorus-containing product present in the reaction mixture. Trithiocyanuric acid was also formed in a process which may

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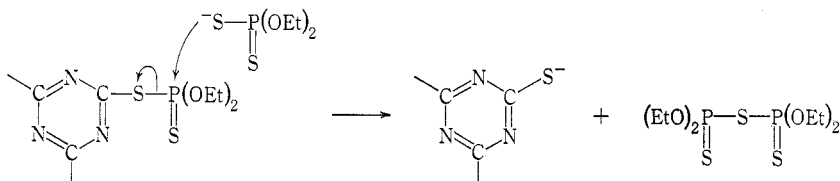
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¹ Margot, A., and Gysin, H., *Helv. chim. Acta*, 1957, **40**, 1562.

² Osborne, G. O., and Page, G., *J. chem. Soc. (C)*, 1967, 1192.

involve attack by diethyl phosphorodithioate anion at the phosphorus atom of the phosphorylated triazine.



An analogous reaction proceeds with even greater facility when sodium diethyl phosphorothioate is employed. This is understandable if the intermediate phosphorylated triazine possesses the phosphorothiolate structure, since triesters containing P=O groups are more readily attacked by nucleophilic reagents than the corresponding P=S derivatives.

It has been reported³ that reaction between cyanuric chloride and ammonium diethyl phosphorodithioate (4 mol. propn.) in boiling benzene yields tris-diethoxyphosphinothiylthio-1,3,5-triazine which was isolated as a coloured oil. However, examination by thin-layer chromatography of the reaction product from cyanuric chloride (1 mol. propn.) and potassium diethyl phosphorodithioate (4 mol. propn.) in acetone reveals that tetraethyl pyrophosphorotrithioate is a major constituent even at room temperature. This anhydride thus seems likely to be present in the above oil. It is known to be highly insecticidal⁴ and may well be responsible for at least part of the insecticidal activity referred to in the above patent.

Experimental

R_F values quoted are those obtained by thin-layer chromatography on silica gel in benzene-hexane (2 : 3) using palladium chloride solution as chromogenic spray.

2-Chloro-4,6-bis(diethoxyphosphinothiylthio)-1,3,5-triazine (II)

Cyanuric chloride (0.184 g, 0.001 mole) and potassium *O,O*-diethyl phosphorodithioate (0.45 g, 0.002 mole) in acetone (10 ml of A.R.) was stirred for 2 hr at room temperature. Precipitated potassium chloride was removed by filtration and solvent evaporated under vacuum to give an oil. This crystallized on standing to give crystals (20%) with m.p. 38°. Recrystallization from light petroleum gave (II), colourless prisms, m.p. 41–42° (Found: C, 27.7; H, 4.3; P, 12.4. Calc. for $C_{11}H_{20}ClN_3O_4P_2S_4$: C, 27.3; H, 4.3; P, 12.8%). The product was homogeneous (R_F 0.35) when examined by thin-layer chromatography. (2,4-Dichloro-6-diethoxyphosphinothiylthio-1,3,5-triazine gave a single spot, R_F 0.7.)

2,4,6-Tris(diethoxyphosphinothiylthio)-1,3,5-triazine

Cyanuric chloride (0.184 g, 0.001 mole) and potassium *O,O*-diethyl phosphorodithioate (0.673 g, 0.003 mole) were stirred in A.R. acetone (10 ml) at ice temperature for 2½ hr and then at room temperature for the same length of time. Potassium chloride was filtered off and the solvent removed under vacuum. The residual oil was dissolved in light petroleum and kept for 4 days in a refrigerator. The product was deposited as colourless prisms (35%), m.p. 32°, unchanged

³ Baker, J. W., and Godfrey, K. L., U.S. Pat. 2,887,432, 1959 (*Chem. Abstr.*, 1959, **53**, 18075e).

⁴ Schrader, G., Lorenz, W., and Mühlmann, R., *Angew. Chem.*, 1958, **70**, 690.

by recrystallization from light petroleum (Found: C, 28.7; H, 4.8; Cl, < 1; P, 14.7. Calc. for $C_{15}H_{30}N_3P_3O_6S_6$: C, 28.4; H, 4.8; P, 14.7%).

When examined by thin-layer chromatography this product gave rise to a single spot, R_F 0.30.

Reaction of Cyanuric Chloride with Excess Sodium Diethyl Phosphorodithioate

Cyanuric chloride (0.500 g, 0.0027 mole) in acetone (20 ml of A.R.) was treated with potassium diethyl phosphorodithioate (4.88 g, 0.0218 mole) at room temperature for 2 hr. Examination by thin-layer chromatography revealed that the principal phosphorus-containing component had R_F 0.75. An authentic sample of *O,O,O,O*-tetraethyl pyrophosphorotrithioate⁴ gave a spot at a similar R_F value. No more than trace amounts of phosphorylated triazines were present.

The reaction mixture was concentrated. Ether was added and the insoluble matter removed by filtration, stirred with dil. HCl, and again recovered by filtration. This material (approx. 0.4 g), m.p. > 300°, was examined by paper chromatography in propan-2-ol-0.880 ammonia (3:1). It was homogeneous with R_F 0.3 (identical with an authentic sample of trithiocyanuric acid). The infrared spectrum was also identical with that of a known sample of trithiocyanuric acid.