

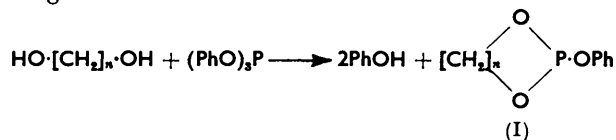
219. *The Organic Chemistry of Phosphorus. Part V.* The Ester-interchange Reaction between Triphenyl Phosphite and Glycols.*

By D. C. AYRES and H. N. RYDON.

Glycols undergo ester-interchange with triphenyl phosphite with the formation of cyclic phosphites, *e.g.* (I). As the separation of the hydroxyl groups increases the yield of cyclic phosphite decreases and increasing amounts of polymeric products are formed. Treatment of the cyclic phosphites with halogens yields halogenoalkyl phenyl phosphorohalidates, while oxidation yields cyclic phosphates. Light-absorption data for the cyclic phosphites and phosphates are recorded and discussed.

LANDAUER and RYDON¹ drew attention to the great ease with which triphenyl phosphite underwent ester-interchange with alcohols, and postulated the intervention of this reaction in one of their new methods for the preparation of alkyl halides.² The present study, which was prompted by difficulties encountered in attempts to prepare halogenohydrins from glycols by the new methods,^{1,2} is concerned with ester-interchange between triphenyl phosphite and glycols.

The initial experiments were carried out with ethylene glycol and trimethylene glycol, both of which react with triphenyl phosphite without added catalyst, the former at room temperature, but the latter with reasonable speed only at 100°, with liberation of two mols. of phenol. In both cases substantial amounts of the cyclic phosphite (I; $n = 2$ and 3) were formed according to the scheme



The cyclic phosphites were accompanied by higher-boiling products, clearly mixtures of the same gross composition as (I).

Further investigation showed that the reaction with ethylene glycol resembled the ester-interchange reactions of silicates^{3,4} in being catalysed by both acid (hydrogen chloride) and base (sodium glycoxide), the former increasing, and the latter decreasing, the rate; both catalysts increased the yield of cyclic phosphite as compared with that of the polymeric material, the glycoxide being the more effective.

For preparative purposes the glycoxide is very convenient and a number of glycols have been caused to react with one mol. of triphenyl phosphite in the presence of catalytic amounts of the corresponding sodium glycoxide. The yields of phenol and of cyclic phosphite so obtained are given in Table 1.

In the aliphatic series the yields of cyclic phosphite show the expected dependence on the degree of separation of the reacting hydroxyl groups, the yield of cyclic phosphite steadily decreasing as n in (I) increases from 2 (five-membered ring) to 5 (8-membered ring), while the 9-membered cyclic phosphite (I; $n = 6$) is not formed at all under our conditions; a similar effect has been observed⁵ in the analogous reaction of glycols with phosphorus trichloride.

* Part IV, Coe, Rydon, and Tonge, *J.*, 1957, 323.

¹ Landauer and Rydon, *J.*, 1953, 2224.

² Cf. Coe, Landauer, and Rydon, *J.*, 1954, 2281.

³ Peppard, Brown, and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 73.

⁴ Helferich and Reimann, *Chem. Ber.*, 1947, **80**, 163.

⁵ Arbuzov, Zoroastrova, and Rizpolozhenskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1948, 208; Arbuzov and Zoroastrova, *ibid.*, 1952, 770.

As expected, the reaction is controlled by the stereochemical configurations of the reacting hydroxyl groups. Of the two *cyclopentane-1:2*-diols, only the *cis*, with favourably placed hydroxyl groups, gives a cyclic phosphite, none being formed from the *trans* compound. On the other hand, both *cis*- and *trans-cyclohexane-1:2*-diol give cyclic phosphites and there is no obvious difference in the ease with which the two reactions proceed. Inspection of models shows that, owing to the size of the phosphorus atom, the phosphite ring can be formed readily from both the *cis*-diol, with one axial and one equatorial hydroxyl, and the *trans*-diol, with two equatorial hydroxyl groups. Neither of the two stereoisomeric (*cis* and *trans*) cyclic phosphites (II) is greatly strained and their formation can require little or no distortion of the *cyclohexane* ring from its preferred chair conformation.

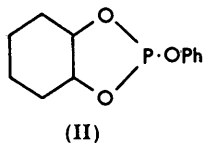
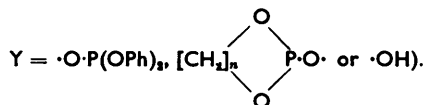
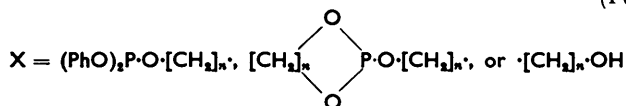
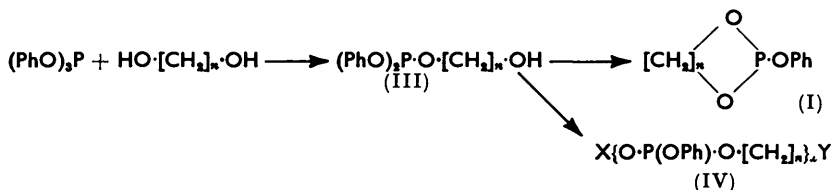


TABLE 1.

Glycol	Yield		Glycol	Yield	
	Phenol (mols.)	Cyclic phosphite (%)		Phenol (mols.)	Cyclic phosphite (%)
Ethylene glycol	1.96	60	Hexane-1:6-diol	1.02 •	0
Propane-1:2-diol	1.98	52	<i>cis-cyclo</i> Pentane-1:2-diol	1.76	49
Propane-1:3-diol	1.76	53	<i>trans-cyclo</i> Pentane-1:2-diol	1.90	0
Butane-1:4-diol	2.00	20	<i>cis-cyclo</i> Hexane-1:2-diol...	1.82	33
Pentane-1:5-diol	1.92	13	<i>trans-cyclo</i> Hexane-1:2-diol	1.86	29

• Considerable loss during working-up.

Attempts to establish the nature of the high-boiling by-products of the interchange reaction, which ranged from oils (from the lower glycols) to a rubber-like solid (from hexane-1:6-diol), were frustrated by formidable difficulties in separation, analysis, and characterisation. The likely course of the reaction is the following :

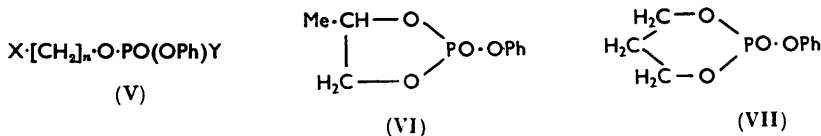


The initial intermediate (III) undergoes either intramolecular ester-interchange to the cyclic phosphite (I), or further intermolecular ester-interchange with eventual formation of polymer (IV). The consistent production of two mols. of phenol indicates that only very small amounts of free hydroxyl can be present in the polymers.

The ester-interchange between triphenyl phosphite and glycerol gave only polymeric material; this is expected in view of the presence of a free hydroxyl group in the cyclic phosphite, which will inevitably lead to further interchange and consequent polymer formation.

On treatment with bromine, ethylene phenyl phosphite (I; $n = 2$) yields the 2-bromoethyl phosphorobromidate (V; $n = 2$; $\text{X} = \text{Y} = \text{Br}$), characterised as the derived

anilide (V; $n = 2$; $X = \text{Br}$; $Y = \text{NPh}$); trimethylene phenyl phosphite and chlorine similarly yield the 3-chloropropyl compound (V; $n = 3$; $X = Y = \text{Cl}$). The formation of halogeno-alkyl phosphorohalidates, such as (V), by way of the cyclic phosphites (I) explains the very poor yields obtained in attempts to prepare halogenohydrins from glycols by reaction with triphenyl phosphite and alkyl halides¹ or halogens.²



Oxidation of propylene and trimethylene phenyl phosphites gave the corresponding cyclic phosphates, *viz.*, propylene phenyl phosphate (VI) and trimethylene phenyl phosphate (VII). These two compounds differ remarkably in their stability to hydrolysis, the latter crystallising unchanged from boiling water whereas the former is readily hydrolysed by water.

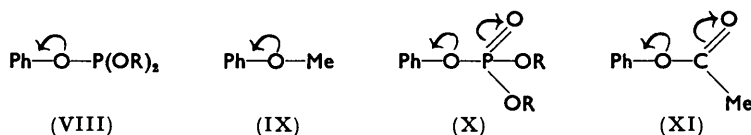
TABLE 2. Light absorption of some phosphites and phosphates. λ_{max} . (m μ) and ϵ_{max} . (in parentheses).

Phosphites			
Ethylene phenyl phosphite	265.5 (970)	270 (1160)	277.5 (1155)
Phenyl propylene phosphite	265.5 (1110)	270 (1440)	277.5 (1510)
Phenyl trimethylene phosphite	264.5 (970)	270.5 (1095)	277 (1010)
Phenyl tetramethylene phosphite	266.5 (760) *	270.5 (1005)	277 (990)
Pentamethylene phenyl phosphite	266.5 (840) *	270 (990)	277 (710)
<i>cis-cyclo</i> Pent-1 : 2-ylyene phenyl phosphite	266 (910)	271 (1090)	277 (1110)
<i>cis-cyclo</i> Hex-1 : 2-ylyene phenyl phosphite	266 (910)	270.5 (990)	277 (770)
<i>trans-cyclo</i> Hex-1 : 2-ylyene phenyl phosphite	265.5 (905)	269 (840) *	—
Triphenyl phosphite	265 (1780)	270 (1870)	278 (1120)
Phosphates			
Phenyl propylene phosphate †	258 (300) *	263 (380)	268 (385)
Phenyl trimethylene phosphate †	256 (355)	262 (430)	268 (330)
Triphenyl phosphate	256 (960)	262 (1180)	268 (910)
Reference compounds			
Anisole	265 (1120)	271 (1580)	278 (1450)
Phenyl acetate †	—	262 (250)	—
Benzene	249 (175)	255 (230)	261 (150)

* Inflection on shoulder.

† In ethanol; all others in hexane.

Light-absorption data for the cyclic phosphites and phosphates, together with those for the corresponding triphenyl esters, are collected in Table 2; full curves are given by Ayres.⁶ All the phosphites have very similar spectra, arising by intensification and bathochromic displacement of the *B*-band system of benzene;⁸ a similar effect is shown by anisole and both effects may be ascribed to electron donation from the oxygen atoms (VIII and IX). The effect is very much smaller, although in the same direction,



in the phosphates; this difference, like the similar one between anisole and phenyl acetate, is clearly due to partial cancellation of the electron drift towards the benzene nucleus by

⁶ Ayres, Ph.D. Thesis, Manchester, 1954.

⁷ Wolf and Strasser, *Z. phys. Chem.*, 1933, **B**, 21, 389.

⁸ Burawoy, *Ber.*, 1930, **63**, 3157; 1931, **64**, 489; Braude, *Ann. Reports*, 1945, **42**, 105; Burawoy and Chamberlain, *J.*, 1952, 2310.

the opposing electron shift in the phosphonyl and carbonyl groups (X and XI). The approximate proportionality between the absorption intensities and the number of phenyl groups in the phosphates, but not in the phosphites, may similarly be due to the overwhelming effect of the phosphonyl group in the phosphates.

EXPERIMENTAL

Ester-interchange Reactions.—Unless otherwise stated all products were worked up by direct vacuum distillation.

Ethylene glycol. (a) Ethylene glycol (31 g.; 0.5 mole) and triphenyl phosphite (155 g.; 0.5 mole) were shaken together in a stoppered flask; much heat was evolved and the mixture became homogeneous within 1 hr. Distillation gave (i) phenol (92.5 g.; 98%), b. p. 99—115°/37 mm., (ii) crude cyclic phosphite (42 g.; 46%), b. p. 59—61°/0.09 mm., n_D^{20} 1.5356, and (iii) polymeric products (41 g.; 45%), b. p. 61—176°/0.1—0.3 mm., n_D^{20} 1.5070—1.5827. Redistillation of fraction (ii) gave pure *ethylene phenyl phosphite* (I; $n = 2$), b. p. 73°/0.3 mm., n_D^{20} 1.5342 [Found: C, 52.9; H, 4.9; P, 16.4%; equiv. (by hydrol.), 189. $C_8H_9O_3P$ requires C, 52.1; H, 4.9; P, 16.8%; equiv., 184].

(b) Four separate portions of triphenyl phosphite (155 g.; 0.5 mole) were mixed with portions of ethylene glycol (31 g.; 0.5 mole), one without addition and the other three containing, respectively, 0.01 mole of sodium glycoxide, sodium phenoxide, and hydrogen chloride. The four mixtures at 37° were shaken by hand for 5 sec. every 10 min. and the time to homogeneity noted; distillation gave ethylene phenyl phosphite. The results were as follows :

Catalyst	Time to homogeneity (min.)	Yield (%)	Phosphite n_D^{20}
None	70	23	1.5336
Sodium glycoxide	> 300 *	49	1.5366
Sodium phenoxide	70	14	1.5347
Hydrogen chloride	20	33	1.5348

* Completed by heating on steam-bath.

(c) The following procedure is the most convenient for preparative purposes: Triphenyl phosphite (155 g.; 0.5 mole) was vigorously stirred on the steam-bath with ethylene glycol (31 g.; 0.5 mole) in which sodium (0.2 g.; 0.01 mole) had been dissolved. Heating and stirring were continued for 1½ hr. after the mixture had become homogeneous. Distillation afforded ethylene phenyl phosphite (55 g.; 60%), b. p. 70—76°/0.2 mm., n_D^{20} 1.5370.

Propylene glycol. (a) Triphenyl phosphite (155 g.; 0.5 mole) was stirred on the steam-bath with the glycol (38 g.; 0.5 mole) in which sodium (0.2 g.; 0.01 mole) had been dissolved. Stirring was continued for 2 hr. after homogeneity was attained (10 min.). Distillation gave phenol (93.3 g.; 99%) and the cyclic phosphite (51.5 g.; 52%), b. p. 81—87°/0.6 mm., n_D^{20} 1.5155; redistillation gave pure *phenyl propylene phosphite*, b. p. 76°/0.4 mm., n_D^{20} 1.5198 (Found: C, 53.7; H, 5.2. $C_8H_{11}O_3P$ requires C, 54.5; H, 5.6%).

(b) Repetition of the above preparation with more sodium (6.9 g.; 0.3 mole) gave the same phosphite (49.5 g.; 50%), b. p. 82—90°/0.3 mm.

(c) Propylene phosphorochloridite⁹ (124 g.; 0.88 mole) and dimethylaniline (109 g.; 0.9 mole) in ether (100 ml.) were treated during 30 min., with stirring and ice-cooling, with phenol (83 g.; 0.88 mole) in ether (75 ml.). After being stirred for a further 2 hr. the product was filtered and distilled, yielding phenyl propylene phosphite (113 g.; 65%), b. p. 94°/2 mm., n_D^{22} 1.5192.

Trimethylene glycol. (a) Triphenyl phosphite (103.3 g.; 0.33 mole) was heated on the steam-bath with the glycol (25.3 g.; 0.33 mole) for 6 hr. with intermittent shaking. Distillation gave (i) phenol (55 g.; 88%), b. p. 85—90°/21—25 mm., (ii) crude cyclic phosphite (18 g.; 27%), b. p. 69—75°/0.07 mm., n_D^{20} 1.5265, and (iii) polymeric material (38 g.; 58%), b. p. 165—173°/0.05—0.1 mm., n_D^{20} 1.5576. Redistillation of fraction (ii) gave pure *phenyl trimethylene phosphite* (I; $n = 3$), b. p. 88°/0.4 mm., n_D^{20} 1.5337 (Found: C, 54.8; H, 5.8.

⁹ Lucas, Mitchell, and Scully, *J. Amer. Chem. Soc.*, 1950, **72**, 5491.

$C_9H_{11}O_3P$ requires C, 54.5; H, 5.6%); this crystallised after some months (m. p. 44–46°, not raised on recrystallisation from acetone–hexane); the supercooled melt had n_D^{27} 1.5230.

(b) Repetition with more glycol (50.6 g.; 0.66 mole) gave the same phosphite, b. p. 68–76°/0.05 mm., n_D^{18} 1.5286, in much reduced yield (4.6 g.; 7%).

(c) Triphenyl phosphite (155 g.; 0.5 mole), stirred on the steam-bath for 2 hr. with sodium (0.2 g.; 0.01 mole) dissolved in trimethylene glycol (38 g.; 0.5 mole), gave the best yield of phenyl trimethylene phosphite (52.5 g.; 53%), b. p. 89°/0.4 mm., m. p. 38–42° [Found: equiv. (by hydrol.), 207. $C_9H_{11}O_3P$ requires equiv., 198].

Butane-1:4-diol. (a) Triphenyl phosphite (62 g.; 0.2 mole), stirred on the steam-bath for 1½ hr. with sodium (0.2 g.; 0.01 mole) dissolved in the glycol (18 g.; 0.2 mole), gave phenol (38 g.; 100%), b. p. 85°/0.3 mm., and the crude cyclic phosphite (8.6 g.; 20%), b. p. 91–95°/0.3 mm., n_D^{20} 1.5359. Redistillation gave pure *phenyl tetramethylene phosphite* (I; $n = 4$), b. p. 94°/0.3 mm., n_D^{20} 1.5361 (Found: C, 56.7; H, 6.3. $C_{10}H_{13}O_3P$ requires C, 56.6; H, 6.1%).

(b) A similar experiment without sodium gave less (5.2 g.; 12%) phosphite, b. p. 90°/0.8 mm., n_D^{20} 1.5336.

Pentane-1:5-diol. Triphenyl phosphite (74.2 g.; 0.24 mole), the glycol (25 g.; 0.24 mole), and sodium (0.2 g.; 0.01 mole) gave phenol (43.4 g.; 96%) and cyclic phosphite (7.3 g.; 13%), b. p. 98–104°/0.0015 mm., n_D^{18} 1.5268–1.5346; redistillation gave pure *pentamethylene phenyl phosphite* (I; $n = 5$), b. p. 99°/0.0015 mm., n_D^{17} 1.5237 (Found: P, 13.2. $C_{11}H_{15}O_3P$ requires P, 13.7%).

Hexane-1:6-diol. The glycol (14.8 g.; 0.125 mole) containing dissolved sodium (0.2 g.; 0.01 mole) was added in portions during 75 min. to stirred triphenyl phosphite (38.8 g.; 0.125 mole) at 90°. After each addition the temporary clouding of the mixture cleared rapidly. After being left overnight the product was a rubber-like mass, insoluble in ether and dioxan, which dissolved slowly in boiling chloroform. Distillation of the chloroform solution gave some phenol (12 g.; 51%) at a bath temp. of 130°/0.3 mm.; raising the bath temp. to 180°/0.004 mm. caused a little more phenol to sublime but the remaining product showed no signs of boiling.

cis-cycloPentane-1:2-diol. Sodium (0.2 g.; 0.01 mole) was dissolved in the glycol¹⁰ (10 g.; 0.1 mole); after addition of triphenyl phosphite (31 g.; 0.1 mole), the mixture rapidly became homogeneous, without external heating. Distillation gave (i) phenol (16.5 g.; 88%), (ii) cyclic phosphite (10.9 g.; 49%), b. p. 72–75°/0.002 mm., n_D^{23} 1.5266, and (iii) polymeric material (3.6 g.; 16%), b. p. 120–130°/0.0015 mm., n_D^{23} 1.5780. Redistillation of fraction (ii) gave pure *cis-cyclopent-1:2-ylyene phenyl phosphite*, b. p. 68°/0.007 mm., n_D^{20} 1.5240 (Found: P, 14.2. $C_{11}H_{13}O_3P$ requires P, 13.8%).

trans-cycloPentane-1:2-diol. The glycol¹⁰ (10 g.; 0.1 mole) was treated with sodium and triphenyl phosphite as for the *cis-isomer*; homogeneity was attained after 10 min. on the steam-bath. Distillation gave phenol (17.8 g.; 95%) and left a very viscous, ether-insoluble residue which showed no signs of distillation at 0.008 mm. from a bath at 200°.

cis-cycloHexane-1:2-diol. Sodium (0.2 g.; 0.01 mole) was added to the glycol¹¹ (11.6 g.; 0.1 mole) in dioxan (30 ml.). When dissolution was complete the solvent was removed under reduced pressure and the residue stirred with triphenyl phosphite (31 g.; 0.1 mole) until homogeneous (15 min.). Phenol (17.1 g.; 91%) was distilled off at 80°/0.2 mm. and the residue stirred into light petroleum (b. p. 40–60°), high-polymeric material (4.8 g.; 20%) remaining undissolved. Distillation of the soluble material gave (i) crude cyclic phosphite (8.8 g.; 37%), b. p. 96–112°/0.004 mm., and (ii) polymeric material (6.1 g.; 26%), b. p. 120–133°/0.003 mm. Fraction (i) partially crystallised; redistillation of the solid (7.8 g.; 33%) afforded pure *cis-cyclohex-1:2-ylyene phenyl phosphite* (II), b. p. 97°/0.004 mm., m. p. 43–45° (Found: C, 61.1; H, 7.0; P, 12.8. $C_{12}H_{16}O_3P$ requires C, 60.5; H, 6.3; P, 13.0%).

Hydrolysis with boiling 4*N*-hydrochloric acid for 4 hr. gave 88% of *cis-cyclohexane-1:2-diol*, m. p. and mixed m. p. 86–89°, characterised as the ditoluene-*p*-sulphonate,¹² m. p. and mixed m. p. 127–129°.

trans-cycloHexane-1:2-diol. The glycol¹³ (11.6 g.; 0.1 mole), treated similarly, but without the treatment with light petroleum, gave (i) phenol (17.4 g.; 93%), (ii) crude cyclic

¹⁰ Owen and Smith, *J.*, 1952, 4026.

¹¹ Clarke and Owen, *J.*, 1949, 315.

¹² Criegee and Stanger, *Ber.*, 1936, 69, 2754.

¹³ Roebuck and Adkins, *Org. Synth.*, 1948, 28, 35.

phosphite (7.0 g.; 29%), b. p. 82—100°/0.0045 mm., n_D^{37} 1.5320—1.5360, and (iii) polymeric material (2.1 g.; 9%). Pure *trans-cyclohex-1:2-ylenyl phenyl phosphite* (II) had b. p. 84°/0.0045 mm., n_D^{37} 1.5330 (Found: C, 60.6; H, 6.7; P, 13.1%).

Hydrolysis by boiling 4*N*-hydrochloric acid for 6 hr. gave 91% of *trans-cyclohexane-1:2*-diol, m. p. and mixed m. p. 100—102°, characterised as the ditoluene-*p*-sulphonate,¹² m. p. and mixed m. p. 104—105°.

Glycerol. Sodium (0.2 g.; 0.01 mole) was dissolved in glycerol (46 g.; 0.5 mole) and the solution stirred on the steam-bath with triphenyl phosphite (155 g.; 0.5 mole) until homogeneous (5 hr.). Distillation afforded phenol (132.7 g.; 94%) and an extremely viscous residue (62 g.; 103%), soluble only in chloroform, which decomposed on attempted distillation. The polymer dissolved completely on boiling for a few min. with 2*N*-hydrochloric acid or with 2*N*-sodium hydroxide.

Reactions of Cyclic Phosphites.—(i) *With halogens.* (a) *Ethylene phenyl phosphite and bromine.* Bromine (26.6 g.; 0.16 mole) was added during 1 hr., with ice-cooling, to the stirred phosphite (30.6 g.; 0.16 g.), moisture being rigorously excluded. After removal of a little unconsumed bromine in a stream of dry air, a portion (2.1 g.) of the residual phosphorobromidate was added to aniline (1.13 g.) at 0°; benzene (5 ml.) was added and the mixture warmed for 20 min. Aniline hydrobromide was filtered off and washed with hot benzene (2 × 5 ml.). Evaporation of the benzene solution followed by recrystallisation of the residue from aqueous ethanol gave *2-bromoethyl phenyl N-phenylphosphoramidate* (V; $n = 2$; X = Br, Y = NHPH) (0.85 g.; 40%), m. p. 128° (Found: N, 4.2; Br, 22.0. C₁₄H₁₆O₃NBrP requires N, 3.9; Br, 22.5%).

(b) *Trimethylene phenyl phosphite and chlorine.* Chlorine (1.1 g.) was passed into an ice-cooled solution of the phosphite (3.3 g.) in chloroform (20 ml.). This solution was then added dropwise, with stirring and ice-cooling, to aniline (3.1 g.) in chloroform (20 ml.). After 2 hr. aniline hydrochloride was filtered off and the filtrate washed with water until free from chloride ion. Evaporation of the dried solution gave *3-chloropropyl phenyl N-phenylphosphoramidate* (V; $n = 3$; X = Cl; Y = NHPH) (4.8 g.; 89%), m. p. 65° after recrystallisation from aqueous ethanol (Found: N, 4.3. C₁₅H₁₇O₃NClP requires N, 4.3%).

(ii) *Oxidation.* (a) *Phenyl propylene phosphite.* The phosphite (13.2 g.) in dry benzene (35 ml.) was stirred for 40 min. with yellow mercuric oxide (16 g.); the vigorous reaction caused the benzene to boil. After filtration and centrifugation to remove mercury and unconsumed mercuric oxide, distillation afforded *phenyl propylene phosphate* (VI) (3.1 g.; 22%), an oil, b. p. 123°/0.007 mm., n_D^{20} 1.5068 (Found: P, 14.4. C₉H₁₁O₄P requires P, 14.5%). This phosphate is readily soluble in ether; it dissolves in water, with evolution of heat, to form a strongly acid solution from which it cannot be recovered unchanged.

(b) *Phenyl trimethylene phosphite.* The cyclic phosphite (9.9 g.) in dry benzene (40 ml.) was added during 1 hr. to a cooled and stirred suspension of active manganese dioxide¹⁴ (45 g.) in dry benzene (60 ml.). After 24 hr. the mixture was filtered, the solid being washed with benzene (3 × 30 ml.). Evaporation of the filtrate and washings gave *phenyl trimethylene phosphate*, (VII), (6.0 g.; 56%), m. p. 71—74°, raised to 76—77° by recrystallisation from carbon tetrachloride containing a little chloroform (Found: C, 50.9; H, 5.5. C₉H₁₁O₄P requires C, 50.5; H, 5.15%). The phosphate is insoluble in light petroleum, slightly soluble in ether and carbon tetrachloride and very soluble in benzene, ethyl acetate, and chloroform; it dissolves readily in boiling water, giving a neutral solution from which it crystallises unchanged on cooling.

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¹⁴ Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.