

Cyclic Organophosphorus Compounds. Part VII.¹ Di-[5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl] Disulphide and its Deoxygenation and Desulphuration with Triphenylphosphine

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Di-[5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl] disulphide, obtainable from 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione and sulphuryl chloride, or from 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione or its salts with sulphur chloride, undergoes both desulphuration and deoxygenation on treatment with triphenylphosphine. The products of the reaction are triphenylphosphine oxide, triphenylphosphine sulphide, *P*-thiono-*P'*-oxodi-[5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl] oxide, and di-[5,5-dimethyl-2-thiono-1,3,2-dioxaphosph(v)an-2-yl] oxide. Possible mechanisms for this reaction are discussed.

A PREVIOUS Paper² describes the synthesis of di-[5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl] disulphide (I). The remarkable ease with which this compound is converted by triphenylphosphine into the trithiopyrophosphate (VII) contrasts with the reported difficulty of the desulphuration of acyclic thioperoxydiphosphorothioic acid esters³ and may be an example of steric acceleration. The present Paper describes the synthesis of the disulphide (II) by routes previously established for acyclic analogues.⁴ 2-Methoxy-5,5-di-

methyl-1,3,2-dioxaphosphorinan-2-thione and sulphuryl chloride gave a moderate yield of compound (II) in a form which proved difficult to purify. Better yields of more readily purified samples of the disulphide were obtained by the action of sulphuryl chloride on the acid (IX), or its potassium or triethylammonium salt. The use of a two-fold quantity of sulphuryl chloride on the acid (IX) furnished a phosphorochloridate (X), presumably by a process similar to that which has been observed with acyclic analogues of these compounds.⁵

Monothiopyrophosphates are thought to exist normally

¹ Part VI, R. S. Edmundson, and A. J. Lambie, *J. Chem. Soc. (B)*, 1967, 577.

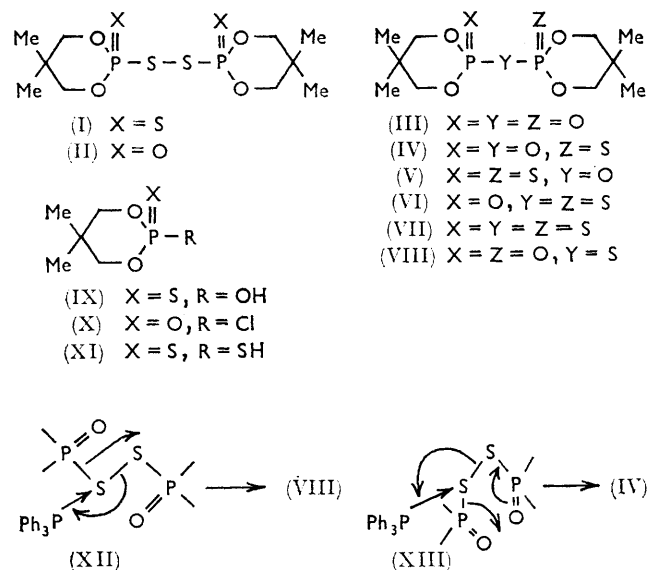
² R. S. Edmundson, *Tetrahedron*, 1965, **21**, 2379.

³ N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, and T. L. Italinskaya, *Zhur. obshchei Khim.*, 1962, **32**, 847.

⁴ J. Michalski, *Bull. Soc. chim. France*, 1963, 11¹

⁵ J. Michalski, M. Mikolajczyk, and A. Skowronzka, *Chem. and Ind.*, 1962, 1053.

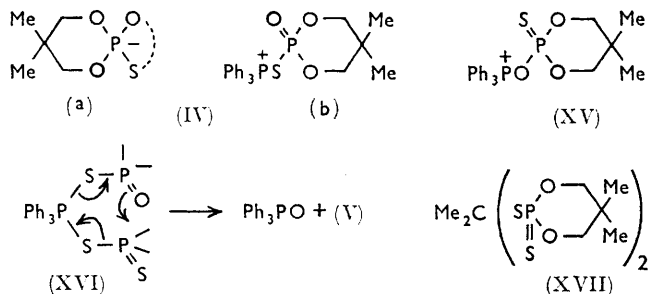
in the thiono-form. However, a compound was recently obtained which isomerised to the stable thiono-structure (IV), and which therefore was thought to have structure (VIII), although more direct proof was then not available.⁶ The desulphuration of di-[5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl] disulphide by triphenylphosphine was investigated as another route to the



symmetrical structure (VIII). The reaction between the disulphide (II) and triphenylphosphine in benzene was mildly exothermic but evidently slower than that between triphenylphosphine and di-[5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl] disulphide (I). The symmetrical dithiopyrophosphate (V) was gradually precipitated, and the filtered solution was shown by thin-layer chromatography to contain a further small amount of the same dithiopyrophosphate, triphenylphosphine sulphide, triphenylphosphine oxide, and the monothiopyrophosphate (IV), all of which were separated by column chromatography.

Two basic mechanisms may be formulated for this reaction sequence. The first involves attack by triphenylphosphine on sulphur followed by a rearrangement as indicated in the partial structure (XII). This mechanism might be satisfactory for the desulphuration of compound (I), but in the present case the process would lead to the symmetrical thiopyrophosphate, unless the process is further complicated by the concomitant rearrangement of thiopyrophosphate to the thiono-structure by the process indicated by Michalski.⁴ The overall process would then be that indicated by the partial structure (XIII). The second mechanism involves the participation of ion-pairs, in this case, (XIV). Interaction of the anion of (XIV) with ring-phosphorus in

the cation (XIVb) would lead by normal desulphuration to either the thiol- or the thiono-form of the monothiopyrophosphate, while isomerisation of the cationic component to (XV) followed by its interaction with the ambident anion (XIVa) *via* the transition state (XVI) would explain the deoxygenation of the disulphide to give triphenylphosphine oxide and the symmetrical dithiopyrophosphate (V). This sequence is not explained by either form of the first mechanism, and the second mechanism is rendered more attractive because of the well known participation of ambident phosphorothiolate anions in thiono-thiolo rearrangements.⁷



During initial experiments on the synthesis of the dithiopyrophosphate (VI), 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan was allowed to react with the ammonium salt of the cyclic phosphorodithiolic acid (XI) in acetone. Structure (XVIII) has been assigned to the product. Attempts to confirm this structure by reaction between the same ammonium salt and 2,2-dichloro- and 2,2-di-bromo-propane failed. The postulated structure is based on elemental analysis and infrared data; the infra-red spectrum showed strong absorption due to *gem*-dimethyls and ring P-O-C bonds, and was similar to those of other cyclic phosphorodithiolic esters,⁸ and indeed almost identical with that of 5,5-dimethyl-2-isopropylthio-1,3,2-dioxaphosphorinan-2-thione.

TABLE 1

Infrared data for the 650—900 cm^{-1} region, indicating grouping into doublets, etc.

(I)	(841sh, 831, 818sh, 812)s; (688, 668, 664)s
(II)	(848, 838)s; (781, 771)s
(III)	862; 835; 788
(IV)	(866, 848, 838, 826)m; 787m; 733m
(V)	853; 841; (797, 778); 681
(VI)	(846, 837, 824)s; (788, 782)s; 684s
(VII)	(836, 821, 812)s; 718; 656s

The infrared spectra of compounds (IV)—(VII) are similar to those of compounds (I) and (II); the main differences are in the 1000—1100 cm^{-1} region, and, particularly, in the 650—900 cm^{-1} region (Table 1). Compared with the compounds with the P-O-P system, those possessing the P-S_n-P grouping (*n* = 1 and 2) give rise to a more complex system of bands in the 810—870

⁶ R. S. Edmundson, *Chem. and Ind.*, 1963, 784.

⁷ J. R. Cox, jun., and O. B. Ramsay, *Chem. Rev.*, 1964, **64**, 317.

⁸ R. S. Edmundson, *Tetrahedron*, 1964, **20**, 2781.

⁹ R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, 1964, **20**, 1679.

¹⁰ J. J. Mann, W. R. Erwin, and H. T. Gordon, *J. Agric. Food Chem.*, 1957, **5**, 601.

cm.⁻¹ region; this absorption is outside the range quoted elsewhere⁹ for the P-S bond.

EXPERIMENTAL

Solvents and solutions were dried by conventional means. Light petroleum had b. p. 40–60°. Infrared spectra were recorded for KBr discs using a Perkin-Elmer 237 spectrometer. Thin-layer chromatography was carried out on Kieselgel. The following solvent systems were employed: (A) dibutyl ether–ethyl acetate (3 : 2), (B) chloroform–ethanol–cyclohexane (1 : 1 : 3), (C) dibutyl ether–chloroform (3 : 2), and (D) acetone–ethyl acetate (1 : 1). Sulphur-containing compounds were detected by a spray of ca. 0.5% w/v 2,6-dibromo-*p*-benzoquinone 4-chloroimine in cyclohexane.¹⁰

2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione.—2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione (20.0 g.) in methanol (40 ml.) was added to methanolic sodium methoxide (from 2.3 g. of sodium in 30 ml. of methanol). The mixture was refluxed for 1.5 hr. and poured into water. The precipitated ester (13.8 g., 71%) was identical (m. p. and infrared spectrum) with a sample prepared by an alternative route.⁸

Di-[5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl] Disulphide.—(a) From 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione. Sulphuryl chloride (2.7 g.) in ethanol-free chloroform (10 ml.) was added in portions to the ester (3.9 g.) in chloroform (25 ml.), and the mixture refluxed for 3 hr. Evaporation of the solution left an oil which was extracted with ethyl acetate–light petroleum, from which the impure disulphide (2.1 g., 58%) separated.

(b) From the potassium salt of 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione. The triethylammonium salt of this acid (8.5 g.) was converted into the potassium salt (6.3 g.) by addition of the calculated amount of potassium hydroxide solution. The solution was evaporated to dryness, and the residue further dried azeotropically (C₆H₆).

The potassium salt was suspended in benzene (30 ml.). Sulphuryl chloride (1.9 g.) was added and the mixture heated over steam for 1 hr., washed with water, and dried. Evaporation of the solution gave the disulphide (4.7 g., 91%), m. p. 126–129° (from ethyl acetate) (Found: C, 33.2; H, 5.55; P, 17.15; S, 17.4. C₁₀H₂₀O₆P₂S₂ requires C, 33.15; H, 5.6; P, 17.1; S, 17.7%).

(c) From 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione. The acid (from 9.4 g. of the triethylammonium salt) was treated with sulphuryl chloride (5.0 g.). The solution developed a deep yellow colour. Evaporation of the solution and extraction of the residual oil with ether gave 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (0.6 g.) (m. p., mixed m. p., and infrared spectrum), the disulphide (1.0 g.), and an unidentified substance (1.5 g.), m. p. 124–126°, containing phosphorus and sulphur, but lacking chlorine.

P-Oxo-P'-thiono-di-[5,5-dimethyl-1,3,2-dioxaphosphorinan-

2-yl] Oxide.—2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (6.2 g.) was added to a hot solution of the triethylammonium salt of 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-thione (8.4 g.) in benzene, and the mixture refluxed for 1 hr. The mixture was filtered (84% triethylammonium hydrochloride recovered), and the filtrate evaporated, to yield the di-[dioxaphosphorinanyl] oxide (8.75 g., 79%), m. p. 154–154.5° (from acetone–light petroleum) (Found: C, 36.25; H, 6.15; P, 19.1; S, 9.4. C₁₀H₂₀O₆P₂S requires C, 36.2; H, 6.05; P, 18.6; S, 9.7%).

TABLE 2
Chromatographic data

<i>R_F</i> in solvent	A	B	C	D
(II)	0.09		0.03	
(IV)	0.31	0.75	0.12	0.94 *
(V)	0.62	0.92	0.62	
(VI)	0.33	0.75	0.14	0.97 *
Ph ₃ PS	0.81		0.90	
Ph ₃ PO †	0.22		0.13	

* Distinguishable by colour of spot. † Visible under u.v. light.

Action of Triphenylphosphine on Di-[5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinan-2-yl] Disulphide.—A solution of the disulphide (0.75 g.) and triphenylphosphine (0.55 g.) in benzene (10 ml.) was allowed to stand. Precipitation commenced after about 1 hr., and after 48 hr. the precipitate of di-[5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-yl] oxide (0.4 g.) (identified by m. p., mixed m. p., infrared spectrum, and chromatography) was collected. The filtrate was evaporated and the residue chromatographed on a column of Kieselgel (2 × 20 cm.) in solvent A, to give triphenylphosphine sulphide (0.20 g.), *P*-oxo-*P'*-thiono-di-[5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl] oxide (0.105 g.), and triphenylphosphine oxide (0.19 g.).

2,2-Di-[5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinan-2-ylthio]propane.—(a) 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinan (1.77 g.) was added to a suspension of the ammonium salt of 5,5-dimethyl-2-mercapto-1,3,2-dioxaphosphorinan-2-thione (2.15 g.) in dry acetone (30 ml.). When the initial exothermic reaction was over, the mixture was boiled for 0.5 hr. and filtered (92% ammonium chloride recovered). Evaporation of the filtrate gave an oil which solidified on trituration with water. The substituted propane (0.5 g.) had m. p. 140–140.5° (from acetone–light petroleum) (Found: C, 35.75; H, 5.9; P, 14.1; S, 29.25. C₁₃H₂₆O₄P₂S₄ requires C, 35.8; H, 6.0; P, 14.2; S, 29.4%), *v*_{max} 688s, 815m, 824m, 916m, 962m, 998s, 1047s, 1114m, 1152w, 1170w, 1212w, 1230w, 1290w, 1310w, 1370 and 1377w (doublet), 1390w, 1408w, 1470m, and 1480m.

(b) The same ammonium salt (4.3 g.) was boiled with a solution of 2,2-dichloropropane (1.2 g.) in acetone for 25 hr. The salt was recovered quantitatively. No reaction took place between the ammonium salt and 2,2-dibromopropane in dimethylformamide during 40 days at room temperature.

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