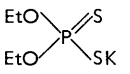
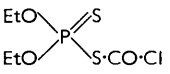
587. *The Reactivity of Organophosphorus Compounds. Part IV.*[1] *The Reaction of Carbonyl Chloride with Some Esters.*

By J. I. G. CADOGAN.

The reaction of carbonyl chloride with potassium *OO*-diethyl phosphorodithioate gives *S*-chlorocarbonyl *OO*-diethyl phosphorodithioate, a new type of organophosphorus compound, whereas potassium *OO*-diethyl phosphorothioate gives diethyl phosphorochloridate and tetraethyl pyrophosphoromonothionate. *S*-Ethyl methylphosphonochloridothioate, also a new type of organophosphorus compound, is readily obtained by reaction of carbonyl chloride with *OS*-diethyl methylphosphonothioate, whereas with the isomeric thionate loss of sulphur occurs to give ethyl methylphosphonochloridate.

ALTHOUGH it is known that carbonyl chloride with dialkyl alkylphosphonates gives alkyl alkylphosphonochloridates [2] and with trialkyl phosphites gives dialkyl phosphorochloridates,[3] its reactions with organophosphorus compounds have generally received little attention. The reactions of other types of organophosphorus compound with carbonyl chloride have now been examined with a view to (*a*) the production of new types of compound or compounds difficult to prepare by other methods, and (*b*) the discovery of new facts likely to lead to the elucidation of the mechanisms of these reactions.


(I)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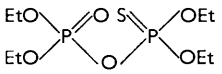
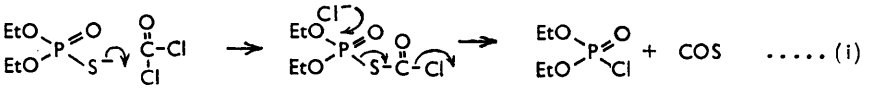

(III)

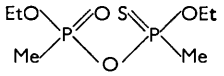
Potassium *OO*-diethyl phosphorodithioate (I) reacted readily with carbonyl chloride, to give *S*-chlorocarbonyl *OO*-diethyl phosphorodithioate (II), a new type of organophosphorus compound formed by nucleophilic displacement on carbonyl chloride. Attempts to characterise this compound by formation of the anilide failed, and *NN'*-diphenylurea, formed by successive displacements on the carbonyl carbon atom, was obtained. Potassium *OO*-diethyl phosphorothioate (cf. IV), on the other hand, gave a mixture of diethyl phosphorochloridate and tetraethyl pyrophosphoromonothionate (III), suggesting the intermediate formation of *S*-chlorocarbonyl diethyl phosphorothioate (V), followed by elimination of carbonyl sulphide by intramolecular decomposition or by bimolecular displacement by chloride ion (reaction i); the chloridate and unchanged potassium salt then give the pyrophosphorothionate (III). The instability of *S*-chlorocarbonyl diethyl phosphorothioate (V) compared with the dithioate (II) is presumably due to the increased electrophilicity of the phosphorus atom and parallels the higher reactivity of diethyl phosphorochloridate than of diethyl phosphorochloridothionate towards nucleophilic reagents.


(IV) (V) ..... (i)

Potassium *O*-ethyl methylphosphonothioate reacted similarly with carbonyl chloride, giving diethyl dimethylpyrophosphonomonothionate (VI). The absence of the corresponding chloridate in this case is in accord with its greater reactivity towards nucleophilic reagents. The presumed formation in the above reactions of the thiolo-isomer, *e.g.*, (V) rather than the isomeric thionate, *e.g.*, (VII) is noteworthy, since Kabachnik and his co-workers [4]

[1] Part III, Cadogan and Thomas, *J.*, 1960, 2248.
[2] Coe, Perry, and Brown, *J.*, 1957, 3604.
[3] Ford-Moore, Lermit, and Stratford, *J.*, 1953, 1776; Pudovik and Platanova, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 507 (U.S. translation).
[4] Kabachnik, Mastryukova, Rodionova, and Popov, *Zhur. obshchei Khim.*, 1956, **26**, 120.

report that *O*-acetyl *OO*-diethyl phosphorothioate results from the reaction of potassium *OO*-diethyl phosphorothioate and acetyl chloride, *i.e.*, C·O·P=S rather than C·S·P=O formation. Thus the behaviour of the bidentate ion (V) towards the carbonyl-carbon atom of carbonyl chloride is similar to its behaviour towards the α-carbon atom of an alkyl halide.[5] The carbonyl-carbon atom in methyl chloroformate, on the other hand, appears to be intermediate in character, because both C·O·P=S and C·S·P=O bond form-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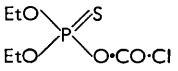
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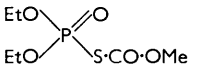
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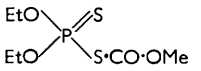
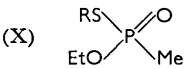

(IX)

ation occur in its reaction with potassium *OO*-diethyl phosphorothioate. This observation apparently conflicts with that of Nesmeyanov and Kabachnik [6] who reported, but without experimental detail, the formation of the thiolo-isomer (VIII) rather than thionate in this reaction. In an earlier paper, however, Kabachnik and his co-workers [4] do not specify which isomer is formed. Our evidence is based on infrared absorptions which can be attributed to P·S·C, P·O·C, P=O, and P=S groups. The analogous reaction between methyl chloroformate and potassium *OO*-diethyl phosphorodithioate gave diethyl *S*-methoxycarbonyl phosphorodithioate (IX).

O-Ethyl *S*-propyl methylphosphonothioate (X; R = Pr^n) and diethyl methylphosphonothiolate (X; R = Et) on reaction with carbonyl chloride gave *S*-propyl (XI; R =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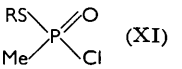
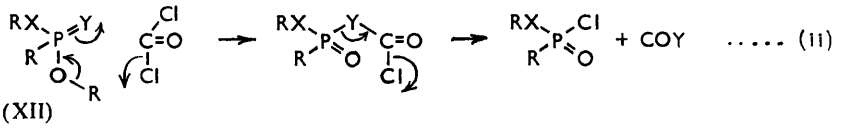

(XI)

Pr^n) and *S*-ethyl methylphosphonochloridothioate (XI; R = Et) respectively, providing a useful method for the preparation of these previously inaccessible compounds. Reaction of carbonyl chloride with diethyl methylphosphonothionate and with the dipropyl homologue, on the other hand, results in the loss of sulphur, presumably as carbonyl sulphide, to give ethyl and propyl methylphosphonochloridate. Triethyl phosphate, triethyl phosphorothionate, triethyl phosphorothiolate, and *OSS*-triethyl phosphorodithioate did not react with carbonyl chloride under the mild conditions employed in these investigations. It is difficult at this stage to arrive at a mechanism which embraces all of the observations made with neutral esters. That the unreactivity of the phosphates is due to the electronic


(XII) ..... (ii)

rather than steric effects, however, is clear from the ready reaction of the hindered diisopropyl propylphosphonate with carbonyl chloride. Mechanism (ii) is proposed for the reactions of carbonyl chloride with esters (XII) where Y = O and X = O or S, and where X = O and Y = S.

Experimental

The infrared spectra in the region 2—15 μ were obtained by using a Perkin–Elmer Model 21 double-beam spectrophotometer fitted with a rock-salt prism. Those in the region 15—25 μ were recorded on a Hilger H800 double-beam spectrophotometer fitted with a potassium bromide prism. Liquids were examined as capillary films between potassium bromide plates, and solids in potassium chloride or bromide discs. The provision of these facilities by Mr.

[5] Stirling, *J.*, 1957, **3597**; Kabachnik, Mastryukova, Kurochkin, Rodionova, and Popov, *Zhur. obshchei Khim.*, 1956, **26**, 2228.

[6] Nesmeyanov and Kabachnik, *Experientia, Suppl.* II, 1955, 67.

L. C. Thomas, and his help in the interpretation of the spectra, which was in part based on his unpublished correlations, are gratefully acknowledged.

Triethyl phosphorothionate, prepared by the addition of sulphur to triethyl phosphite, had b. p. 96°/12 mm., n_D^{25} 1·4458. Triethyl phosphorothiolate [1] had b. p. 100°/12 mm., n_D^{25} 1·4565. Triethyl *OOS*-phosphorodithioate had n_D^{25} 1·5030. Diethyl methylphosphonothiolate, prepared from ethyl methylphosphonochloridate [2] and ethanethiol in the presence of triethylamine, had b. p. 90°/12 mm., n_D^{25} 1·4738. Potassium diethyl phosphorothioate, m. p. 197°, was prepared by Mastin's method.[7] *Potassium ethyl methylphosphonothioate*, m. p. 137—138° (sealed tube) (from ether–ethanol) (Found: C, 19·6; H, 4·7. $C_3H_8KO_2PS$ requires C, 20·2; H, 4·5%), was obtained as hygroscopic crystals by the hydrolysis of diethyl methylphosphonothionate by Mastin's method.[7] *O-Ethyl S-propyl methylphosphonothiolate* (50%), b. p. 106°/10 mm., n_D^{25} 1·4718 (Found: C, 39·7; H, 8·6. $C_6H_{15}O_2PS$ requires C, 39·5; H, 8·3%), was prepared by boiling diethyl methylphosphonothionate with an excess of propyl iodide for 92 hr.

Dipropyl methylphosphonothionate, prepared from sodium propoxide and methylphosphonothioic dichloride in propan-1-ol at room temperature (24 hr.), had b. p. 62—64°/0·03 mm., n_D^{23} 1·4603 (Found: C, 43·5; H, 8·7. $C_7H_{17}O_2PS$ requires C, 42·9; H, 8·8%).

Reaction of Carbonyl Chloride with Organophosphorus Esters.—(i) *With diethyl methylphosphonothiolate.* Dry (H_2SO_4) carbonyl chloride was bubbled through the ester for 12 hr. at room temperature in an apparatus protected by drying tubes (SiO_2 gel). The mixture was degassed by drawing dry air through it. Distillation of the residue gave *ethyl methylphosphonochloridothiolate* (75%), b. p. 46°/0·1 mm., n_D^{25} 1·5100 (Found: C, 23·1; H, 5·3. C_3H_8ClOPS requires C, 22·8; H, 5·05%). The infrared spectrum showed absorption at 8·15 (P=O), 7·7, 11·3 (P·Me [8]), and 18·7 μ (P·S·C [8]). The chloridate (1·71 g.) in benzene (3 ml.) was added to aniline (1·80 g.) in benzene (4·5 ml.) at 0°. After 30 min. the mixture was filtered and the residue (3·2 g.) was washed with water and filtered. The residue (2·0 g.) was recrystallised to constant m. p. (155°) from methanol–benzene, to give S-*ethyl* N-*phenylmethylphosphonamidothioate* in needles (Found: C, 50·3; H, 6·9. $C_9H_{14}NOPS$ requires C, 50·3; H, 6·5%). The infrared spectrum showed absorption at 8·55 (P=O), 3·2 (NH), 18·7 μ (P·S·C).

O-Ethyl *S*-propyl methylphosphonothioate was similarly treated with carbonyl chloride for 9 hr. and left overnight before being degassed; it gave *S*-propyl methylphosphonochloridothioate, n_D^{25} 1·4930. This was confirmed by conversion (75%) into S-*propyl* N-*phenylmethylphosphonamidothioate* which, on recrystallisation from benzene–light petroleum (b. p. 60—80°), had m. p. 98—100° (Found: C, 52·1; H, 7·2. $C_{10}H_{16}NOPS$ requires C, 52·5; H, 7·0%).

(ii) *With dialkyl methylphosphonothionates.* The diethyl ester (4·75 g.; n_D^{25} 1·4620) was treated with carbonyl chloride at room temperature for 3½ hr. during which the volume of the mixture had doubled. The product, after being degassed on the next day by passage of dry air, had n_D^{25} 1·4485. Treatment with carbonyl chloride was resumed for 1½ hr. and the next day degassing gave ethyl methylphosphonochloridate (4·0 g.), n_D^{25} 1·4374, having an infrared spectrum identical with that of authentic material. Coe, Perry, and Brown [2] reported n_D^{25} 1·4320.

The dipropyl ester (4·75 g.; b. p. 62—64°/0·03 mm., n_D^{23} 1·4603) was similarly treated but was kept for 3 days before excess of carbonyl chloride was removed; it gave propyl methylphosphonochloridate (3·0 g.), n_D^{20} 1·4350 (correct infrared spectrum). A portion (1·6 g.) of the chloridate on treatment with aniline (1·86 g.) gave propyl *N*-phenylmethylphosphonamidate (2·00 g.), b. p. 134°/0·05 mm. (Found: C, 55·6; H, 7·6. Calc. for $C_{10}H_{16}NO_2P$: C, 56·4; H, 7·5%).

(iii) *With di-isopropyl propylphosphonate.* Reaction with carbonyl chloride, which was vigorous at first, was allowed to proceed for 3 hr. The mixture was degassed on the next day to give isopropyl propylphosphonochloridate (80%), n_D^{23} 1·4310 (correct infrared spectrum).

(iv) *With potassium* OO-*diethyl phosphorodithioate.* The salt (20 g.) in light petroleum (b. p. 60—80°; 350 ml.; Na-dry) was stirred magnetically during the reaction, which was slow (by heat evolution), until the addition of dry ($MgSO_4$) acetone (50 ml.). The mixture was degassed after 3 hr., filtered, and evaporated at 20 mm. to leave an oil (19 g.), n_D^{25} 1·5130, which was distilled. This gave S-*chlorocarbonyl* OO-*diethyl phosphorodithioate*, b. p. 80°/0·05 mm., n_D^{25} 1·5198 (Found: C, 24·7; H, 3·9. $C_5H_{10}ClO_3PS_2$ requires C, 24·2; H, 4·0%). The infrared spectrum showed absorption at 12·05 (P=S [8]), 9·9, 10·25 [$(EtO)_2P$], 5·7 (C=O), 15·5 μ

[7] Mastin, *J. Amer. Chem. Soc.*, 1945, **67**, 1663.
[8] Thomas, *Chem. and Ind.*, 1957, 198.

($\sim PS_2\sim$ [9]). The product gave *NN'*-diphenylurea, m. p. and mixed m. p. 238°, on treatment with aniline (2 mol.).

(v) *With potassium* OO-*diethyl phosphorothioate.* The salt (15 g.) in light petroleum (b. p. 60—80°; 500 ml.; Na-dry), after reaction with carbonyl chloride (12 hr.), degassing, filtration, and evaporation (20 mm.), afforded an oil (12 g.), n_D^{25} 1·4628, which was not diethyl phosphorochloridate and had a spectrum similar to that of *S*-chlorocarbonyl *OO*-diethyl phosphorodithioate. The product was sealed in soda-glass to await purification by distillation, but decomposed violently after 4 days with the evolution of a gas. The experiment was repeated as follows: The salt (15 g.) was added during 10 min. to light petroleum (b. p. 60—80°; 150 ml.; Na-dry) which had been saturated with dry carbonyl chloride. Reaction occurred at once. The carbonyl chloride was passed through the magnetically stirred mixtured for 3 hr. The mixture was degassed on the next day, filtered, and evaporated at 20 mm. to leave an oil (5 g.), n_D^{23} 1·4570, which, on distillation at 0·05 mm. gave (*a*) diethyl phosphorochloridate, b. p. 40° (2 g.), n_D^{25} 1·4150 (correct infrared spectrum), and (*b*) tetraethyl pyrophosphoromonothionate, b. p. 90° (2·2 g.), n_D^{25} 1·4430 (infrared spectrum identical with that of authentic material [2]). Fraction (*a*) gave diethyl *N*-phenylphosphoramidate, m. p. and mixed m. p. 96°, on treatment with an excess of aniline. The unstable compound formed in the first experiment is therefore assumed to have been *S*-chlorocarbonyl diethyl phosphorothioate, which on decomposition would give diethyl phosphorochloridate, as discussed above.

(vi) *With potassium ethyl methylphosphonothioate.* The salt (15 g.) was added during 10 min. to light petroleum (b. p. 60—80°; 250 ml.) which had been saturated with carbonyl chloride. The reaction was very vigorous and required cooling; it was allowed to continue for 2 hr. After being degassed and filtered the solution was evaporated at 20 mm. to leave an oil (6 g.) which was distilled; this gave diethyl dimethylpyrophosphonomonothionate (4·9 g.), b. p. 80°/0·05 mm., n_D^{24} 1·4640. The infrared spectrum was identical with that of an authentic specimen. Coe, Perry, and Brown [2] reported b. p. 73°/3 × 10^{-4} mm., n_D^{20} 1·4679.

(vii) *With other esters.* The following esters did not react with carbonyl chloride at room temperature; the duration of reaction in hours is given in each case: triethyl phosphorothionate (18), triethyl phosphorothiolate (7), *OSS*-triethyl phosphorodithioate (12), triethyl phosphate (4 + overnight).

Reaction of Potassium OO-*Diethyl Phosphorodithioate with Methyl Chloroformate.*—The potassium salt (5·0 g.) and methyl chloroformate (2·6 g.) were boiled under reflux in ethyl methyl ketone (25 ml.) for 2 hr. Evaporation of the cooled, filtered mixture gave OO-*diethyl* S-*methoxycarbonyl phosphorodithioate* (5 g.), b. p. 80°/0·05 mm., n_D^{25} 1·5040 (Found: C, 30·2; H, 5·8. $C_6H_{13}O_4PS_2$ requires C, 29·6; H, 5·4%).

Reaction of Potassium OO-*Diethyl Phosphorothioate with Methyl Chloroformate.*—The reaction of the potassium salt (5·0 g.) with methyl chloroformate (2·4 g.), as described above, gave a colourless oil (4·0 g.), b. p. 86°/0·05 mm., n_D^{23} 1·4560 (Found: C, 32·6; H, 6·3. $C_6H_{13}O_5PS$ requires C, 31·6; H, 5·8%). The infrared spectrum showed bands at 9·8, 10·25 (P·O·Et), 7·9 (P=O), 12·25 (P=S), 17·85, 16·95 (P·S·C), and 5·65, 5·8 μ (C=O).

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, December 21st,* 1960.]

[9] Thomas, 16th Internat. Congr., I.U.P.A.C., Paris, 1957, Resumé of Communications, Vol. II, p. 103.