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ORGANOPHOSPHORUS CHEMISTRY—I

PHOSPHORYLATION VIA VERY REACTIVE INTERMEDIATES FORMED BETWEEN ORGANOPHOSPHONODICHLORIDATES AND DIMETHYL SULPHOXIDE.*

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Abstract—Organophosphonodichloridates react exothermically with DMSO in anhydrous solvents to give P^1P^2-disubstituted pyrophosphoric and pyrophosphonic acids. $MeSCH_2Cl$, $(MeS)_2CH_2$, Me_2S and Me_2S_2 were the sulphur compounds identified as by-products of the reaction. Our findings are consistent with the assumption that the active phosphorylating agents are compounds of the P-XYZ type. A mechanism for the phosphorylation reaction is proposed.

INTRODUCTION

EXOTHERMIC reaction of some cyclic phosphorus (V) chlorides with dimethyl sulphoxide (DMSO) has been described by Ratz and Sweeting.[1] Reaction of DMSO with organic phosphorus (III) dichlorides has been investigated by Amonoo-Neizer *et al.*,[2] who found that DMSO is an oxidizing agent able to react with tervalent phosphorus compounds to give phosphoryl compounds. In addition, with phosphorus (V) chlorides, another reaction takes place in which chlorine is replaced by hydroxyl to give the corresponding phosphorus (V) acid and phosphorus-free materials.

Preliminary experiments have shown that methyl phosphonodichloridate reacts instantaneously and explosively with DMSO to give P^1P^2-dimethyl pyrophosphonic acid. As described in the present communication the reaction may be extended to a number of organophosphonodichloridates, to give high yields of anhydrides.

RESULTS AND DISCUSSION

The "activation" of phosphorus compounds to give phosphorylating agents (usually not isolated) able to produce pyrophosphates or diesters of phosphoric acid has been previously described.[3–8] Here we describe a new activating agent (DMSO).

No reports exist on the isolation and identification of phosphates having anhydride P—O—P bonds obtained from reactions involving phosphorus halides and DMSO.

To study the reaction in more detail, we used a simple substrate, methyl phosphonodichloridate (I). The over-all reaction of I with DMSO is rapid and exothermic and dilution with an anhydrous solvent and cooling with ice is necessary. A highly hygroscopic solid product (II) m.p. 138–141° was obtained clearly not the expected methyl phosphonic acid (m.p. 104–106°).[9–11] PMR spectra of the unknown solid (II) in D_2O showed the presence of five peaks, two of which continuously increased at the expense of the other three. Analysis of the PMR spectra suggested that the methyl

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phosphonic acid (III) as well as its anhydride (IV) are present in solution. This assumption was confirmed by running PMR spectra of the pure compounds. Pure III was obtained by hydrolysis of I according to McKay *et al.*[9] and Neale and Williams[12] and IV was prepared from the corresponding acid according to Grunze, Distol and Thilo.[13]

Reaction of I with DMSO in anhydrous solvents showed from the material balance that all the phosphorus remained in the insoluble fraction. Several products were detected and separated from the supernatant solution by prep. GLC and identified as methylchloromethyl sulphide (V) (main product), dimethylsulphide (VI), bis-methylthiomethane (VII) and dimethyldisulphide (VIII).

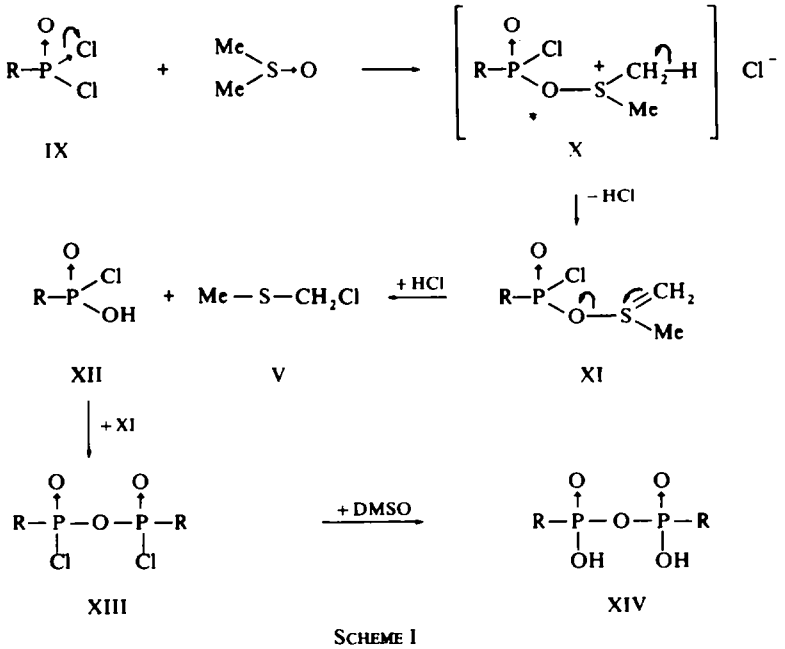
P^1P^2-Dialkyl and diaryl pyrophosphoric and pyrophosphonic acids were obtained from the corresponding organophosphonodichloridates by the described reaction and isolated as their cyclohexylammonium salts.

Reaction of organophosphonodichloridates with DMSO presumably proceeds *via* formation of very reactive intermediate XI, a P-XYZ phosphorylating system.[3,7]

A reaction mechanism (Scheme I), would be initial activation of the phosphoryl dichloride (IX) and the DMSO to give X as a reactive intermediate.

Analogous structures to X have been postulated for the case of the reactive adducts formed from DMF and phosphoryl chloride[14] or organophosphorodichloridates,[15] which can be isolated as deliquescent solids at low temperatures. Similar unstable intermediate is formed between DMSO and 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5) undecane 3,9-dioxide.[1]

As is typical for sulphonium compounds[16] X will readily lose a proton to give a d orbital stabilized sulphur ylid (XI). The presence of a positively charged sulphur atom facilitates subsequent proton abstraction by a nucleophile, e.g. Cl^-.



SCHEME I

The oxygen atom attached to sulphur favours the resonance forms, ylid ↔ ylene (XI), which combine readily with nucleophilic reagents.

The action of HCl resulting from X gives rise to the formation of free acid (XII) and methyl chloromethyl sulphide (V).

The phosphorylating agent (XI) reacts with XII to give pyrophosphates (XIII) and the thermodynamically stable sulphoxide.[5]

Further, XIII reacts with DMSO according to the stages described, to give pyrophosphoric acids (XIV).

Since methyl chloromethyl sulphide (V) is an alkylating agent it might be expected to react with phosphoric acids (XII) to give pyrophosphates.[8] This is a P-XYZ system,[3,7] protonation of which might be expected to lead to phosphoryl transfer. On this basis an alternative step for the production of XIII could be postulated. However, we were not able to observe any reaction between methyl phosphonic acid and methyl chloromethyl sulphide in 1,2-dimethoxyethane with or without DMSO.

A complex mixture of side products V, VI, VII and VIII, together with other minor products, not identified, was obtained. The formation of VI, VII and VIII can be assumed to proceed by attack of HCl on DMSO.[17] Other possible mechanisms have been discussed.[18–20] Water produced in these reactions can react with V[21–25] to give methanethiol, formaldehyde, HCl and VII. Besides, some unreacted DMSO can react with the methanethiol to give VIII.[18–26]*

The formation of HCl and formaldehyde arising from the reaction was detected by conventional methods.

Our laboratory has extended the phosphorylation reaction to organophosphorodichloridites and phosphorothiodichloridates. Besides, we found that other sulphoxides behave like DMSO in promoting phosphoryl transfer. Full experimental results will subsequently be reported.

The experimental conditions described in this paper for phosphoryl transfer were not adequate for acyl transfer.

EXPERIMENTAL

M.ps. were determined with a Buchi apparatus and are uncorrected. PMR spectra were obtained with a Varian T-60 spectrometer using TMS and DSS as internal standards. GLC was carried out using an Aerograph 1522-B and a Varian Aerograph Autoprep 700 gas chromatograph. IR spectra were measured with a Perkin-Elmer 337 spectrometer. Elemental analysis were performed by A. Bernhardt's laboratory (W. Germany). All reactions were carried out in a moisture-free N_2 atmosphere. All solvents were reagent grade and further dried by usual procedures. DMSO was purified by recrystallization.[27] Methyl phosphonodichloridate was prepared as described[28] b.p. 73°/14 mm. PMR in Cl_3CD consisted of a P—CH_3 doublet at τ 7·5 (J_{P-CH_3} 16 cps). Phenyl phosphorodichloridate was prepared according to Kalyshkina and Kraft,[29] b.p. 127–132°/30 mm. PMR in Cl_3CD showed one peak centred at τ 2·7 assigned to the aromatic protons. Ethyl phosphonodichloridate was synthetized according to Kinnear and Perren,[30] b.p. 52–57°/22 mm. PMR in CCl_4 consisted in a complex multiplet at τ 7·3 and two triplets centred at τ 8·7 (J_{P-C-CH} 30 cps, J_{CH-CH} 8 cps) in the ratio 2:3. Cyclohexyl phosphonodichloridate was prepared according to Clayton *et al.*,[31] b.p. 124–126°/18·5 mm. PMR in C_6D_6 showed a broad signal over the range τ 9·6–7·6. Methyl chloromethyl sulphide was synthetized by reaction between DMSO and benzoyl chloride,[32] b.p. 107–112°, n_D^{20} = 1·4985. PMR in CCl_4 consisted in a CH_2 singlet at τ 5·3 and a CH_3 singlet at τ 7·7 in the ratio 2:3. The product was checked for homogenity by GLC. Bismethylmethanethiol was

* Reaction of V with aqueous DMSO was found to give VI, VII and VIII by GLC analysis of the $CHCl_3$ extracts. (column: 6 ft × ⅛ in., o.d. S.S. packed with 15% Carbowax 20M on 60/80/Chromosorb A/W DMCS. Carrier gas: N_2, flow rate 30 ml/min. Column temp: 75°. Pyrex injector insert).

obtained from methyl chloromethyl sulphide by hydrolysis,[25] b.p. 150-151°, 50-50·5°/12 mm. PMR in Cl_3CD consisted of a CH_2 singlet at τ 6·4 and a CH_3 singlet at τ 7·8 in the ratio 1:3. The product shows one peak by GLC. (Calc. for $C_3H_8S_2$: C, 33·31; H, 7·45; S, 59·27. Found: C, 33·52; H, 7·29; S, 59·2%). To confirm its identity the sulphone was prepared by oxydation with H_2O_2 (200 vol.) in glacial AcOH, m.p. 147·5°. (Calc. for $C_3H_6O_4S_2$: C, 20·92; H, 4·72; S, 37·24. Found: C, 21·20; H, 4·57; S, 37·38%). PMR in $(CD_3)_2CO$ consisted of a CH_2 singlet at τ 5·0 and a CH_3 singlet at τ 6·7 in the ratio 1:3.

No impurities were observed in the PMR spectra of any of the synthetized compounds.

Reaction of methylphosphonodichloridate (I), (IX, R = Me) *with* DMSO *in* MeCN, *1,2-dimethoxyethane, ether,* C_6H_6, CH_2Cl_2 and *dioxane.* A solution of DMSO (1·563 g, 20 mmoles/2 ml) was added slowly while stirring, to a solution of I(1·330 g, 10 mmoles/2 ml) in the same solvent, cooling to moderate the the exothermic reaction (ice bath) and maintain the temperature between 10 to 15°. Then the mixture was allowed to rise to room temp and further heated at 30–40° for 1 hr. The solid (II) separated was removed by centrifuging and washed twice with 0·5 ml of MeCN and once with 0·5 ml dry acetone. The supernatant was examined by GLC as described below. Solvents were removed from the residue by vacuum over P_2O_5, weighted and the yield calculated. Yield of II in MeCN was 99%. M.p. and m.m.p. 141–142° (lit.[9] 141–141·5°). (Calc. for $C_2H_8O_5P_2$: C, 13·79; H, 4·63; P, 35·62. Found: C, 13·98; H, 4·71; P, 35·51%). Yields in other solvents were: 82% (1,2-dimethoxyethane), 75% (dioxane), 72% (CH_2Cl_2), 64% (C_6H_6) and 60% (ether). Elemental analysis, PMR and IR spectra, and m.p. comparison with that of an authentic sample of P^1P^2-dimethyl pyrosphosphonic acid (IV) prepared as described below, indicated that they were identical. No paraformaldehyde was detected in crude II by conventional methods.

Preparation of dicyclohexylammonium P^1P^2*-dimethyl pyrophosphonate.* A sample of 0·80 g of II was treated with a solution (10%) of cyclohexylamine in acetone until precipitation was complete (pH 8). Water was added dropwise with stirring until the solid just dissolved. The solution was filtrated and to the clear, colourless solution obtained, sufficient anhydrous acetone was added until precipitation was complete. The precipitate was filtered, washed with dry acetone, dried and recrystallized from acetone–water (92%), m.p. 234–236° (no depression by m.m.p. with authentic product). Elemental analysis, PMR and IR spectra were identical with those of an authentical sample.

Methyl phosphonic acid (III) *from methylphosphonodichloridate* (I). Redistilled I (1·330 g, 10 mmoles) was dissolved in 1,2-dimethoxyethane (2 ml) and hydrolyzed by stirring with water,[9,12] and the solution evaporated. The acid was dissolved in water, treated with charcoal, filtered and the filtrate evaporated giving, after drying *in vacuo* over P_2O_5, 0·94 g (98%) of III m.p. 104–106°, m.p. 106° from methyl ethyl ketone. (Calc. for CH_5O_3P: C, 12·50; H, 5·25; P, 32·25. Found: C, 12·53; H, 5·25; P, 32·17%). PMR (D_2O) two peaks at τ 8·5 (J_{PCH_3} 17 cps). IR (nujol): 765 (s); 950 cm^{-1} (vs closed doublet); 1010 (vs); 1110 (s) (P═O); 1310 cm^{-1} (s) (P—CH_3).[33]

Cyclohexylammonium salt was obtained as above (96%): m.p. 201–202°. (Calc. for $CH_5O_3P(C_6H_{11}NH_2)_2$: C, 53·03; H, 10·62; N, 9·52; P, 10·53. Found: C, 48·37; H, 10·07; N, 9·32; P, 10·24%) (low carbon determination believed due to colloidally dispersed carbon in analysis residue, 1·91%). IR (nujol): bands at 940 (s); 1010 (vs); 1130 (vs) (P═O); 1305 cm^{-1} (m) (P—CH_3).[33,34]

By comparison of the PMR spectrum of cyclohexylammonium methyl phosphonate with that of cyclohexylammonium sulphate, we found signals between τ 7·7–9·0 which could be assigned to the protons of cyclohexylammonium cation and a superimposed doublet at τ 8·9 (J_{PCH_3} 17 cps) corresponding to the P—CH_3 group. The integrated areas obtained by comparison of the molar solutions (in D_2O) of both showed protons in the ratio of 28 (cation) to 3 (anion).

P^1P^2*-dimethyl pyrophosphonic acid from methyl phosphonic acid.* The dehydration was conducted according to the directions of Grunze, Dostal and Thilo.[13] Methyl phosphonic acid (1·12 g) was suspended in 2 ml Ac_2O. Refluxing for 1·5 hr gave a clear, yellowish solution from which crystals separated on cooling. The crude solid was washed (4 ×) with 1 ml portions of acetone and centrifugated. Each time the solid was crushed and the last traces of solvents eliminated by prolonged vacuum drying over P_2O_5, giving 1·00 g (90%), m.p. 139·5–141·5°. The product was 99·9% pure by PMR and no AcOH or acetone found. (Calc. for $C_2H_8O_5P_2$: C, 13·79; H, 4·63; P, 35·62. Found: C, 13·91; H, 4·65; P, 35·58%). IR (nujol): 775 (vs), 890 (vs), 940 (vs), 975 (s), 1000 (vs) and 1120 (vs) (P—O—P); 1210 (vs) (P═O); 1310 cm^{-1} (s) (P—CH_3).[34,35] PMR (D_2O) superimposed peaks of the anhydride and the acid. Augmentation of the acid peaks is always observed at the expense of the anhydride peaks. PMR spectra in water basified with NH_4OH shows six stabilized peaks over the range τ 8·5–8·7.

Cyclohexylammonium salt obtained as before had m.p. 234–236° (90%). (Calc. for $C_2H_8O_5P_2(C_6H_{11}NH_2)_2$: N, 7·53; P, 16·63. Found: N, 7·33; P, 16·96%). IR (nujol): 755 (s), 870 (m), 945 (vs) and 1055 (vs) cm^{-1}

(P—O—P); 1200 (vs) (P=O); 1295 (m) cm^{-1} (P—CH_3).[34, 35] PMR (D_2O) protons of cyclohexylammonium cation over the range τ 7·7–9·0 and partially superimposed peaks over the range τ 8·5–8·7 corresponding to the anhydride anion.

Methyl phosphonic acid from P^1P^2*-dimethyl pyrophosphonic acid.* A sample (0·348 g, 2 mmoles) of anhydride was hydrolyzed by warming with water. Complete hydrolysis was checked by PMR. The water was removed under red. press. the solid dissolved in acetone and the solution evaporated. This operation was repeated twice to remove all water. The acetone solution was concentrated, filtered and just enough petroleum ether added to cause cloudiness. When cooled with ice, pure phosphonic acid separated as colourless crystals in a nearly quantitative yield. Two recrystallizations from methyl ethyl ketone gave m.p. 106° (m.m.p. undepressed).

P^1P^2*-Diphenyl pyrophosphate from phenylphosphorodichloridate* (IX; R = PhO) *and DMSO.* DMSO (1·560 g, 20 mmoles) in MeCN (1·5 ml) were added with stirring to a solution of IX (R = PhO) (2·100 g, 10 mmoles) in MeCN (2 ml) at such a rate that with ice-water bath cooling the temp was maintained at 15–20°. After stirring at 30–35° for 1 hr the solution was evaporated under red. press and the residual oil taken up in acetone to which cyclohexylamine was added to pH 8. The mixture was kept at 0° for 1 hr, then filtered. The precipitate, washed with acetone, was crystallized from water containing cyclohexylamine (a few drops). The salt (2·06 g, 84%) has m.p. 255–257° (lit. 258–260°[5]; 252–254°[6]; 250–255°[33]). (Calc. for $C_{12}H_{12}O_7P_2(C_6H_{11}NH_2)_2$: C, 54·58; H, 7·25; N, 5·31; P, 11·74. Found: C, 54·74; H, 7·34; N, 5·45; P, 11·50%). Residue: 2·34%. IR (nujol): 500 (s), 510 (m), 555 (m), 695 (m), 735 (s), 765 (s), 900 (vs), 980 (vs), 1085 (vs) and 1245 (vs) cm^{-1}. The following assignments are made: 735 and 980, P—O—P; 900, P—O—Ph; 1245, P=O.[34, 35]

P^1P^2*-Diethyl pyrophosphonate from ethylphosphonodichloridate* (IX; R = Et) *and DMSO.* As above for IX (R = PhO), 1·563 g (20 mmoles) of DMSO and 1·430 g (10 mmoles) of IX (R = Et) were reacted and the mixture treated with cyclohexylamine in acetone to pH 8. The diester was isolated as its cyclohexylammonium salt (70%) and recrystallized from acetone-water, m.p. 210–211°. (Calc. for $C_4H_{12}O_5P_2(C_6H_{11}NH_2)_2$: C, 47·99; H, 9·60; N, 6·99; P, 15·48. Found: C, 46·85; H, 9·48; N, 7·12; P, 14·97%). PMR: a signal corresponding to the cyclohexyl group (cation) and the P-Et complex multiplet (anion) superimposed over the range τ 7·7–9·2. IR spectra (nujol mull) showed absorption bands at: 725 (m) and 900 (m), (P—O—P), 1070 (s), 1125 (vs) (P=O?), 1240 (w) (P-Et) cm^{-1}.[34, 35]

P^1P^2*-Dicyclohexyl pyrophosphonate from cyclohexylphosphonodichloridate* (IX; R = C_6H_{11}) *and DMSO.* 1·563 g (20 mmoles) of DMSO and 2·01 g (10 mmoles) of IX (R = C_6H_{11}) were reacted. The anhydride was isolated as its cyclohexylammonium salt, 2·4 g (96%) which is soluble in cold water but separates by heating. Recrystallized from warm water, m.p. 242–243°. (Calc. for $C_{12}H_{24}O_5P_2(C_6H_{11}NH_2)_2$: C, 56·65; H, 9·91; N, 5·51; P, 12·19. Found: C, 56·45; H, 9·78; N, 5·31; P, 12·06%). IR (nujol): 510 (m), 580 (m), 760 (w), 855 (w), 890 (m), 925 (vs), 1000 (w), 1055 (vs), 1180 (vs) and 1210 (s) cm^{-1}. The following assignments are made: 760 and 925 P—O—P, 1180 P=O.[34, 35] PMR: a signal corresponding to the cyclohexyl group (cation and anion) superimposed over the range τ 7·7–9·0.

Attempted reaction between methyl phosphonic acid, methyl chloromethyl sulphide with or without DMSO. The methyl chloromethyl sulphide (5 mmoles) was added dropwise to a solution of methyl phosphonic acid (10 mmoles) in DMSO (10 mmoles) and 1,2-dimethoxyethane (1·5 ml). No heat was evolved. The mixture was heated under reflux for 1 hr, cooled and worked up to give the dicyclohexylammonium salt. PMR analysis gave no evidence of pyrophosphate formation.

When DMSO was omitted an identical result was obtained.

Attempted preparation of benzoic anhydride from DMSO *and benzoyl chloride.* 1·560 g (20 mmoles) of DMSO in 1,2-dimethoxyethane (1 ml) was added with stirring to a solution of BzCl (1·400 g, 10 mmoles) in 1,2-dimethoxyethane (2 ml). It was necessary to moderate the exothermic reaction by cooling (ice-water) to get the mixture between 5–10°. The mixture was then heated at 30–35° for 1 hr. GLC analysis of the mixture gave no evidence of anhydride formation. (The column was 6 ft × $\frac{1}{8}$ in. o.d., pyrex, packed with 3% OV 17 on 100/120 mesh Varaport 30. Carrier gas: N_2; flow rate 25 ml/min.; column temp. 200°).

Identification of the sulphur compounds. The upper and lower layers of the two-phase solvent system (one-phase system when using MeCN) were separated and examined by GLC. The qualitative chemical composition of both phases was identical. The main compounds observed were identified as methyl chloromethyl sulphide (V), dimethyl sulphide (VI), bismethylmethanethiol (VII) and dimethyldisulphide (VIII) by comparison of their retention times with those of authentic samples (pyrex column, 10 ft × $\frac{1}{8}$ in. o.d., packed with 5% QF1-DC200 on 100/120 mesh Varaport 30. Carrier gas: N_2; flow rate: 20 ml/min.; column temp.: 30°). Pure fractions of these compounds were isolated by prep GLC (column: 20 ft × $\frac{1}{8}$ in.

o.d., aluminium, packed with 30% SE52 on 45/60 mesh Chromosorb W. Carrier gas: H_2, flow rate 120 ml/min., column temp.: 120°). Physical constants and PMR spectra of V and VII were in good agreement with those of authentic samples. The IR and PMR spectra of VI and VIII corresponded to those tabulated (Sadtler catalog, No. 6.299) 6·344 and 14·500; 6·345 respectively.

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