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Mechanism of Phosphinyl Disulfide Formation from a Phosphorodithioate Ester

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3–Chloroperbenzoic acid oxidation of *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate (I) gave the oxon, 4–chlorophenyl diethoxyphosphinyl disulfide (IV), *O,O*–diethyl phosphorothioic acid (VI), 4–chlorothiophenol (VII), bis(4–chlorophenyl) disulfide and elemental sulfur. Production of compounds VI and VII, which are seemingly the hydrolysis products of compound I as judged from their chemical structures, occurred actually under oxidative condition, accompanied with the formation of the oxon. Therefore, an intermediate which links the starting material I with products VI and VII can be assumed. The disulfide compound IV which was found among the peracid oxidation products of compound I was also produced from peracid oxidation of compounds VI and VII. This must be one way of the disulfide production from peracid oxidation of compound I, because ^{18}O was incorporated into the molecule of compound IV when peracid oxidation was carried out in the presence of $H_2{}^{18}O$ (99.5 atom%). Incorporation of ^{18}O was 100% with a higher level of water, while it was none with a low level of water. With an intermediate level, both water-derived and peracid-derived oxygen are incorporated into the disulfide molecule IV. This indicates the presence of another pathway for production of compound IV. All these facts as well as production of elemental sulfur indicate the involvement of an unstable phosphorus oxythionate type intermediate, which gives the oxon by desulfuration and the phosphinyl disulfide IV by rearrangement and/or oxidation of compounds VI and VII which produce by hydrolysis of the intermediate.

INTRODUCTION

Organophosphorus insecticides represent a most important group of insecticides and most of them are in the form of the thiono or dithio type, which are oxidized either chemically and biologically to give the activated form, the oxons. There are evidences that at the same time of the oxon formation, the *P–O*(or *S*)-aryl bond cleaves to form the seemingly hydrolyzed products of the starting materials.[1–9]

The puzzle was solved by assuming the formation of a common intermediate, named later as "phosphorus oxythionate".[7,10–13] The intermediate has not been isolated yet for any kind of phosphorothioate or phosphorodithioate esters, but in certain cases the corresponding isomer has been isolated and identified.[12–14] If the formation of the isomer can be shown to occur by the rearrangement of the proposed intermediate, the structure of the isomer is a good indication of the structure of the intermediate. Probably the formation of *N*–dimethoxyphosphinylthio derivative from *N*–(dimethoxyphosphinothioyl)carbamate by peracid oxidation may be explained by assuming such rearrangement.[12] In the case of the forming phosphinyl disulfide derivatives from phosphorodithioate esters, such rearrangement was assumed, but not evidenced.[13] Rather they are produced by peracid oxidation of the corresponding phosphorothioic acids and thiol compounds.[14] The present study concerns the

mechanism of formation of the phosphinyl disulfide from *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate and provides further evidences for the structure of phosphorus oxythionate intermediate.

MATERIALS AND METHODS

1. *Chemicals*

The chemical structures and names of compounds used in the present study, identified by number, and the *Rf* values on thin-layer chromatography (TLC) are shown in Fig. 1 and Table 1, respectively.

Compound I, *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate, was prepared by the reaction of potassium 4–chlorothiophenoxide with diethyl phosphorochloridothioate. 3.0 g of 4–chlorothiophenol and 1.2 g of powdered potassium hydroxide were mixed together in 20 ml of acetone and stirred at room temperature for 1 hr. To this solution was added dropwise with stirring 4.0 g of diethyl phosphorochloridothioate at room temperature and stirring was continued for 3 hr. After removing acetone, chloroform and 5% aqueous potassium hydroxide solution were added to the reaction mixture, the organic layer was separated and the aqueous layer was extracted with chloroform. The combined extract was washed with water, dried with anhydrous magnesium sulfate, and concentrated. It was purified by gradiently eluting through a silica gel column with hexane/benzene (100/0, 95/5 and then 90/10). The IR spectrum indicated the presence of *P*=*S* (800, 660 cm^{-1}), *P*–*O*–alkyl (1015, 965 cm^{-1}), *P*–*O*–C_2H_5 (1160 cm^{-1}), and the benzene ring (1580, 1480, 810 cm^{-1}). The PMR spectrum in $CDCl_3$ showed δ=1.30 ppm ($2\underline{CH_3}CH_2O$ 6H, t), δ=4.00–4.40 ppm ($2CH_3\underline{CH_2}O$ 4H, m) and δ=7.30–7.60 ppm (aromatic 4H). The MS fragments appeared at *m/e* 298, 296 (M^+).

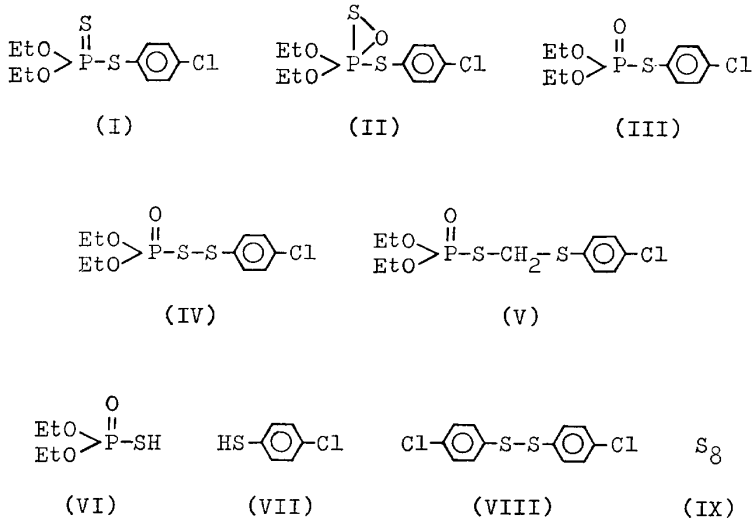

Fig. 1 Chemical structures and numbering. Et: ethyl.

Compound III, *O,O*–diethyl *S*–(4–

Table 1 TLC *Rf* values of related compounds.

Compound	Solvent system[a]					
	A		B		C	D
	S[b]	U[c]	S	U	S	S
I	0.47	0.80	0.03	0.05	0.32	0.72
III	0.09	0.19	—	—	0.02	0.40
IV	0.14	0.26	—	—	0.02	0.47
V	0.08	0.17	—	—	0	0.41
VI	0	0	—	—	0	0
VII	0.39	0.67	0.22	0.39	0.34	0.71
VIII	0.57	0.86	0.27	0.54	0.48	0.74
IX	0.58	0.88	0.47	0.79	0.54	0.73

[a] (A) hexane-ethyl acetate (4 : 1 v/v)
(B) hexane
(C) hexane-ethyl acetate (19 : 1 v/v)
(D) dichloromethane-ethyl acetate (9 : 1 v/v)

[b] Developed in a vapor-saturated tank with 15 cm development.

[c] Developed in a vapor-unsaturated tank with 15 cm development.

chlorophenyl) phosphorothiolate, was prepared by oxidation of compound I with 3-chloroperbenzoic acid (MCPBA) (see peracid oxidation of compound I). The reaction mixture was washed with 5% aqueous sodium bicarbonate solution, dried with anhydrous magnesium sulfate, concentrated, and separated preparatively on TLC using hexane-ethyl acetate (4 : 1 v/v) system (*Rf* value: 0.19). The IR spectrum showed the presence of *P=O* (1240 cm^{-1}), *P–O*-alkyl (1025, 970 cm^{-1}), *P–O*-C_2H_5 1160 cm^{-1}), and the benzene ring (1577, 1470 cm^{-1}). The PMR spectrum in $CDCl_3$ gave δ= 1.32 ppm ($2\underline{CH_3}CH_2O$ 6H, *t*), δ=4.04–4.40 ppm ($2CH_3\underline{CH_2}O$ 4H, *m*) and δ=7.28–7.72 ppm (aromatic 4H). The MS fragments were observed at *m/e* 282, 280 (M^+), 145, 143 ($[SC_6H_4Cl]^+$), 137 ($(EtO_2)\overset{+}{P}(O)$), 109 $\left(\begin{matrix}HO\\EtO\end{matrix}>\overset{+}{P}(O)\right)$ and 81 $((HO)_2\overset{+}{P}(O))$.

Compound IV, 4–chlorophenyl diethoxyphosphinyl disulfide, was formed as a major product of peracid oxidation of compound I. It was synthesized as follows: $HSC_6H_4Cl + Cl_2 \longrightarrow ClSC_6H_4Cl(X) + HCl$; $(EtO)_2P(O)SK + ClSC_6H_4Cl \longrightarrow (EtO)_2P(O)SSC_6H_4Cl + KCl$. Compound X was prepared by chlorination of 4–chlorothiophenol. 3.0 g of 4–chlorothiophenol and 0.5 g of triethyl phosphate were mixed together in 20 ml of chloroform and chlorine was added under ice-cooling until the weight of the reaction mixture showed an increase of 5.5 g. The temperature of the reaction solution was maintained below 25°C. To this solution was added with stirring 4.6 g of potassium salt of *O,O*–diethyl phosphorothioic acid at room temperature and stirring was continued at 40°C for 3 hr. The reaction mixture was washed with 5% aqueous potassium hydroxide solution and water, dried with anhydrous magnesium sulfate, and concentrated. It was chromatographed on a silica gel column with dichloromethane as the eluting solvent. The IR spectrum showed the presence of *P=O* (1250 cm^{-1}), *P–O*-alkyl (1040, 1010, 970 cm^{-1}), *P–O*-C_2H_5 (1160 cm^{-1}), and the benzene ring (1560, 1470, 810 cm^{-1}). The PMR spectrum in $CDCl_3$ indicated δ=1.30 ppm ($2\underline{CH_3}CH_2O$ 6H, t), δ=3.90–4.40 ppm ($2CH_3\underline{CH_2}O$ 4H, m), δ=7.40 ppm (aromatic 2H, d) and δ=7.70 ppm (aromatic 2H, d). The MS fragments appeared at *m/e* 314, 312 (M^+), 177, 175 ($[SSC_6H_4Cl]^+$), 145, 143 ($[SC_6H_4Cl]^+$), 137 ($(EtO)_2\overset{+}{P}(O)$), 109 $\left(\begin{matrix}HO\\EtO\end{matrix}>\overset{+}{P}(O)\right)$ and 81 $((HO)_2\overset{+}{P}(O))$. Compound IV was also produced by peracid oxidation of 4–chlorothiophenol and *O,O*–diethyl phosphorothioic acid: $(EtO)_2P(O)SH + HSC_6H_4Cl \xrightarrow{\text{peracid}} (EtO)_2P(O)SSC_6H_4Cl$. 183.2 mg of *O,O*–diethyl phosphorothioic acid and 147.1 mg of 4–chlorothiophenol were mixed together in 4 ml of dichloromethane and 207.4 mg of MCPBA in 4 ml of dichloromethane was added dropwise to the solution with stirring under ice-cooling. After keeping for 24 hr in a freezer, the reaction mixture was washed with 5% aqueous sodium bicarbonate solution, dried with anhydrous magnesium sulfate, and concentrated. It was subjected to a silica gel column chromatographic separation eluted with dichloromethane. The spectroscopic data was identical with that of compound IV prepared by the above method.

Compound V, *O,O*–diethyl *S*–(4–chlorophenylthiomethyl) phosphorothiolate, was a product from reaction of compound IV with diazomethane. It was synthesized as follows: $HSC_6H_4Cl + CH_2O + HCl \longrightarrow ClCH_2SC_6H_4Cl$ (XI); $(EtO)_2P(O)SK + ClCH_2SC_6H_4Cl \longrightarrow (EtO)_2P(O)SCH_2SC_6H_4Cl$. Compound XI was prepared by the reaction of 4–chlorothiophenol with formalin and hydrochloric acid. 2.9 g of 4–chlorothiophenol was dissolved in 2.1 g of 37% formalin and 10.0 g of 35% hydrochloric acid and the reaction solution was warmed at 60–70°C for 4 hr. The reaction mixture was extracted with ether, dried with anhydrous magnesium sulfate, and distilled to obtain transparent oil (1.3 g, 36.2% yield), bp 125–133°C/16–17 mmHg. To 0.6 g of sodium salt of *O,O*–diethyl phosphorothioic acid in dichloromethane was added dropwise 0.6 g of compound XI in dichloromethane with stirring at room temperature for 90 min. After washing with water the reaction mixture was extracted with dichloromethane, dried with anhydrous magnesium sulfate, and concentrated. It was purified by gradiently eluting through a silica gel column with hexane/ethyl acetate (90/10 and then 80/20). The IR spectrum indicated the presence of

P=O (1265 cm^{-1}), *P–O*–alkyl (1025, 985 cm^{-1}), *P–O*–C_2H_5 (1175 cm^{-1}), and the benzene ring (1580, 1480 cm^{-1}). The PMR spectrum in $CDCl_3$ showed δ=1.33 ppm ($2\underline{CH_3}CH_2O$ 6H, t), δ=3.87–4.23 ppm ($2CH_3\underline{CH_2}O$ 4H, m), δ=4.26 ppm (SCH_2S 2H, d) and δ=7.30 ppm (aromatic 4H, s). The MS fragments gave *m/e* 328, 326 (M^+), 183 ($[(EtO)_2P(O)SCH_2]^+$), 159, 157 ($[CH_2SC_6H_4Cl]^+$), 137 ($(EtO)_2\overset{+}{P}(O)$), 109 $\left(\begin{matrix}HO\\EtO\end{matrix}>\overset{+}{P}(O)\right)$ and 81 ($(HO)_2\overset{+}{P}(O)$).

Compound VI, *O,O*–diethyl phosphorothioic acid, was prepared by alkaline hydrolysis of diethyl phosphorochloridothioate. 9.4 g of diethyl phosphorochloridothioate was dissolved in 50 ml of ethanol-water mixed solution (1 : 1) containing 5.6 g of potassium hydroxide and heated at 80–90°C for 90 min. After removing ethanol and acidifying with 10% hydrochloric acid the reaction mixture was extracted with dichloromethane with salting out, dried with anhydrous magnesium sulfate, and concentrated. The IR spectrum showed the presence of *P=S* (805, 660 cm^{-1}), *P–O*–alkyl (1010, 965 cm^{-1}), *P–O*–C_2H_5 (1155 cm^{-1}), and OH (3360 cm^{-1}). This compound was also identified as compound VI because compound IV was prepared from MCPBA oxidation of this compound with 4–chlorothiophenol.

Compound VII, 4–chlorothiophenol, was purchased.

Compound VIII, bis(4–chlorophenyl) disulfide, was purchased.

Compound IX, elemental sulfur, identified by the *Rf* value and solubility in carbon disulfide.

$H_2{}^{18}O$ (99.5 atom %) was obtained from Prochem, The British Oxygen Company Ltd..

2. *Chromatography and Analytical Procedures*

TLC was carried out for analytical purpose on 0.25 mm precoated silica gel $60F_{254}$ plastic sheets (Merck) and for preparative isolations on 0.50 mm hand coated silica gel GF_{254} Type 60 (Merck) glass plates. Chromogenic reagent used for detection was 0.5% palladium chloride in diluted hydrochloric acid.

Column chromatography on 100 mesh analytical grade silica gel was used. The solvent systems are described in individual experiment.

Infrared (IR) spectra were determined as liquid or as mix with nujol using JASCO IRA–1 Grating Infrared Spectrophotometer.

Proton nuclear magnetic resonance (PMR) spectra were obtained in deuterochloroform solution on JEOL JNM–PMX60 NMR Spectrometer.

Electron impact mass (MS) spectra were obtained on JEOL JMS–D100 Mass Spectrometer.

Gas chromatography was done with YANACO G1800–FPD Gas Chromatograph equipped with a column (1.0 m×2 mm *i.d.*) containing 1% XE–60 on AW DMCS Chromosorb–W (60–80 mesh) and a Model G1800-flame photometric detector (S or P channel) under operating conditions of nitrogen pressure, 0.50 kg/cm^2 and column temperatures, 80, 170 or 185°C.

3. *Peracid Oxidation of Compound I*

To a magnetically stirred solution of compound I (0.4 mmol) in 2 ml of dichloromethane under ice-cooling was added in portions an equivalent mole of 3–chloroperbenzoic acid (MCPBA) in 2 ml of dichloromethane. The reaction mixture was kept for 24 hr in a freezer. For qualitative determination the reaction mixture was washed with 5% aqueous sodium bicarbonate solution to remove the acids and the remaining dichloromethane solution was analyzed by TLC. For quantitative analysis the reaction mixture was treated with an excess amount of diazomethane in ether for 2 days at room temperature, then analyzed gas chromatographically. *O,O*–diethyl phosphorothioic acid (VI) was converted almost quantitatively to *O,O*–diethyl *S*–methyl phosphorothiolate (formation of *O,O*–diethyl *O*–methyl phosphorothioate was scanty), 4–chlorothiophenol (VII) to the methyl thioether, while compound IV to compound V in a 50% yield. Retention times (given in parentheses) at 170°C of column temperature were as follows: compound I (3.6 min), compound III (4.2 min), compound V (20.7 min; 10.8 min at 185°C of column temperature). Also retention times of the methyl thioether of compound VII and the methyl ester of compound VI at 80°C of column temperature were 2.7 min and 11.0 min, respectively. Peracid oxidation was also done with more ratio

of MCPBA in the presence of aqueous solution of different acidity.

4. Peracid Oxidation in the Presence of $H_2^{18}O$

To a stirred suspension of compound I (110 mg) in 4 ml of dichloromethane and $H_2^{18}O$ (99.5 atom%, 1, 10 or 140 mg) was added an equivalent mole of MCPBA dissolved in 4 ml of dichloromethane under ice-cooling and the reaction mixture was kept overnight in a freezer. After washing with 5% aqueous sodium bicarbonate solution, the dichloromethane solution was concentrated under a reduced pressure at 35°C and separated preparatively on TLC. The region corresponding to compound IV was scraped and extracted with dichloromethane and compound IV was submitted to MS. The ratio of ^{18}O–containing peak and the corresponding ^{16}O–containing peak directly represents the ratio of ^{18}O and ^{16}O incorporated in the case.

5. Reaction of Compound IV with Diazomethane

A dichloromethane solution (10 ml) of compound IV (0.2 g) was reacted with an excess of diazomethane at room temperature for overnight, then concentrated and submitted to preparative TLC using dichloromethane–ethyl acetate (9 : 1 v/v) system (*Rf* value: 0.42).

RESULTS AND DISCUSSION

1. The Reaction of 4–Chlorophenyl Diethoxyphosphinyl Disulfide (IV) with Diazomethane

The reaction mixture from peracid oxidation of starting material I gave the same TLC pattern before and after diazomethane treatment except the spot corresponding to compound IV which changed to *O,O*–diethyl *S*–(4–chlorophenylthiomethyl) phosphorothiolate (V) and an unknown. Treatment of the isolated compound IV with diazomethane gave two major products, compound V (*Rf* value: 0.07) and the unknown (*Rf* value: 0.46) when developed with the solvent system of hexane–ethyl acetate (4 : 1 v/v) mixture. The chemical structures of compounds IV and V were established by unequivocal synthesis as well as IR, PMR, MS spectroscopies. Proposed reaction mechanism for formation of compound V is shown in Fig. 2 by analogy with the reaction

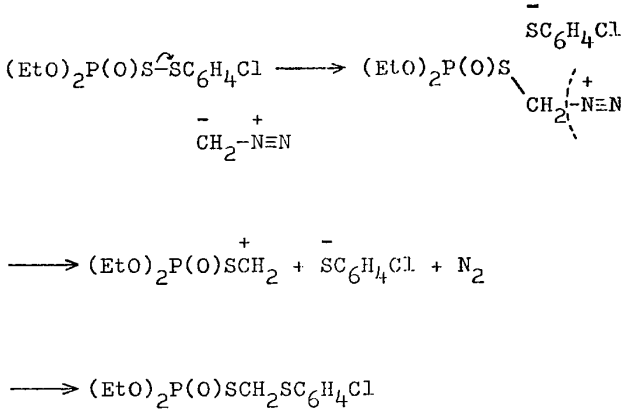

Fig. 2 Proposed mechanism for reaction of 4–chlorophenyl diethoxyphosphinyl disulfide with diazomethane to form *O,O*–diethyl *S*–(4–chlorophenylthiomethyl) phosphorothiolate.

of polysulfide with the nucleophiles. The same type of reaction was found for the organophosphorus compound, Amiphos®, *O,O*–dimethyl *S*–(2–acetylaminoethyl) phosphorodithioate (unreported). The yield of compound V was 50±4% when 3.2 mg to 34.1 mg of compound IV in 5 ml of dichloromethane reacted with excess amounts of diazomethane at 15°C for 2 days. As compound IV was unable to be detected under the gas chromatographic conditions used, this conversion was useful for semiquantification of the phosphinyl disulfide IV.

2. Peracid Oxidation of the Phosphorus Dithioate Ester I

The findings which indicate or imply the presence of an unstable intermediate, "phos-

Table 2 Products formed on MCPBA oxidation of *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate in dichloromethane.

	Compound	% of SM[a)]
I	$(EtO)_2P(S)SC_6H_4Cl$	23
III	$(EtO)_2P(O)SC_6H_4Cl$	22
IV	$(EtO)_2P(O)SSC_6H_4Cl$	39
VI	$(EtO)_2P(O)SH$	trace
VII	HSC_6H_4Cl	trace
VIII	$(SC_6H_4Cl)_2$	<8
Other compounds		not analyzed

a) SM: starting material.

phorus oxythionate" will be discussed.

Gas chromatographic analysis of the products obtained by peracid oxidation of compound I under an anhydrous condition (Table 2) indicates the production of compound IV followed by the oxon III as major products. Compounds VI, VII and VIII and at least 2 other unknowns were found in smaller amounts. Elemental sulfur was detected on TLC. Compounds VI and VII (and its further oxidation product VIII) are seemingly the hydrolyzed products of starting material I, but actually they produced only under oxidative conditions. To know whether or not hydrolysis occurs, dichloromethane solution of compound I or III was stirred with water, 5% aqueous sodium bicarbonate solution or 5% aqueous 3-chlorobenzoic acid solution for 5 hr, but the starting material was recovered quantitatively. Therefore, an oxidized intermediate which links the starting material I with products VI and VII (or VIII) must be considered.

Formation of compound IV in peracid oxidation of starting material I may be from the oxidative combination of compounds VI and VII. Indeed, peracid oxidation of compounds VI and VII gave roughly equal production of compounds IV (41%) and VIII (37%). However, as shown in Table 2, far more compound IV produced than compound VIII from peracid oxidation of the starting material I. Therefore, the results imply the presence of another pathway of forming compound IV.

More direct evidence was obtained by peracid oxidation of starting material I in the presence of $H_2{}^{18}O$ (99.5 atom%).

Authentic sample IV and the product IV obtained in the presence of 1 mg of $H_2{}^{18}O$ gave

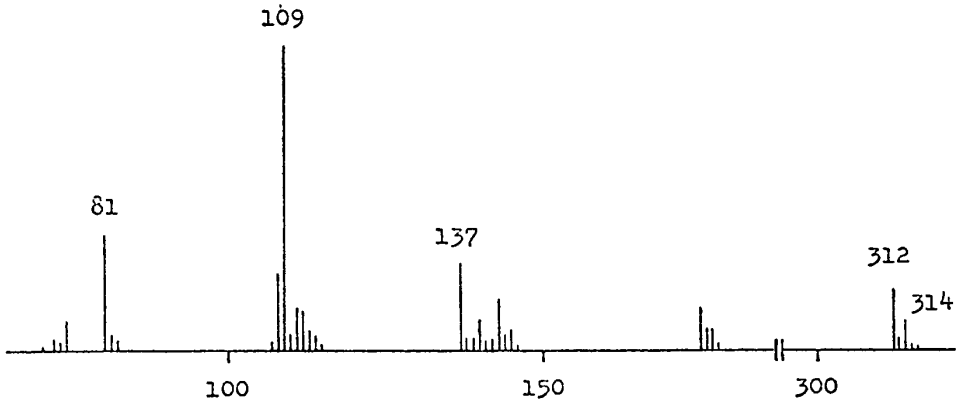

Fig. 3 Mass spectrum of $(EtO)_2P(O)SSC_6H_4Cl$ obtained on MCPBA oxidation of $(EtO)_2P(S)SC_6H_4Cl$ in 4 ml of CH_2Cl_2 with or without 1 mg of $H_2{}^{18}O$ (99.5 atom%).

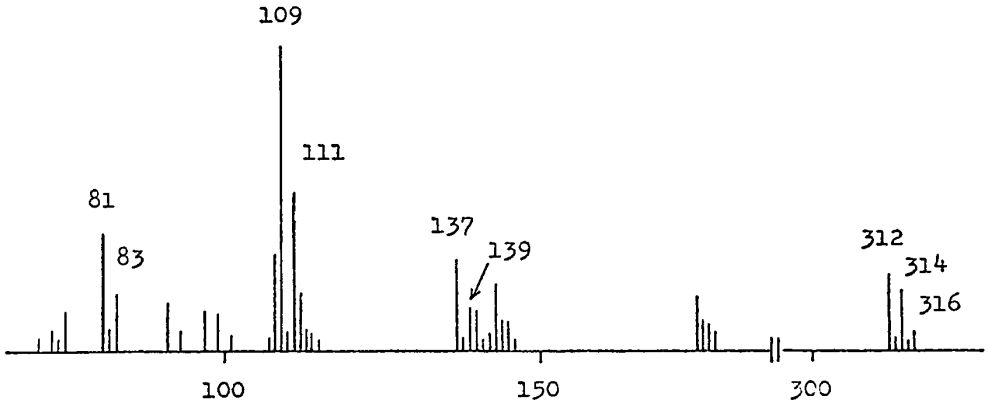

Fig. 4 Mass spectrum of $(EtO)_2P(O)SSC_6H_4Cl$ obtained on MCPBA oxidation of $(EtO)_2P(S)SC_6H_4Cl$ in 4 ml of CH_2Cl_2 and 10 mg of $H_2{}^{18}O$ (99.5 atom%).

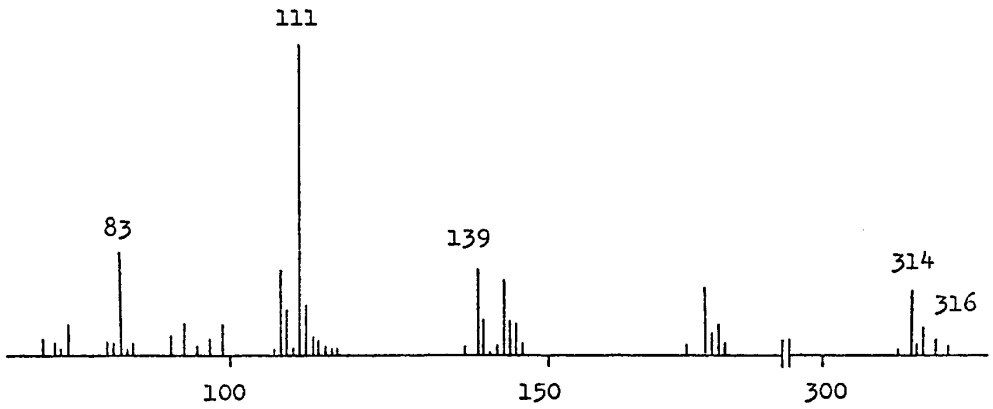

Fig. 5 Mass spectrum of $(EtO)_2P(O)SSC_6H_4Cl$ obtained on MCPBA oxidation of $(EtO)_2P(S)SC_6H_4Cl$ in 4 ml of CH_2Cl_2 and 140 mg of $H_2{}^{18}O$ (99.5 atom%).

Table 3 The oxon formation on MCPBA oxidation of *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate under various conditions.

Solvent system	Molar ratio of MCPBA to SM[a)]	The oxon	SM
CH_2Cl_2	1.0	22%	23%
CH_2Cl_2	3.5	18	0
CH_2Cl_2–H_2O (1 : 1)	3.5	41	0
CH_2Cl_2–5%$NaHCO_3$ (1 : 1)	3.5	81	0
CH_2Cl_2–5%HCl (1 : 1)	3.5	21	0

a) Starting material. 100 mg of SM in 4 ml of a solvent system shown in the table added with 2 ml of dichloromethane solution of MCPBA, kept at room temperature for one day.

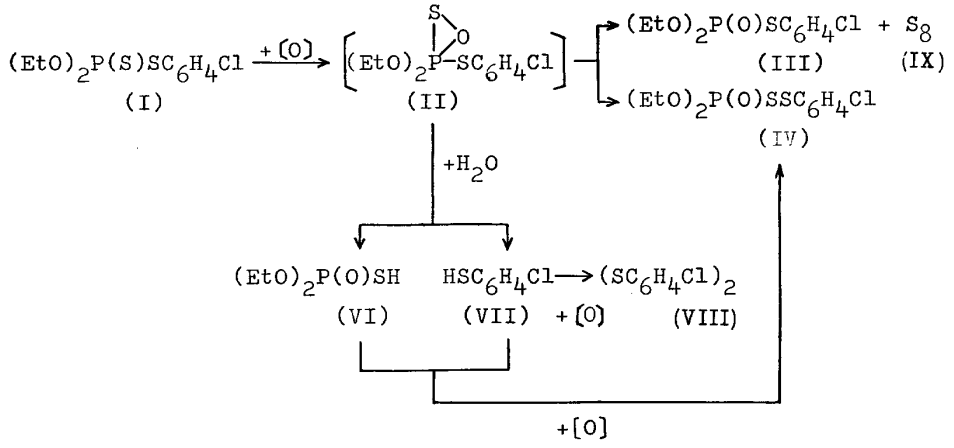

Fig. 6 Proposed pathway leading to formation of various products on MCPBA oxidation of *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate.

key peaks of 314, 312 (M^+), 137 ($(EtO)_2\overset{+}{P}(O)$), 109 $\left(\begin{matrix}HO\\EtO\end{matrix}>\overset{+}{P}(O)\right)$ and 81 ($(HO)_2\overset{+}{P}(O)$) (Fig. 3), while the product IV obtained in the presence of 140 mg of $H_2{}^{18}O$ gave 316, 314, 139, 111 and 83, indicating complete incorporation of one ^{18}O into the molecule (Fig. 5). In the presence of 10 mg of $H_2{}^{18}O$ an intermediate mass fragmentation pattern was obtained (Fig. 4). The fact clearly indicates that two mechanisms function for production of compound IV: one which involves oxygen from peracid, and another which requires water oxygen as a source of P(O) oxygen.

The simplest structure for the intermediate which matches the first mechanism and links starting material I and compound IV is structure II. One of the hydrolysis products of structure II, that is compound VI, includes oxygen derived from water. Therefore, compound IV as the oxidized product of compounds VI and VII should have water originated oxygen. The oxon (III) formation is governed by solvent factors. Table 3 shows the yield of the oxon III under different conditions. Presence of water increased the oxon formation than anhydrous conditions and far more oxon formation was obtained in a basic condition. On the contrary an acidic condition decreased oxon formation.

The overall picture of the peracid oxidation is shown in Fig. 6. The starting material I receives oxygen from peracid to form the phosphorus oxythionate intermediate II, which, under anhydrous condition or in the presence of small amount of water, rearranges to give the phosphinyl disulfide IV, and loses sulfur to form the oxon III. Hydrolysis of phosphorus oxythionate intermediate occurs in the presence of water. In the presence of much water both the oxon formation and hydrolysis are prefered ways, particularly under basic condition, and the hydrolyzates, compounds VI and VII, are further oxidized to form compound IV and compound VIII.

要　　約

ジチオ型有機リン化合物 *O,O*–diethyl *S*–(4–chlorophenyl) phosphorodithioate (I) を 3–chloroperbenzoic acid で酸化したところ，オキソン体 III，4–chlorophenyl diethoxyphosphinyl disulfide (IV)，*O,O*–diethyl phosphorothioic acid (VI)，4–chlorothiophenol (VII)，bis (4–chlorophenyl) disulfide (VIII)，元素イオウ (IX) を得た．VI と VII は化学構造上，一見出発物質 I の単なる加水分解物のようであるが，実際は酸化条件下でのみ III とともに生成することから，これらの物質 VI，VII と出発物質をつなぐ反応中間体 phosphorus oxythionate II の存在が推定される．IV は VI と VII を過酸で酸化すれば得られた．出発物質 I を ^{18}O で標識した水 (99.5 Atom %) 存在下で過酸酸化したところ，IV の分子内に ^{18}O が取り込まれ VI と VII からの IV の生成が少なくとも出発物質の過酸酸化の際にも起こっていることがわかる．しかし，取り込まれる ^{18}O の割合は水の量により異なり，多量の ^{18}O 水の存在下では IV の $P{=}O$ 酸素は 100% ^{18}O に由来するが無水条件か少量の水の存在下では ^{16}O のみである．したがって IV についてもう一つ別の生成経路の存在が示唆される．これらの事実から出発物質 I を過酸で酸化すると，まず不安定な反応中間体 phosphorus oxythionate II が形成され，このものの分子内転位により，また水が存在すればこのものの加水分解物VIとVIIの再酸化によってもIVが生成，他方において脱イオウによりオキソン体が生成すると結論し，phosphorus oxythionate 中間体の存在をいっそう明確にした．

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