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Oxidation of Diphosphine Dioxides, Disulfides and Phosphinothioite and Photolysis of Diphosphine Disulfides. Formation of Phosphinic and Phosphinothioic Anhydrides

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Oxidation of tetraphenyldiphosphine dioxide with an equimolar amount of peroxybenzoic acid (III) gave diphenylphosphinic anhydride in a good yield. Similarly, diphosphine disulfides (II) with 1.5—2.0 mol times of III, gave the corresponding phosphinothioic anhydrides (V), together with the corresponding phosphinic acid and sulfur. II gave V in air in refluxing xylene or *o*-dichlorobenzene. The yields of V increased with reaction temperature and with reaction time, indicating a homolytic fission of the P(S)–P(S) bond. Reaction of tetraphenyldiphosphine disulfide with sulfur in refluxing *o*-dichlorobenzene gave bis(diphenylphosphinothioyl) sulfide. Photolysis of II with a low pressure mercury lamp gave phosphinic acid and sulfur under oxygen, and gave phosphine sulfide and *O*-methyl phosphinothioate in methanol. Phenyl diphenylphosphinothioite gave diphenyl disulfide and diphenylphosphinic acid with silver nitrate.

Diphosphine dioxides (I) and disulfides (II) undergo heterolytic cleavage of the P–P bond with various reagents.[1] Phosphinic anhydrides are considered to be the intermediate in the oxidation of diphosphines[2] and the corresponding disulfides (II),[3–5] with oxidizing reagents such as hydrogen peroxide and mercuric oxide to the corresponding phosphinic acids.

It has been reported that II inserts ethylene molecules between their phosphorus atoms.[6] In the course of unsuccessful attempts to insert heterocumulenes into the P(S)–P(S) bond of II, it was found that phosphinothioic anhydrides were always obtained in small yields in refluxing benzene or xylene in air.

We thus carried out oxidation of I and II with peroxybenzoic acid, anticipating the formation of the corresponding anhydrides through Baeyer-Villiger type reaction[7] and the air oxidation of II. This paper describes the results, photolysis of II and also oxidation of phenyl diphenylphosphinothioite with silver nitrate.

Results and Discussion

Oxidation of Diphosphine Dioxide (I) and Disulfides (II) with Peroxybenzoic Acid (III). Tetraphenyldiphosphine dioxide (Ia) was chosen as a sample of diphosphine dioxide, since tetraalkyldiphosphine dioxides are scarcely known.

When Ia was allowed to react with an equimolar amount of peroxybenzoic acid (III) in dichloromethane for 40 min at room temperature, diphenylphosphinic anhydride (IVa) was obtained in 83% yield.

Longer reaction time or use of excess amounts of III gave mainly diphenylphosphinic acid. The low yields of IVa may be attributed to decomposition of IVa by benzoic acid produced during the reaction or by excess of III. Anhydride (IVa) could not be purified by column chromatography or by recrystallization, because of easy hydrolysis with moisture.

$R_2P(=X)\text{–}P(=X)R_2 + PhCO_3H \longrightarrow$
I, $X=O$ III
II, $X=S$
$R_2P(=X)\text{–}O\text{–}P(=X)R_2 + PhCO_2H$
IV, $X=O$
V, $X=S$
a, $R=Ph$; b, $R=Et$

A similar oxidation of diphosphine disulfides (II) gave phosphinothioic anhydrides (V). Typical results are listed in Table 1.

V was obtained in poor yield with an equimolar amount of III, but in fairly good yield with 1.5—2.0 mol times of III. Phosphinic acid and sulfur were always produced in small yields, indicating that the oxygen atom insertion into the P(S)–P(S) bond competes with the oxidative desulfurization of the P=S groups. Therefore, use of the above 3 mol times of III gave no V but the corresponding phosphinic aicd and sulfur.

In order to clarify the oxidative desulfurization of the P=S group, triphenylphosphine sulfide was oxidized with III as a model compound under similar conditions. The reaction products were triphenylphosphine oxide and sulfur. It is known that triphenylphosphine sulfide is oxidized to the corresponding oxide with various oxidizing reagents.[8]

Recently the oxidation of diethyl aroylphosphonates with III has been reported to produce aroyl diethyl phosphates.[9] The present reactions are also explained by the Baeyer-Villiger type reaction.

However, the structures VI and VII may be considered to be the actual structures of so-called "diphosphine dioxides and disulfides", respectively.

$R_2P(O)\text{–}OPR_2$ $R_2P(S)\text{–}SPR_2$
VI VII

Both samples of Ia prepared by air oxidation of tetraphenyldiphosphine[2] and by air oxidation of diphenylphosphinous chloride in the presence of *t*-amine

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Table 1. Oxidation of diphosphine disulfides (II) with peroxybenzoic acid (III) in dichloromethane

II		Temp. (°C)	Time (hr)	III/II (mol/mol)	Mol %		
					$[R_2P(S)]_2O$	$R_2P(O)OH$	S
IIa	R=Ph	18—35	2	1.2	13	22	11
		ca. 2	2	2.0	54	4	3
IIb	R=Et	*ca.* 7	24	3.8	0	58	46
		ca. −50	5	1.5	37	25	33
		18—31[a)]	14	2.0	40	17	21

a) In benzene.

and water,[10)] and those of IIa or IIb prepared by sulfurization of diphosphines[2)] and reaction of ethylmagnesium bromide with diphenylphosphinothioyl chloride[11)] or phosphorus thioxychloride,[12)] were quite the same as each other with respect to melting point, IR spectrum, and reactivity toward III. Uncertainty as to structure was thus eliminated.

Air Oxidation of Diphosphine Disulfides (II). When diphosphine disulfides (II) were refluxed in toluene, xylene or *o*-dichlorobenzene in the air for a longer time, phosphinothioic anhydrides (V) were obtained but not under nitrogen. Typical data are summarized in Table 2.

Table 2. Phosphinothioic anhydrides (V) from diphosphine disulfides (II)

II	R	Solvent	Temp. (°C)	Time (hr)	V (%)
IIa	Ph	PhH	80	24	8
		PhMe	110	64	45
		Xylene	140	72	98
IIb	Et	PhH	80	29	0
		Xylene	140	93	12
		o-$Cl_2C_6H_4$	180	33	35
IIc	*n*-Bu	o-$Cl_2C_6H_4$	180	42	48

We see that both higher temperature and longer reaction time favor the formation of V. No V was formed in benzene at room temperature after a longer period even under oxygen stream. These observations suggest the homolytic cleavage of the P(S)–P(S) bond in II.

$$\underset{\mathrm{II}}{\mathrm{R_2P(S){-}P(S)R_2}} \xrightarrow{\Delta} \mathrm{2R_2\dot{P}{=}S} \xrightarrow{\mathrm{O_2}} \underset{\mathrm{V}}{\mathrm{R_2P(S){-}O{-}P(S)R_2}}$$

a, R=Ph; b, R=Et; c, R=*n*-Bu

IIa reacts at lower temperature because of the formation of more stable $Ph_2P(S)\cdot$ radical.

In the cases of aliphatic diphosphine disulfides, especially IIc, the formation of unidentified decomposition products was observed by tlc.

Thus, ethylene insertion reaction of II[6)] is considered to proceed through homolysis of the P(S)–P(S) bond followed by the addition of $R_2P(S)\cdot$ radicals to ethylene, since the reaction is carried out at 275°C for 48 hr.

Similarly the reaction of IIa with sulfur gave bis(diphenylphosphinothioyl) sulfide (VIII) in refluxing *o*-dichlorobenzene under nitrogen.

$$\underset{\mathrm{IIa}}{\mathrm{Ph_2P(S){-}P(S)Ph_2}} \longrightarrow \mathrm{2Ph_2\dot{P}{=}S} \xrightarrow{\mathrm{S_8}} \underset{\mathrm{VIII}}{\mathrm{Ph_2P(S){-}S{-}P(S)Ph_2}}$$

Photolysis of Diphosphine Disulfides (II). It has been reported that tetraphenyldiphosphine undergoes homolysis on irradiation of light or on heating at above 180°C,[13,14)] but there is no report on the homolytic fission of II, except for the above results.

In the photolysis of II, evidences for the homolytic fission of the P(S)–P(S) bond were also obtained.

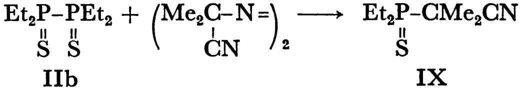
At room temperature, no Vb could be detected on irradiation of IIb with a high pressure mercury lamp in carbon disulfide or in methanol for 18—28 hr, even in the presence of rose bengal as a sensitizer, and IIb was recovered. On the other hand, irradiation of IIb in benzene with a low pressure (LP) mercury lamp for 19 hr under oxygen gave 59% of sulfur and 18% of diethylphosphinic acid, along with a trace amount of Vb.

The result is explained by a homolytic cleavage of the P(S)–P(S) bond and oxidative desulfurization of the P=S groups.

$$\underset{\mathrm{IIb}}{\mathrm{Et_2P(S){-}P(S)Et_2}} \xrightarrow{\mathrm{LP}\,h\nu} \mathrm{2Et_2\dot{P}{=}S} \xrightarrow{\mathrm{O_2}} \underset{\mathrm{Vb}}{\mathrm{[Et_2P(S){-}O{-}P(S)Et_2]}}$$

$$\xrightarrow[\mathrm{O_2}]{h\nu} \mathrm{1/4S_8 + [Et_2P(O){-}O{-}P(O)Et_2]} \xrightarrow{\mathrm{H_2O}} \mathrm{2Et_2P(O)OH}$$

Although IIb did not react with α,α′-azobisisobutyronitrile (AIBN) in refluxing benzene under irradiation with a high pressure mercury lamp, IIb gave a small amount of diethyl-1-cyano-2-methylethylphosphine sulfide (IX) on irradiation with a low pressure mercury lamp. Sulfide (IX) could not be isolated in pure state, but its presence was determined by IR (2240 cm^{-1}) and MS (*m/e* 189, M^+).



$$\underset{\mathrm{IIb}}{\mathrm{Et_2\underset{\underset{S}{\|}}{P}{-}\underset{\underset{S}{\|}}{P}Et_2}} + \left(\mathrm{Me_2\underset{\underset{CN}{|}}{C}{-}N{=}}\right)_2 \xrightarrow{\mathrm{LP}\,h\nu} \underset{\mathrm{IX}}{\mathrm{Et_2\underset{\underset{S}{\|}}{P}{-}CMe_2CN}}$$

When IIa was irradiated in methanol under nitrogen for 6 hr with a low pressure mercury lamp, 52% of diphenylphosphine sulfide and 65% of *O*-methyl diphenylphosphinothioate were obtained. This reaction is also explicable in terms of homolysis as follows.

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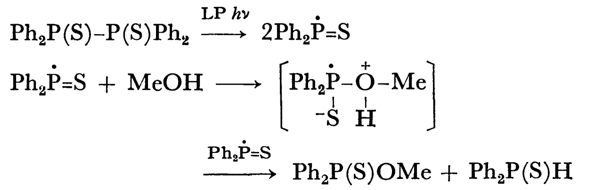


$$\mathrm{Ph_2P(S){-}P(S)Ph_2} \xrightarrow{\text{LP } h\nu} \mathrm{2Ph_2\dot{P}{=}S}$$

$$\mathrm{Ph_2\dot{P}{=}S + MeOH} \longrightarrow \left[\begin{array}{l}\mathrm{Ph_2\dot{P}{-}\overset{+}{O}{-}Me} \\ \quad\mathrm{{}^{-}S\ \ H}\end{array}\right]$$

$$\xrightarrow{\mathrm{Ph_2\dot{P}{=}S}} \mathrm{Ph_2P(S)OMe + Ph_2P(S)H}$$

A similar reaction has been reported in photolysis or thermolysis of tetraphenyldiphosphine in alcohols.[14)]

The above results indicate that II undegoes homolytic cleavage of the P(S)–P(S) bond on irradiation with a low pressure mercury lamp, and are reasonable from the fact that the disulfides (II) in methanol exhibit absorption maximum at 236—248 nm.

Oxidation of Phenyl Diphenylphosphinothioite (X) with Silver Nitrate. When X was allowed to react with silver nitrate in carbon disulfide at room temperature, silver metal (70%), diphenyl disulfide (87%), and diphenylphosphinic acid (60%) were obtained. The reaction might be attributed to electron transfer from X to silver ion.

$$\underset{\text{X}}{\mathrm{Ph_2P{-}SPh}} + \mathrm{AgNO_3} \longrightarrow \underset{\text{XI}}{\mathrm{[Ph_2P{-}SPh]^{\cdot +}}} + \mathrm{Ag} + \mathrm{NO_3^-}$$

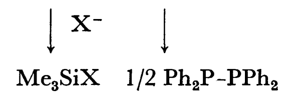
$$\mathrm{[Ph_2P{-}SPh]^{\cdot +}} \longrightarrow \mathrm{Ph_2P^+ + PhS\cdot}$$

$$\mathrm{2PhS\cdot} \longrightarrow \mathrm{PhS{-}SPh}$$

$$\mathrm{Ph_2P^+ + NO_3^-} \longrightarrow \underset{\text{XII}}{\mathrm{[Ph_2PONO_2]}} \xrightarrow[\mathrm{H_2O}]{\mathrm{O_2}} \mathrm{Ph_2P(O)OH}$$

The formation of diphenylphosphinic acid is explained by oxidation of an intermediate XII followed by hydrolysis during isolation.

A similar reaction of trimethylsilyldiphenylphosphine with silver halides has been reported.[15)] The reaction is also considered to proceed through a similar mechanism.



$$\mathrm{Ph_2P{-}SiMe_3 + AgX} \longrightarrow \underset{\text{XIII}}{\mathrm{[Ph_2P{-}SiMe_3]^{\cdot +}}} + \mathrm{Ag + X^-}$$

$$\begin{tikzcd}[column sep=small] \mathrm{[Ph_2P{-}SiMe_3]^{\cdot +}} \arrow[r] & \mathrm{[Me_3Si^+]} \arrow[d, "\mathrm{X^-}"] & + & \mathrm{Ph_2P\cdot} \arrow[d] \\ & \mathrm{Me_3SiX} & & \mathrm{1/2\ Ph_2P{-}PPh_2} \end{tikzcd}$$

In the radical cations (XI and XIII), it is shown that more electronegative group generates the free radical.

Experimental

Materials. The following compounds were prepared by the methods given in literature: tetraphenyldiphosphine dioxide[2,10)] (mp 164—165°C), tetraethyl-[12,16)] (mp 76—76.5°C), tetra-*n*-butyl-[12,16)] (mp 71—72°C), tetraphenyldiphosphine disulfides[11)] (mp 170—171.5°C), phenyl diphenylphosphinothioite[17)] (mp 46—48°C) and peroxybenzoic acid.[18)]

Oxidation with Perbenzoic Acid (III). Only typical examples are given.

a) Tetraphenyldiphosphine Dioxide (Ia): To 10 g (25 mmol) of Ia in 100 ml of dichloromethane was added dropwise III (30 mmol) in 150 ml of dichloromethane at room temperature for 40 min under stirring. The reaction was exothermic. When addition was completed, III had been almost consumed. After removal of the solvent, the residual solid was extracted with ether to remove benzoic acid. Crude anhydride thus obtained was dissolved in carbon tetrachloride followed by precipitation with petroleum ether, mp 137—138°C (lit,[19)] 142—143°C), *m/e* 418 (M^+); yield 9.2 g (83%).

b) Tetraphenyldiphosphine Disulfide (IIa): To 4.35 g (10 mmol) of IIa in 100 ml of dichloromethane was added dropwise III (20 mmol) in 100 ml of dichloromethane at room temperature over a period of 2 hr. The mixture was stirred for further 30 min and extracted with 5% aqueous sodium carbonate. The organic layer was washed three times with 400 ml of water and dried with anhydrous sodium sulfate. After removal of the solvent, the residual tarry material was dissolved in benzene and the solution was concentrated to give crude anhydride. After removal of the solvent from the filtrate, the residue gave 18.5 mg (3%) of sulfur as the insoluble in dichloromethane. The solution was separated by preparative tlc. In total, 2.4 g (54%) of anhydride (Va), mp 192—194°C (lit,[19)] 196—198°C), *m/e* 450 (M^+), was obtained and 0.62 g (14%) of IIa was recovered. The first aqueous layer was acidified with hydrochloric acid to give 0.187 g (4.3%) of diphenylphosphinic acid, mp 190—191°C (lit,[20)] 194—196°C).

c) Tetraethyldiphosphine Disulfide (IIb): To 4.85 g (20 mmol) of IIb in 100 ml of dichloromethane was added dropwise III (30 mmol) in 100 ml of dichloromethane at about −50°C over a period of 2 hr under stirring. 5% of III remained after addition was completed. After standing for 3 hr at this temperature, the reaction mixture was extracted with 5% aqueous sodium bicarbonate. The organic layer was dried with anhydrous magnesium sulfate and the solvent was removed. The oily residue was chromatographed on alumina to separate sulfur (0.42 g, 33%), unchanged IIb (1.2 g, 25%) and anhydride (Vb). Crude anhydride thus obtained was again chromatographed on silica gel, and recrystallized repeatedly from petroleum ether, mp 34—36°C (lit,[21)] 42.5°C), *m/e* 258 (M^+); yield 1.9 g (37%) (Found: C, 36.92; H, 8.14%). The aqueous alkaline layer was acidified with hydrochloric acid, and extracted with dichloromethane. After removal of dichloromethane the residue was extracted with water, and dried to give viscous liquid (1.2 g, 25%). The IR spectrum was superimposable with that of diethylphosphinic acid.

d) Triphenylphosphine Sulfide: To 1.47 g (5 mmol) of triphenylphosphine sulfide in 10 ml of dichloromethane was added dropwise III (15 mmol) in 15 ml of dichloromethane at room temperature under stirring. After standing for 6 days, the solvent was removed. The residue was washed with ether and then aqueous sodium bicarbonate, and recrystallized from benzene to give triphenylphosphine oxide (0.98 g, 71%), mp 154—155°C (lit,[22)] 156°C). The ethereal washings were washed with 10% aqueous sodium bicarbonate to give 98 mg (61%) of sulfur.

Air Oxidation of Diphosphine Disulfides (II). a) Tetraphenyl Derivative (IIa): A solution of IIa (4.4 g, 10 mmol)

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in xylene (40 ml) was refluxed for 72 hr. Removal of the solvent under reduced pressure and washing of the residue, with ether gave 4.4 g (98%) of crude anhydride (Va), which was recrystallized from benzene, mp 198—199°C (lit,[19] 197—198°C), 3.9 g (87%).

b) Tetraethyl Derivative (IIb): A solution of IIb (0.72 g 3.0 mmol) in *o*-dichlorobenzene (30 ml) was refluxed for 33 hr. After removal of the solvent *in vacuo*, the residual brown oil (0.96 g) was chromatographed on silica gel. Elution with petroleum ether gave colorless oily material. Recrystallization from petroleum ether gave 0.27 g (35%) of Vb, mp 31—32°C (lit,[21] mp 42.5°C). The IR spectrum and R_f value on tlc were in agreement with those of an authentic sample.

*c) Tetra-*n*-butyl Derivative (IIc)*: A solution of IIc(0.60g, 1.7 mmol) in *o*-dichloromethane (30 ml) was refluxed for 42 hr. After removal of the solvent *in vacuo*, the residual brown tarry material (0.64 g) was purified by means of preparative tlc (silica gel, with petroleum ether–acetone (8:2)) to obtain pure Vc (0.30 g, 48%), which was oily. IR (liquid film), ν_{max} 920 (P–O–P) and 520 cm^{-1} (P=S); *m/e* 370 (M$^+$, 41%), 314 (M$^+$–C_4H_8, 28), 257 (M$^+$–C_4H_8–C_4H_9, 80), 193 ($Bu_2P(S)O^+$, 77), and 177 (Bu_2PS^+, 100).

Found: C, 52.02; H, 9.62%. Calcd for $C_{16}H_{36}OP_2S_2$: C, 51.85; H, 9.81%.

Reaction of IIa with Sulfur. A mixture of IIa (0.55 g, 1.3 mmol) and sulfur (58 mg, 1.8 mg-atom) in *o*-dichlorobenzene (50 ml) was refluxed for 8 hr under nitrogen. After removal of the solvent *in vacuo*, the residual brown solid was purified by preparative tlc (silica gel, with *n*-hexane–benzene (1:1)). Crude sulfide (VIII) (0.45 g) was recrystallized twice from 2-propanol, mp 120—121°C (lit,[23] 118—121°C), 0.39 g (66%).

Photochemical Oxidation of IIb. The disulfide (IIb) (0.86 g, 3.55 mmol) in benzene (50 ml) was irradiated with a low pressure mercury lamp (10 W) under oxygen at room temperature for 19 hr. After removal of the solvent, a small amount of benzene was added for the purpose of obtaining sulfur. The solution was chromatographed on silica gel to give sulfur (in total, 0.134 g, 59%), a small amount of Vb and diethylphosphinic acid (0.142 g, 18%) with petroleum ether and ether as eluent, respectively. The IR spectrum of diethylphosphinic acid was superimposable with that of an authentic sample.[20]

Photolysis of IIb in the Presence of AIBN. A mixture of IIb (1.2 g, 5 mmol) and AIBN (5.1 g, 31 mmol) in dichloromethane (100 ml) was irradiated for 10 hr with a low pressure mercury lamp (160 W) under nitrogen. After removal of the solvent and sublimation of tetramethylsuccinodinitrile *in vacuo*, the oily residue containing about ten components was separated by silica gel dry column chromatography (with petroleum ether–acetone (3:2)). The fraction of R_f 0.66 exhibited a peak at *m/e* 189, corresponding to the parent peak of diethyl-1-cyano-1-methylethylphosphine sulfide, and a weak band at 2240 cm^{-1} (C≡N). The fraction was also impure and further purification was difficult.

Photolysis of IIa in Methanol. A solution of IIa (0.54 g, 1.2 mmol) in absolute methanol (80 ml) and dichloromethane (40 ml) was irradiated with a low pressure mercury lamp (10 W) for 5 hr with water-cooling under nitrogen. After removal of the solvent, the residual viscous oil was separated into two components by silica gel dry column chromatography (with chloroform). One component was *O*-methyl diphenylphosphinothioate (0.20 g, 65%) mp 82—84°C (from *n*-hexane) (lit,[24] 84.5—85.5°C), and the other was diphenylphosphine sulfide (0.14 g, 52%), mp 93—95°C (lit,[25] 95—97°C).

Oxidation of Phenyl Diphenylphosphinothioite (X) with Silver Nitrate. To a solution of X (0.81 g, 2.76 mmol) in carbon disulfide (20 ml) was added under nitrogen silver nitrate (0.48 g, 2.8 mmol), the surface of which turned yellow at first and then black. After being stirred at room temperature overnight, a black precipitate containing mainly metallic silver and a small amount of silver diphenylphosphinate (by IR), was filtered off and the filtrate was evaporated. The residue was extracted with ether to leave 0.36 g (60%) of diphenylphosphinic acid, mp 190—191°C. The extract gave 0.26 g (87%) of diphenyl disulfide, mp 58—60°C.

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