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Reaction of P-N Compounds with Alkylating Reagents such as Alkyl Benzenesulfonates and Dialkyl Sulfates[1)]

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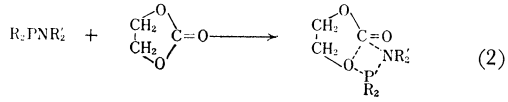
The reaction of *N,N*-dialkyl-diphenylphosphinous amides (I) with alkyl benzenesulfonates (III) or dialkyl sulfates (IV) took place exothermally, giving phosphonium salts (V). When phosphonium salts (V) were heated at 100°C for 5—10 hr, asymmetric phosphine oxide (VI) and *N,N*-dialkyl-benzenesulfonamides (VII) or polymeric materials were obtained. In the case of diphenyl dialkylphosphoramidites (II), no quaternization was observed at room temperature. However, diphenyl alkylphosphonates (VIII) and *N,N*-dialkylbenzenesulfonamides (VII) or the same polymeric materials were obtained through intermediate phosphonium salts when the mixture was heated.

The reaction of P–N compounds with phenyl cyanate[2)] or cyclic carbonate esters[3)] have been studied. In the reaction, the P–N compound behaved as an ambident reagent. When it was treated with an onium ion, the reaction took place at the phosphorus center, as exemplified by the reaction with phenyl cyanate:

$$R_2PNR_2' + PhOCN \rightarrow [R_2P^+(NR_2)(OPh)][CN^-] \rightarrow R_2POPh + R'_2NCN \quad (1)$$

In contrast, when the reaction partners were ester-carbonyl compounds, the P–N compound reacted as the N base and the phosphorus atom would attack ester oxygen or carbonyl oxygen synchronously:



$$\longrightarrow R_2POCH_2CH_2OC(O)NR'_2 \quad (2)$$

In reaction (2), predominancy of the nucleophilic attack of the nitrogen atom to the carbonyl carbon was confirmed by the kinetic study of the reaction of P–N compounds with acetic anhydride.[4)]

The reaction between *N,N*-dialkyl-diphenylphosphinous amide (I) or diphenyl dialkylphosphoramidites (II) and alkyl benzenesulfonates (III) or dialkyl sulfates (IV), which would give phosphonium salts through a reaction similar to (1) are reported in this publication.

Results

A: Reaction of *N,N*-Dimethyl-diphenylphosphinous Amide (Ia) with Alkyl Benzenesulfonates (III) or Dialkyl Sulfates (IV). When Ia was added to equimoler amounts of III or IV at room temperature, an exothermic reaction took place with the formation of stable phosphonium salts (V), as shown in the following equations.

$$Ph_2PNMe_2 + PhSO_2OR''$$

Ia; IIIa: R″=Me, IIIb: R″=Et

$$\longrightarrow [Ph_2P^+(R'')NMe_2][PhSO_2O^-] \quad (3)$$

Va: R″=Me, Vb: R″=Et

$$Ph_2PNMe_2 + SO_2(OR'')_2$$

Ia; IVa: R″=Me, IVb: R″=Et

$$\longrightarrow [Ph_2P^+(R'')NMe_2][(R''O)SO_2O^-] \quad (4)$$

Vc: R″=Me, Vd: R″=Et

These phosphonium salts (Va—Vd) are insoluble to benzene, petroleum ether, dioxane, or carbon tetrachloride, but soluble to chloroform, acetone, or water. IR (KBr disk) and NMR (in $CDCl_3$) spectral data of Vb and Vd are shown in the Table 1.

When the phosphonium salts were heated at 100°C for 5 hr in a sealed tube under an atmosphere of nitrogen, the corresponding asymmetric phosphine oxides (VI) were obtained, along with

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Table 1. IR and NMR spectra of phosphonium salts; Vb and Vd

Compounds	IR spectra ν (cm^{-1})	NMR spectra τ (TMS)
Vb	3060(w), 2980(w), 2940(w), 2910(w), 1585(w), 1480(m), 1438(m), 1352(s), 1220—1180(vs, br), 1118(s), 1165(m), 1033(m), 1019(m), 997(m), 915(w), 755(s), 730(s), 698(s), 611(s), 586(w), 562(s).	8.55—9.10(m); $PCH_2\mathbf{CH_3}$ 6.60—7.45(m); $\mathbf{PCH_2}CH_3$ 7.22(d); J=11 Hz; $PN\mathbf{Me_2}$ 2.30—2.80(m); $P\mathbf{Ph_2}$
Vd	3055(w), 2980(w), 2945(w), 2910(w), 1585(w), 1484(m), 1440(s), 1385(m), 1250—1190(vs, br), 1119(s), 1060(m), 1023(s), 996(m), 915(s), 759(s), 732(s), 698(s), 620(s), 578(s), 564(m).	8.40—9.00(m); $PCH_2\mathbf{CH_3}$ and $\mathbf{CH_3}CH_2OSO_2O$ 6.40—7.30(m); $\mathbf{PCH_2}CH_3$ 5.90(q); J=7Hz; $-\mathbf{CH_2}CH_3$ 2.30—2.80(m); $P\mathbf{Ph_2}$

N,N-dimethylbenzenesulfonamide (VIIa) in the case of two phosphonium salts Va and Vb (Eq. (5)). However, pyrolysis (100°C for 5 hr) products of Vc and Vd were phosphine oxides (VIa and VIb) and polymeric materials which showed a broad ν_{SO_2} band at 1220—1180 cm^{-1}.

$[Ph_2P^+(R'')NMe_2][PhSO_2O^-]$

Va: R″=Me
Vb: R″=Et

$\longrightarrow Ph_2P(O)R'' + PhSO_2NMe_2$ (5)

VIa: R″=Me VIIa
VIb: R″=Et

$[Ph_2P^+(R'')NMe_2][(R''O)SO_2O^-]$

Vc: R″=Me
Vd: R″=Et

$\longrightarrow Ph_2P(O)R''$ + Polymeric materials (6)

VIa: R″=Me
VIb: R″=Et

N,N-dimethylbenzenesulfonamide (VIIa) was identified by comparison of its IR and NMR spectra with those of an authentic sample.

B: Reaction of *N,N*-Diethyl-(Ib) and *N,N*-Di-*n*-propyl-diphenylphosphinous Amide (Ic) with Alkyl Benzenesulfonates (III) and Dialkyl Sulfates (IV). In the same manner as Ia, Ib and Ic reacted with III or IV, affording stable phosphonium salts. The phosphonium salts were subsequently heated to afford the corresponding phosphine oxide (VIa) and *N,N*-dialkylbenzenesulfonamides (VIIb and VIIc) or polymeric materials:

$Ph_2PNR'_2 + PhSO_2OR''$

Ib: R′=Et IIIa: R″=Me
Ic: R′=Pr^n

$\longrightarrow Ph_2P(O)R'' + PhSO_2NR_2'$ (7)

VIa: R″=Me VIIb: R′=Et
VIIc: R′=Pr^n

$Ph_2PNR'_2 + SO_2(OR'')_2 \rightarrow Ph_2P(O)R''$

Ib: R′=Et IVa: R″=Me VIa: R″=Me
+ Polymeric material (8)

C: Reaction of Diphenyl Dialkylphosphoramidites (II) with Alkyl Benzenesulfonates (III) or Dialkyl Sulfates (IV). Diphenyl dialkylphosphoramidite (II) did not react with III or IV at room temperature. However, when a mixture of equimolar amounts of II and III or IV was heated at 100°C under an atmosphere of nitrogen in a sealed tube for about 10 hr, a similar reaction took place with the formation of final deoxygenation products and counter products (probably through unstable phosphonium salts, Eqs. (9) and (10)). The results were supported by the appearance of the IR band characteristic of benzenesulfonamide at 1360 cm^{-1} ($\nu_{SO_2asym.}$) and 1160 cm^{-1} (ν_{SO_2sym}), and also by a sharp singlet at τ (in CCl_4) 7.40 for NMe_2 protons and complex ethyl protons at τ (in CCl_4) 7.9—9.2 for P(O)Et in the NMR spectra. After distillation and subsequent column chromatographic treatments of the reaction mixtures, diphenyl alkylphosphonates (VIII) and *N,N*-dialkylbenzenesulfonamides (VII) or polymeric materials were obtained:

$(PhO)_2PNR'_2 + PhSO_2OR''$

IIa: R′=Me IIIb: R″=Et
IIb: R′=Et IIIa: R″=Me

$\longrightarrow (PhO)_2P(O)R'' + PhSO_2NR'_2$ (9)

VIIIb: R″=Et VIIa: R′=Me
VIIIa: R″=Me VIIb: R′=Et

$(PhO)_2PNR_2' + SO_2(OR'')_2$

IIa: R′=Me IVb: R″=Et
IIb: R′=Et IVa: R″=Me

$\rightarrow (PhO)_2P(O)R''$ + Polymeric materials (10)

VIIIb: R″=Et
VIIIa: R″=Me

The structures of VIIIa and VIIIb were determined by IR and NMR spectra and elemental analyses, and those of VIIa and VIIb by comparison of their IR and NMR spectra with those of authentic samples.

Discussion

In the reaction with electrophilic reagents, the P–N compound exhibited an ambident property. When the reaction partners were typical soft acids such as carbonium ions and PhO^+, the P–N compound behaved as the P base. In this case, *N,N*-dialkyl-diphenylphosphinous amide (I) reacted more readily than diphenyl dialkylphosphoramidite (II). This can be ascribed to the fact that the phosphorus atom of I has higher electron density than II, because II has more electronegative oxygen atoms as substutients on the phosphorus atom. In addition, the phenyl group attached to the phosphorus atom donates an electron to the phosphorus center because of (p–d)π interaction between electrons of phenyl groups and an empty 3d orbital of the phosphorus atom.[5] On the other hand, when reaction partners were hard acids, *i.e.* ester-carbonyl compounds, the reverse reactivity order II>I was observed.[6] In this case the nucleophilic site of P–N compounds is considered as the nitrogen atom, and the phosphorus atom would attack ester or carbonyl oxygen synchronously as seen in Eq. (2). The different reactivity order between I and II (II>I) stems from the different affinity of the phosphorus atom to the oxygen atom. That is, II has more electronegative oxygen atom bonded to the phosphorus atom directly, hence, electron density on the phosphorus atom of II is reduced considerably. This electron attractive effect of oxygen gives large octet expansion ability,[7] *i.e.* an oxygen affinity to the phosphorus atom.

The structures of the phosphonium salts (V) resulting from the reaction between I and III or IV were confirmed by IR and NMR spectra (see Table 1) In the IR spectra, there were absorption bands characteristic of sulfonate ion at 1220—1180 cm^{-1} ($\nu_{SO_2asym.}$), 1120 cm^{-1} ($\nu_{SO_2sym.}$), and 610 cm^{-1} ($\nu_{SO_2-O^-}$). In the NMR spectra, NMe_2 protons showed doublet near τ (in $CDCl_3$) 7.1 (d, J=11 Hz) and PCH_2CH_3 protons showed complex multiplet signals at τ (in $CDCl_3$) 6.6—7.4 (PCH_2-CH_3) and 8.4—9.1 (PCH_2CH_3) as the result of large J_{PCCH} and J_{HCCH}[8]. The results indicate that quaternization occurred at the phosphorus center, being consistent with the results of Trippett[9] and Burg.[10] They suggested that the phosphorus atom has larger nucleophilicity than the nitrogen atom owing to (p–d)π conjugation between the phosphorus atom and the nitrogen atom. II could not be quaternized at room temperature. This phenomenon was already observed in the reaction of II with phenyl cyanate.[2] When the phosphonium salts (V) or the mixture of II with III or IV, were heated at 100°C, not only alkylation reaction of the phosphorus atom but also deoxygenation reaction from the sulfonate group took place, giving phosphine oxide (VI) or phosphonate (VIII). This reaction was assumed to proceed *via* a four centered mechanism as follows.

$$R_2PNR_2' + R'''SO_2(OR'') \rightarrow [R_2P^+(R'')NR_2'][R'''SO_2O^-] \xrightarrow{\text{heat}} \text{(cyclic transition state)} \rightarrow R_2P(O)R'' + R'''SO_2NR_2' \quad (11)$$

The alkylation reactions of phosphorus by alkylbenzenesulfonate and dialkyl sulfate can be applied generally to P–N compounds as well as the alkylation reaction of P–N compounds by the Grignard reagent.[10]

Experimental

General Remarks. IR and NMR spectra were measured on a Nippon Bunko IR 403 G Spectrometer and a Japan Electron Minimer Spectrometer. By using benzene as solvent, thin layer chromatography (TLC) was carried out on 250μ thick WAKO Gel-5G (silica gel) layer. Column chromatography was performed in a column 50 cm long (ratio of column to diameter= 20 : 1). Into the column filled with 40 g of 100 mesh silica gel (Mallinckrodt Chemical Works) was put 1—2 g of the sample by the wet method (solvent benzene) which was then eluted by benzene.

Reagents. *N,N*-Dialkyl-diphenylphosphinous amides (I) and diphenyl dialkylphosphoramidites (II) were prepared by the same method as described previously.[2] Alkyl benzenesulfonates (III) and dialkyl sulfates (IV) were purified by distillation before use.

N,N-Dialkylbenzenesulfonamides (VII) were prepared from benzenesulfonyl chloride and the corresponding amine.

$PhSO_2NMe_2$(VIIa): bp 103—110°C/0.1 mmHg; mp 46—47°C; TLC, R_f=0.30; IR (KBr disk), 1324 (ν_{SO_2asym}), and 1158 cm^{-1} (ν_{SO_2sm}).

$PhSO_2NEt_2$(VIIb): bp 120—121°C/1.0 mmHg; n_D^{23} 1.5361; TLC, R_f=0.23; IR (KBr disk), 1332 (ν_{SO_2asym}), and 1158 cm^{-1} (ν_{SO_2sym}).

$PhSO_2NPr_2^n$(VIIc): bp 154—156°C/2.5 mmHg; n_D^{23} 1.5181; TLC, R_f=0.28; IR (KBr disk), 1338 (ν_{SO_2asym}), and 1170 cm^{-1} (ν_{SO_2sym}).

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Reaction of *N,N*-Dimethyl-diphenylphosphinous Amide (Ia) with Methyl Benzenesulfonate (IIIa). An equimolar mixture of Ia and IIIa reacted exothermally, and the product became turbid and separated into two layers. Further stirring of the product for 5 hr gave a homogeneous and clear solution. This product was heated at 100°C for 5 hr in a sealed tube under a nitrogen atmosphere. When the reaction mixture was distilled, a distillate with boiling point range 104—140°C/mmHg was obtained *viz.*, two spots on TLC at R_f=0.0 and R_f=0.3. From the mixture, 1.17 g (82% yield) of diphenylmethylphosphine oxide (VIa) was separated as crystals from cyclohexane solution, and the filtrate gave 0.81 g (78% yield) of *N,N*-dimethylbenzenesulfonamide (VIIa).

VIa: bp 132—134°C/0.04 mmHg; mp 111.5—112.5°C (lit, 112.5—113°C,[11] 111°C[12]), IR (KBr disk) 1170 cm^{-1} ($\nu_{P=O}$); NMR (in $CDCl_3$) τ 7.79 (d, 3H, J=11Hz, P-CH_3), 2.20 and 1.86 (m, 10H, phenyl). Found: C, 71.99; H, 6.06; P, 14.35%. Calcd for $C_{13}H_{13}PO$: C, 72.22; H, 6.06; P, 14.33%.

VIIa was identified by a comparison of IR and NMR spectra with those of an authentic sample.

Reaction of *N,N*-Diethyl-diphenylphosphinous Amide (Ib) with Methyl Benzenesulfonate (IIIa). When the product from equimolar reaction (6.30 mmol) of Ib and IIIa was heated at 100°C for 5 hr, IVa and VIIb were obtained in 87% and 92% yield, respectively. The structure of VIIb was confirmed by comparison with the corresponding product by a standard procedure.

Reaction of *N,N*-Dimethyl-diphenylphosphinous Amide (Ia) with Ethyl Benzenesulfonate (IIIb). A mixture of 6.19 mmol of Ia and 6.25 mmol of IIIb reacted at room temperature to give the phosphonium salt (Vb) (see Table 1). The subsequent heating of Vb at 100°C for 6 hr in a sealed tube afforded 1.23 g (90% yield) of diphenylethylphosphine oxide (VIb) and 0.82 g (85% yield) of VIIa.

VIb: bp 145—147°C/0.2 mmHg; mp 120—122°C (lit, 124°C,[13] 121°C[12]); IR (KBr disk) 1178 cm^{-1} ($\nu_{P=O}$); NMR (in $CDCl_3$) τ 7.20—7.90 (m, 2H, P**C**H_2-CH_3), 8.45—9.10 (m, 3H, PCH_2**C**H_3), 2.18 and 1.86 (m, 10H, phenyl).

Reaction of *N,N*-Di-*n*-propyl-diphenylphosphinous Amide (Ic) with Methyl Benzenesulfonate (IIIa). From equimolar reaction of Ic and IIIa, 88% yield of VIa and 78% yield of VIIc were obtained.

Reaction of *N,N*-Dimethyl-diphenylphosphinous Amide (Ia) with Diethyl Sulfate (IVb). When 7.95 mmol of Ia was added to IVb (7.90 mmol), phosphonium salt (Vd) was formed exothermally (see Table 1). When Vd was heated in a sealed tube at 100°C for 7 hr, 82% yield of VIb was obtained, which was identified by comparison with the above products. The distillation residue was dark polymeric material, which showed a broad IR absorption band at 1220—1180 cm^{-1} attributable to ν_{SO_2} frequency, and was assumed to be the decomposition product of "$ROSO_2$-NR_2."

Reaction of *N,N*-Diethyl-diphenylphosphinous Amide (Ib) with Dimethyl Sulfate (IVa). In the same manner as in the above experiment, VIa was isolated in 50% yield by the reaction of equimolar mixture of Ib and IVa. The viscous distillation residue had the same IR spectrum as that obtained in the above experiment.

Reaction of Diphenyl Dimethylphosphoramidite (IIa) with Ethyl Benzenesulfonate (IIIb). When IIa was added to an equimolar amount of IIIb, heat evolution could not be observed. Even after standing for one week at room temperature, the IR and NMR spectrum of the mixture showed no change. When the mixture was heated in a sealed tube under a nitrogen atmosphere at 100°C for 10 hr, the mixture turned to yellowish brown. The reaction products showed IR and NMR spectra corresponding to the final alkylation-deoxygenation products as described (see Result). By distillation under reduced pressure, 2.70 g of the distillate with boiling point range 130—150°C/0.03 mmHg was obtained. The distillate gave two reaction products, which were separated on a chromatographic column. Thus, 73% yield of diphenyl ethylphosphonate(VIIIb) and 86% yield of *N,N*-dimethylbenzenesulfonamide (VIIa) were obtained.

VIIIb: bp 113.5—114.0°C/0.03 mmHg; n_D^{23} 1.5540; TLC, R_f=0.14; IR(KBr disk), 1265 cm^{-1} ($\nu_{P=O}$); NMR (in CCl_4), τ 7.80—9.00 (m, 5H, P**C**H_2**C**H_3), 2.85 (s, 10H, phenyl), (Found: P, 11.65% Calcd: P, 11.80%.)

Reaction of Diphenyl Diethylphosphoramidite (IIb) with Methyl Benzenesulfonate (IIIa). When an equimolar mixture of IIb and IIIa was heated at 100°C for 10 hr in a sealed tube under a nitrogen atmosphere, diphenyl methylphosphonate (VIIIa) and VIIb were isolated by distillation and subsequent column chromatography in 87% and 77% yields, respectively.

VIIIa: bp 110—112°C/0.01 mmHg; n_D^{23} 1.5480; TLC, R_f=0.17; IR (KBr), 1264 cm^{-1} ($\nu_{P=O}$); NMR (in CCl_4) τ 8.33 (d, 3H, J=18 Hz, PCH_3), 2.23 (S, 10H phenyl). Found: C, 62.69; H, 5.75; P, 12.20%. Calcd for $C_{13}H_{13}PO_3$: C, 62.91; H, 5.23; P, 12.43%.

Reaction of Diphenyl Dimethylphosphoramidite (IIa) with Diethyl Sulfate (IVb). No reaction took place between equimolar amounts (8.10 mmol) of IIa and IVb at room temperature. However when the mixture was heated at 100°C, VIIIb was isolated in 63% yield by distillation. The distillation residue was 2.0 g of dark polymeric material which showed the same IR spectrum as those of the above experiments.

Reaction of Diphenyl Diethylphosphoramidite (IIb) with Dimethyl Sulfate (IVa). By the same treatment as that mentioned above, VIIIa was obtained in 54% yield from an equimolar mixture (6.50 mmol) of IIb and IVa. In this case too, the counter product was dark polymeric material (1.80 g).

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