

N-PHOSPHORANYLIDENE SULPHENAMIDES

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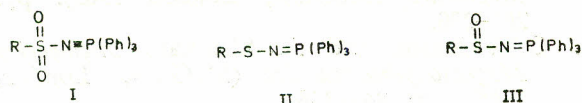
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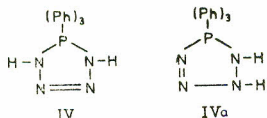
Abstract. *N*-Phosphoranylidene sulphenamides were obtained by the reaction of dibromotriphenylphosphorane with sulphenamides and also by the reaction of hydrazoic acid-triphenylphosphineimine complex with sulphenyl chlorides, where the sulphenyl aromatic residue was substituted with an electro-negative group.

N-Phosphoranylidene sulphenamides on photolysis did not give the expected nitrenes but instead a low yield of disulphides and good yield of triphenylphosphine were obtained.

The reaction of dichlorotriphenylphosphorane with aromatic sulphonamides, and sulphenamides yield *N*-(triphenylphosphoranylidene)-arenesulphonamides (I), *N*-(triphenylphosphoranylidene)-arenesulphenamides (II) respectively.¹⁻³ The sulphenamides have also been reported to give (II) and not *N*-triphenylphosphoranylidene)-arenesulphenamides (III) by the above mentioned reaction.³

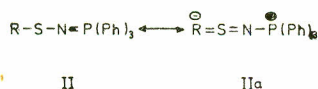


N-Phosphoranylidene sulphenamides (II) have been reported to be obtained by the acylation of triphenylphosphineimide with sulphenyl chloride.⁴ Our studies have shown that (II) can also be obtained by the reaction of dibromotriphenylphosphorane with aromatic sulphenamides which have electronegative substituents. It has also been prepared by the reaction of sulphenyl chloride with hydrazoic acid-triphenylphosphineimine complex (IV). The complex (IV) has a nonionic structure (IV) or (IVa)⁵ and was obtained by the method described by Staudinger and Hauser.⁶



Complex (IV) is more easily accessible than triphenylphosphineimide and gave similar results to that of triphenylphosphineimide which proves this method particularly more convenient when the sulphenamides are not accessible or difficult to get.

The *N*-phosphoranylidene sulphenamides can have nonpolar structure (II) and polar structure (IIa), their existence and colour are certainly determined by electronic equilibrium between the two structures.



In our present work we have concentrated only on the aromatic sulphenamides and have successfully prepared *N*-phosphoranylidene sulphenamides having electronegative group bearing aromatic systems.

Our efforts have been unsuccessful with insufficiently electronegative systems. The general equation of the reaction is as follows:

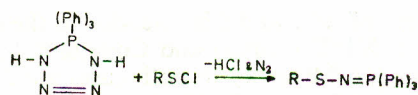
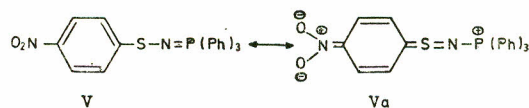


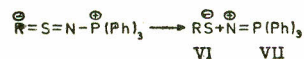
TABLE 1.

R	RSNP (Ph) ₃		RSSR	
	Yield (%)	M.p.(°C)	Yield (%)	M.p.(°C)
4-Nitrophenyl	37	148-151	62	180-181
2-Nitrophenyl	25-30	174-175	40-50	195
2,4-Dinitrophenyl	20	193-195	50	303
Tolyl	—	—	100	45-46
Phenyl	—	—	100	55-56

The results reveal the fact that the presence of an electronegative group on the aromatic residue helps the long conjugated polar structure (IIa) to become stable. This fact is better explained by structures (V) and (Va).

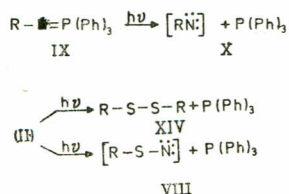


In the case of a less electronegative group (—CH₃) or an unsubstituted phenyl ring the electronic equilibrium between structures (II) and (IIa) takes place whereby the negative charge is born by the phenyl ring. The sulphenyl group as an anion is a good leaving group⁷ and the only product obtained in quantitative yield is disulphide.

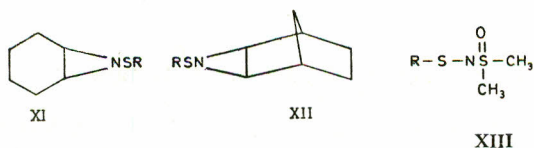


The *N*-phosphoranylidene sulphenamides were synthesised as prospective precursors for the generation of sulphenyl nitrenes (VIII), as phosphoneimines (IX) on photolysis give nitrenes (X).^{8,9} The photolysis of *N*-phosphoranylidene (II) was carried out both in pyrex and in silica apparatus under nitrogen and the temperature was altered in the range

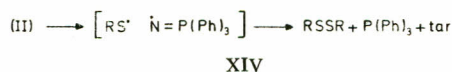
of 25–40°C in the presence of nitrene trapping agents, i.e. dimethyl sulphoxide, cyclohexene and norbornylene.



Products (XI)–(XIII) were not obtained but the corresponding disulphides (XIV) were the products isolated in low yield along with triphenylphosphine in a good yield.



It may be suggested in the light of these results that the break up of the molecule (II) gave rise to sulphenyl radical which could give the corresponding disulphide, and amide radicals which could react with another radical of the same, followed by the loss of nitrogen to give triphenylphosphine. The polymeric tar shows the presence of sulphur which indicates that the sulphenyl radical is involved in the process of polymerization and it also explains the poor yield of disulphide (XIV).



Experimental

N-Phosphoranylidene-2,4-dinitrobenzene sulphenamide. (a) Bromine (2.4 g, 15 mmole) in CCl_4 (15 ml) was added to triphenylphosphine (3.9 g, 15 mmole) in cold CCl_4 (30 ml). Triethylamine (3.0 g, 4.1 ml) was added to the resulting suspension followed by ground 2,4-dinitrobenzene sulphenamide (3.22 g, 15 mmole). The reaction mixture stirred at room temperature for 15 min, refluxed for another $\frac{1}{2}$ hr and filtered. The precipitate washed several times with hot CCl_4 . The solvent was evaporated off and the residue recrystallized from ethanol; *N*-phosphoranylidene-2,4-dinitrobenzene sulphenamide (4.312 g, 60%; m.p. 193–195°; lit. m.p. 193–195°) was obtained as dark red crystalline compound. The IR spectrum fits the structure, and the UV spectrum shows absorption in the visible regions. λ_{max} in alcohol 415 $\text{m}\mu$. ϵ_{max} Ca 12,000.

(b) To a solution (suspension) of hydrazoic acid-triphenylphosphineimine complex (1.28 g, 4 mmole) in a mixture of benzene (60 ml) and dimethylsulphoxide (10 ml), 2,4-dinitrobenzenesulphenyl chloride (1.872 g, 8 mmole) in benzene (30 ml) was added dropwise at 10°C in about 20 min and the reaction mixture was allowed to warm up to the room temperature. The stirring continued for 2 hr, the solvent evaporated and the residue poured into water, precipitate filtered,

dried and chromatographed on a short silica column in benzene. Two fractions were obtained: (i) Yellow band, 2,4-dinitrobenzenedisulphide (0.798 g, 50%; m.p. 303° decomp). (ii) Dark red band gave *N*-phosphoranylidene-2,4-dinitrobenzene sulphenamide (0.773 g, 20%; m.p. 193–195°). The spectral data fits the compound and is similar to the one mentioned in experiment (a).

N-Phosphoranylidene-4-nitrobenzene sulphenamide. (a) Bromine (2.4 g, 15 mmole) in CCl_4 was added to triphenylphosphine (3.9 g, 15 mmole) in cold CCl_4 (30 ml). Triethylamine (3.0 g, 4.1 ml) was added to the resulting suspension, followed by 4-nitrobenzene sulphenamide (2.55 g, 15 mmole), stirred at room temperature for 15 min and refluxed for another $\frac{1}{2}$ hr. Reaction mixture filtered and washed several times with hot CCl_4 . Solvent evaporated and the residue recrystallized from ethanol. *N*-phosphoranylidene 4-nitrobenzene sulphenamide obtained as orange prisms (4.312 g, 95%; m.p. 148–150° lit. m.p. 147–149°) UV spectrum showed λ_{max} in alcohol 402 $\text{m}\mu$. ϵ_{max} 14,700.

(b) Same method as described for *N*-phosphoranylidene-2,4-dinitrobenzene sulphenamide under the heading (b). The product was chromatographed on a short silica column in benzene. Two fractions were obtained: (i) Yellow band gave 2-nitrobenzenedisulphide in 62%; m.p. 180–181°. (ii) Orange band gave *N*-phosphoranylidene-4-nitrobenzene sulphenamide 37%, m.p. 149–151°.

N-Phosphoranylidene-2-nitrobenzene sulphenamide. Similar methods were used for the preparation of the compound as has been described for *N*-phosphoranylidene-4-nitrobenzene sulphenamide under heading (a) and (b). The yields of the two methods are: (a) Dark red prisms of *N*-phosphoranylidene-2-nitrobenzene sulphenamide, m. p. 174–157° (lit. m.p. 174–175), 75% yield.

(b) The chromatography of the reaction mixture gave:

- (i) 2-Nitrobenzenedisulphide, m.p. 195°; 40–50% yield.
- (ii) *N*-Phosphoranylidene-2-nitrobenzene sulphenamide, m.p. 174–175°; 25–30%; UV spectrum shows absorption in the visible region λ_{max} 455 $\text{m}\mu$, ϵ_{max} 50,000

Attempted Preparation of N-Phosphoranyldiene-benzene sulphenamide and N-Phosphoranyldiene-p-toluenesulphenamide

N-Phosphoranyldiene-benzenesulphenamide. To a solution (some suspension) of hydrazoic acid-triphenylphosphineimine complex (2.56 g, 4 mmole) in a mixture of benzene (20 ml) and dimethylsulphoxide (9 ml) benzene sulphenyl chloride (1.52 g, 8 mmole) in benzene (20 ml) was added dropwise at 10°C in ten min. The reaction mixture was allowed to warm up to the room temperature and stirred for 2 hr. The solvent evaporated, the residue poured into water, filtered, the precipitate dried and chromatographed on a short column of silica in benzene. Benzene disulphide was obtained (0.864 g, m.p. 55–56°, 100% yield).

N-Phosphoranyldiene-p-toluene sulphenamide. Similar method as described for *N*-phosphoranyldiene-benzene sulphenamide was used and *p*-toluene disulphide, m.p. 45–46°, was obtained in 100% yield.

Photolysis of N-Phosphoranyldiene-2,4-dinitrobenzene sulphenamide. (a) *N*-Phosphoranyldiene-2,4-dinitrobenzene sulphenamide (0.712 g, 15 mmole) was dissolved in a mixture of methylene chloride (140 ml) and dimethyl sulphoxide (100 ml) and irradiated under nitrogen in pyrex apparatus for 10 hr by 125 W (Mazda mercury lamp). The solvent was evaporated and the crude brown tar was chromatographed on silica column in benzene (200 ml) followed by benzene-ethyl-acetate mixture (1:1). The following fractions were obtained: (i) Triphenylphosphine (0.2196 g; 61% on the basis of the reacted material), m.p. 79–81°. (ii) Starting material, 0.0461 g. (iii) 2,4-dinitrobenzene disulphide (0.0281 g, 11% on the basis of reacted material), m.p. 303 decomp.

(b) When the reaction was carried under the same condition but using silica apparatus, the only product obtained from the brown polymeric tar was triphenylphosphine in about 20% yield.

Similar results were obtained by photolysis of *N*-phosphoranyldiene-2-nitrobenzene sulphenamide and *N*-phosphoranyldiene-4-nitrobenzene-sulphenamide in the presence of dimethylsulphoxide, cyclohexene and norbornylene.

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