246. *The Reactivity of Organophosphorus Compounds. Part XII.*[1] *Nitrosation of Phosphoramidates.*

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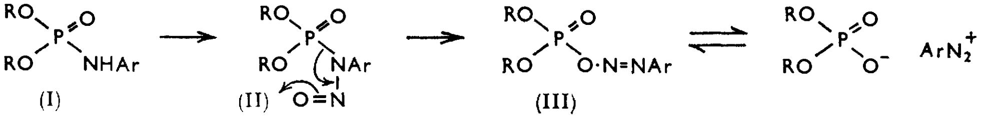
Nitrosation of *N*-arylphosphoramidates by nitrosylsulphuric acid * or nitrosyl chloride leads to the corresponding diazonium phosphate, probably produced by rapid rearrangement of the first formed *N*-nitrosophosphoramidates which were too reactive to be isolated. The resulting diazonium salts undergo the usual reactions, *e.g.*, Sandmeyer type, azo-coupling with phenols, and free-radical aromatic phenylation. Comparisons are made with the rearrangement of the analogous *N*-nitrosoacylarylamines.

Few reactions involving the nitrogen atom of phosphoramidates have been reported. Hydrolysis in acid involves *N*-protonation,[2] and oxidation of *NN*-disubstituted amidates with peracetic acid probably proceeds by way of the corresponding *N*-oxide.[3] *N*-Chloroamidates have been prepared and their reactions under heterolytic and homolytic conditions have been studied.[4] *N*-Nitrosation of phosphoramidates, a reaction not previously reported, is described in the present paper.



(I) (II) (III)

Reaction of diphenyl *N*-phenylphosphoramidate (I; R = Ar = Ph) with nitrosyl chloride or its precursor, nitrosylsulphuric acid, in acetic acid–acetic anhydride in the presence of sodium acetate, followed by treatment with water and removal of unchanged amidate, gave a clear solution which slowly evolved nitrogen and on basification gave 4-hydroxyazobenzene and diphenyl hydrogen phosphate. The reaction is, therefore, assumed to proceed by way of *N*-nitrosation to give diphenyl *N*-nitroso-*N*-phenylphosphoramidate (II; R = Ar = Ph) which very rapidly rearranges to the diazophosphate (III) and thence to the ionic benzenediazonium diphenyl phosphate. Decomposition of the last to phenol followed by coupling with unchanged diazonium cation in alkaline solution then gives 4-hydroxyazobenzene. In accordance with this interpretation, experiments in which aliquot parts of the aqueous reaction mixture were neutralised at fixed intervals indicated that the yields of azo-compound passed through a maximum (12 hr.). A logarithmic plot of undecomposed diazonium salt against time based on this rationalisation showed that decomposition of the benzenediazonium salt under these conditions (pH 5) followed first-order kinetics having $t_{\frac{1}{2}}$ 12·5 hr. Calculations based on Snow's data [5] reveal that benzenediazonium chloride at 20° has $t_{\frac{1}{2}}$ 9·2 hr. Diethyl *N*-phenylphosphoramidate (I; R = Et, Ar = Ph), diphenyl *N*-*p*-tolylphosphoramidate (I; R = Ph, Ar = C_6H_4Me-*p*), and ethyl *NN'*-diphenylphosphorodiamidate behaved similarly. In no case was a compound having the characteristics of a covalent *N*-nitroso-compound isolated, nor could such a compound be isolated when reactions were carried out under anhydrous conditions in benzene; the latter gave a benzene-insoluble solid whose infrared absorption was consistent with the presence of the diazonium cation and which dissolved in water and gave 4-hydroxyazobenzene on subsequent basification. The benzene solution, however, contained material that could not be isolated without decomposition. Such decomposition,

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* The authors are particularly grateful to Dr. Y. Ahmad who suggested the use of this reagent and provided details in advance of publication of his work.

[1] Part XI, Cadogan, *J.*, 1962, 18.

[2] Heath and Casapieri, *Trans. Faraday Soc.*, 1951, **47**, 1093.

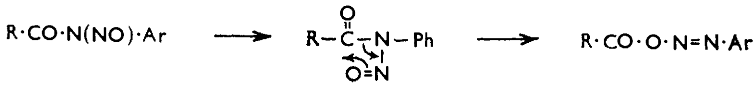
[3] Spencer, *Chem. Soc. Special Publ.*, 1957, **8**, 171.

[4] Cadogan and Foster, *J.*, 1961, 3076.

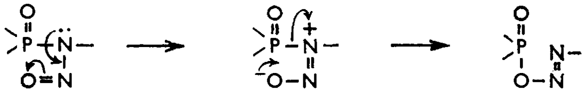
[5] Snow, *Ind. Eng. Chem.*, 1932, **24**, 1420.

which was catalysed by copper powder and led to the evolution of gas and the formation of biphenyl, presumably involved phenyl radicals formed by homolysis of the covalent form of the diazophosphate (III).

The rearrangement of *N*-aryl-*N*-nitrosophosphoramidates to diazonium phosphates is analogous to that of the more stable *N*-nitrosoacylarylamines, *e.g.*, *N*-nitrosoacetanilide (IV; R = Me, Ar = Ph), which can be isolated and are known to rearrange to the corresponding diazonium salts by way of a four-membered intermediate: [6]



The very fast rearrangement of nitrosophosphoramidates, compared with that of nitrosoacylarylamines, is in keeping with the high reactivity of phosphorus compounds towards compounds containing the (=N–O)$^-$ group, *e.g.*, the reactions of oximes with isopropyl methylphosphonofluoridate.[7] Further, in phosphoramidates the probability of finding the lone pair of electrons on the nitrogen is higher than in the corresponding amides,[8] as a result of the lower conjugative effect of P=O; hence the driving force for rearrangement of the nitrosoamide is probably greater in the former case:



That diazonium salts are formed by nitrosation of phosphoramidates is further supported by the result of decomposition. Addition of the aqueous nitrosated mixture from diphenyl *N*-phenylphosphoramidate to aqueous cuprous bromide–hydrogen bromide led to bromobenzene (55%) and diphenyl hydrogen phosphate, formed by a Sandmeyer reaction. Iodobenzene was obtained by the use of potassium iodide. Treatment of the nitrosated mixture with benzene under conditions of the Gomberg reaction gave biphenyl. Decomposition in the presence of pyridine gave excellent yields of a mixture of phenylpyridines of isomeric composition 2- 53%, 3- 36%, and 4- 11%. From consideration of the yields of isomeric phenylpyridines produced by standard methods of free-radical phenylation of pyridine,[9] it is clear that phenylation of pyridine by nitrosated diphenyl *N*-phenylphosphoramidate is also homolytic in nature, and the yields are the highest recorded for this type of preparation (see Table).

Free-radical phenylation of pyridine.

	Phenylpyridines				
Source of Ph·	Yield (mol.)	2- (%)	3- (%)	4- (%)	Ref.
(BzO·)$_2$	0·62	54	32	14	9
Pb(OBz)$_4$	0·42	52	32·5	15·5	9
Ph·I(OBz)$_2$	0·23	58	28	14	9
Ph$_3$C·N:N·Ph	0·40	53	31	16	9
Ph·N(NO)Ac	0·47	46	43	11	9
BzOH, electrolysis	—	56	35	9	10
(PhO)$_2$PO·NHPh + NOCl	0·73	53	36	11	

EXPERIMENTAL

"AnalaR" benzene was dried over sodium, and "AnalaR" pyridine was dried by, and redistilled from, potassium hydroxide. Nitrosylsulphuric acid and nitrosyl chloride were

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[6] Hey, Stuart-Webb, and Williams, *J.*, 1952, 4657.
[7] Green and Saville, *J.*, 1956, 3887.
[8] Cadogan, *J.*, 1957, 1079; Burn, Cadogan, and Moulden, *J.*, 1961, 5542.
[9] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[10] Bunyan and Hey, *J.*, 1960, 3787.

prepared in the normal manner;[11] the former was stored under a guard tube ($CaCl_2$) at 0°, and the latter in 25% acetic anhydride solution at 0° for several months without deterioration.

Preparation of Amidates.—The following amidates were prepared by interaction of the appropriate chloridate and amine in benzene (previous m. p.s are in parentheses): diphenyl *N*-phenylphosphoramidate, m. p. 129—130° (128—129°);[12] diphenyl *N-p*-tolylphosphoramidate, m. p. 135° (134°);[13] *diphenyl* N-o-*tolylphosphoramidate* (15%), m. p. 119—120° (from ethanol) (Found: C, 67·0; H, 5·0. $C_{19}H_{18}NO_3P$ requires C, 67·2; H, 5·3%); *diphenyl* N-o-*ethylphenylphosphoramidate* (60%), prepared in toluene at 105° (110 hr.), and recrystallised from ethanol, rhombs, m. p. 105—106° (Found: C, 68·0; H, 5·9. $C_{20}H_{20}NO_3P$ requires C, 68·0; H, 5·7%); diethyl *N*-phenylphosphoramidate, m. p. 96° (96·5°);[14] ethyl *NN'*-diphenylphosphorodiamidate, m. p. 114·5° (114°).[15]

Nitrosoacetanilide.—Solid nitrosylsulphuric acid (4·6 g.) was added in small portions during 10 min. to a *vigorously* stirred solution of acetanilide (4 g.) and fused potassium acetate (3·2 g.) in acetic acid (28 ml.) and acetic anhydride (12 ml.) at 5°. Stirring was continued for 1 hr., the mixture was poured into ice-cold water, and the yellow precipitate of *N*-nitrosoacetanilide[16] (3·3 g.) filtered off; it had m. p. 49—50° (decomp.) (lit.,[16] 50—51°).

Nitrosation of Diphenyl N-*Phenylphosphoramidate.*—The nitrosation was carried out by solid nitrosylsulphuric acid and by nitrosyl chloride in acetic anhydride with identical results, although the latter failed unaccountably occasionally, probably as a result of the heterogeneous nature of the reaction. The following are typical examples.

(i) Nitrosylsulphuric acid (2·3 g.) was added in small portions in 5 min. to a stirred suspension of diphenyl *N*-phenylphosphoramidate (4·8 g.) and sodium acetate (1·6 g.) in glacial acetic acid (14 ml.) and acetic anhydride (6 ml.) at 0°. Stirring was continued for a further 20 min., and the gel-like mixture was added to ice-cold water (200 ml.). Unchanged amidate (0·6 g.), when filtered off, had m. p. and mixed m. p. 127—129°.

(ii) Nitrosyl chloride (1·25 g.) in acetic anhydride (4 ml.) was substituted for the nitrosylsulphuric acid in (i). The unchanged amidate (1·3 g.) had m. p. and mixed m. p. 120—129°.

The colourless filtrates obtained from such nitrosations were used in the following experiments, unless otherwise stated. Yields are based on amidate consumed.

Decomposition of Nitrosated Diphenyl N-*Phenylphosphoramidate in Aqueous Solution.*—(i) The aqueous filtrate, which slowly evolved nitrogen and darkened, was neutralised with sodium hydrogen carbonate after 24 hr. A yellow precipitate (0·7 g.), dried *in vacuo* over phosphorus pentoxide, had m. p. 120—145°. Recrystallisation from benzene–light petroleum (b. p. 80—100°) yielded 4-hydroxyazobenzene, m. p. and mixed m. p. 156—157°. The aqueous filtrate yielded, on continuous extraction with ether, an impure sample of phenol (0·5 g.) (benzoate, m. p. and mixed m. p. 68—69°) and, after acidification and ether-extraction, an oil (24 ml.) with an odour of acetic acid. Evaporation yielded a sticky solid (2·66 g.), which on treatment with chloroform–light petroleum (b. p. 60—80°) gave diphenyl hydrogen phosphate (needles), m. p. 34—39°, identified by comparison of the infrared spectrum with that of an authentic specimen.

(ii) *In the presence of benzene and alkali.* The filtrate, immediately neutralised with solid sodium hydrogen carbonate and then made alkaline by 2N-sodium hydroxide (50 ml.), was stirred vigorously with benzene (250 ml.) at 5° for 3 hr. and then at room temperature for 45 hr. The benzene layer was separated from the resultant dark brown mixture, washed, and dried ($MgSO_4$). Evaporation yielded a brown gum (0·68 g.) from which biphenyl (0·162 g., 10%), m. p. 59—66°, was sublimed at 50—70°/0·03 mm., and identified by its mixed m. p. and infrared spectrum (Nujol mull). The residue was adsorbed on active alumina and eluted with a variety of solvents; small amounts of highly coloured solids were slowly and continuously eluted, but were not identified.

(iii) *In the presence of pyridine.* Duplicate experiments (A and B) were performed. After nitrosation, the mixture was added to water (100 ml.), unchanged diphenyl *N*-phenylphosphoramidate was filtered off (A 0·6 g.; B 0·9 g.), and the filtrate was added dropwise, with stirring, to pyridine (150 ml.) at 30°. Stirring was continued at room temperature for 48 hr. Working

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[11] Coleman, Lillis, and Goheen, *Inorg. Synth.*, 1939, **1**, 55.
[12] McCombie, Saunders, and Stacey, *J.*, 1945, 380.
[13] Michaelis and Schulze, *Ber.*, 1894, **27**, 2572.
[14] Foster, Overend, and Stacey, *J.*, 1951, 980.
[15] Michaelis, *Annalen*, 1903, **326**, 129.
[16] France, Heilbron, and Hey, *J.*, 1940, **370**.

up of the basic products gave a pale yellow oil which partly solidified (A 1·594 g.; residue 0·227 g. B 1·342 g.; residue 0·277 g.), b. p. 53°/0·01 mm. This oil, initially considered to contain only the isomeric phenylpyridines from consideration of the infrared spectra, exhibited some abnormally high absorption peaks in its ultraviolet spectra. These were removed by dissolving the entire fraction in 4N-hydrochloric acid (100 ml.), boiling under reflux for 5 hr., extracting the mixture with chloroform (4 × 25 ml.), pouring the aqueous acid residue into ice-cold 8N-sodium hydroxide (100 ml.), and recovering the basic mixture of phenylpyridines by chloroform-extraction and distillation (A 1·486 g., 73%; B 1·232 g., 66%), b. p. 140°/13 mm. (Found, from A: C, 84·9; H, 5·9. From B: C, 85·0; H, 5·8. Calc. for $C_{11}H_9N$: C, 85·15; H, 5·8%).

The isomer ratio of the mixture of phenylpyridines in each fraction was determined by ultraviolet spectrophotometry with the aid of a " Unicam S.P.500 " quartz spectrometer as described by Cadogan, Hey, and Williams.[17] The solvent was ethanol. The calibration spectra of each of the pure isomers used in the calculations were those recorded by Stirling [18] for isomers obtained from the pure picrates. The composition of the mixtures thus obtained was 2- 53, 3- 36, 4- 11%, in each case.

Sandmeyer Reactions.—(i) After nitrosation, treatment of the aqueous solution with cuprous bromide in the usual manner gave bromobenzene (50·5%) (identified by its infrared spectrum and refractive index), phenol, m. p. and mixed m. p. 35—40° (18·5%), and diphenyl hydrogen phosphate (isolated as the hydrate, m. p. 48—52°).

(ii) The aqueous solution was added slowly to a stirred solution of potassium iodide (10 g.) in water (15 ml.) at 0°. The initial yellow precipitate was allowed to decompose at room temperature during 20 hr., and the resultant brown liquid steam-distilled, to yield iodobenzene, b. p. 60°/10 mm. (1·347 g., 52%), identified by its refractive index and infrared spectrum. Neither phenol nor diphenyl hydrogen phosphate was isolated.

Nitrosation in Benzene.—(i) Solid nitrosylsulphuric acid (2·9 g.) was added slowly to a stirred solution of diphenyl *N*-phenylphosphoramidate (4·8 g.) in benzene (100 ml.) containing fused sodium acetate (2 g.) at 5°. A white solid separated from the pale yellow solution, and after 1 hr. it was filtered off, washed with dry ether (which afterwards left no residue on evaporation), and dried at 20°/10 mm. over phosphorus pentoxide. The solid (3·53 g.) charred and decomposed at 70—74°, but could be kept for three months at 0° over phosphorus pentoxide without deterioration except for slight coloration. The infrared spectrum (Nujol mull) had a continuous high background absorption, but a slight peak was detectable at 1562 cm.$^{-1}$ which could be due to the diazonium cation.[19] The solid (1·3 g.) was readily soluble in water (50 ml.), yielding a green solution of pH 2, which slowly evolved nitrogen. Neutralisation by sodium hydrogen carbonate after 22 hr. yielded 4-hydroxyazobenzene (0·22 g.), m. p. and mixed m. p. 130—148°.

The benzene filtrate appeared to be stable at room temperature; nitrogen evolution did not occur (48 hr.) until addition of a trace of freshly prepared copper powder, and continued for *ca.* 4 hr. Working up of the resultant red solution gave diphenyl *N*-phenylphosphoramidate (0·54 g.), m. p. 128—131°, and biphenyl (0·04 g.), m. p. 62—68°, identified as above.

When the above experiment was repeated in the absence of sodium acetate, a colourless oil separated and was isolated by decantation. The oil, which decomposed slowly in air, had an infrared spectrum similar to that of the solid above, and it dissolved in sodium acetate solution and afforded 4-hydroxyazobenzene on neutralisation by sodium hydrogen carbonate. Re-acidification of the filtrate and continuous ether-extraction did not yield diphenyl hydrogen phosphate, which suggests that the oil consists mainly of the benzenediazonium salt of an inorganic acid.

(ii) Nitrosyl chloride (1·5 g.) in dry benzene (10 ml.) was added slowly to a stirred solution of diphenyl *N*-phenylphosphoramidate (4·8 g.) in benzene (100 ml.) containing fused sodium acetate (2 g.) at 5°. A white solid separated, which decomposed slowly with the evolution of nitrogen. The mixture was stirred at room temperature for 21 hr., boiled under reflux for a further 3 hr., cooled, and filtered. A small amount of sodium chloride (0·75 g.) was recovered. Standard methods of working up gave acetic acid, diphenyl hydrogen phosphate (2·34 g.), m. p. 43—51°, biphenyl (0·44 g., 28%), m. p. and mixed m. p. 65—68°, and a brown solid

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[17] Cadogan, Hey, and Williams, *J.*, 1954, 794.

[18] Stirling, Ph.D. Thesis, London, 1955; cf. ref. 9.

[19] Le Fèvre, O'Dwyer, and Werner, *Chem. and Ind.*, 1953, 378.

(1·5 g.) that gave some diphenyl *N*-phenylphosphoramidate after several recrystallisations but was considered to be pure for the purpose of calculating the yield of biphenyl.

Nitrosation of Other Amidates.—*Diethyl* N-*phenylphosphoramidate.* This amidate (3·4 g.) was treated with nitrosyl sulphuric acid (2·3 g.) as described for diphenyl *N*-phenylphosphoramidate. The reaction appeared easier, all the suspended solid having dissolved in 20 min. to yield a pale green solution. No unchanged amidate separated when the solution was poured into ice-cold water (75 ml.). The solution (100 ml.) was allowed to decompose, 20-ml. aliquot parts being neutralised at intervals, and the precipitated 4-hydroxyazobenzene, m. p. 130—148°, was filtered off, dried, and weighed. From the results the approximate kinetics showed that the rate of decomposition (to *ca.* 75%) was of the same order as that measured for diphenyl *N*-phenylphosphoramidate.

(ii) *Diphenyl* N-p-*tolylphosphoramidate.* This amidate (5·0 g.) was nitrosated with nitrosylsulphuric acid (2·3 g.) in the normal manner; the solution was poured into water (150 ml.), and unchanged amidate (0·4 g.), m. p. and mixed m. p. 132—135°, was removed. The aqueous liquor was allowed to decompose, and 30-ml. aliquot parts were neutralised as above at intervals from 17 to 160 hr., yielding red precipitates, m. p. 106—112°. Only the quantitative observation that the decomposition was considerably slower than that recorded above could be made. Combination of the precipitates and recrystallisation from benzene–light petroleum (b. p. 60—80°) yielded 2-hydroxy-5,4′-dimethylazobenzene in bright red plates, m. p. 113° (lit.,[20] 113°) (Found: C, 74·6; H, 6·65. Calc. for $C_{14}H_{14}N_2O$: C, 74·3; H, 6·25%).

(iii) *Diphenyl* N-o-*ethylphenylphosphoramidate.* Nitrosation of this amidate (5·2 g.) by nitrosylsulphuric acid or nitrosyl chloride in the normal manner proved both difficult and unreliable, the bulk of the amidate being recovered unchanged in most instances, even after prolonged stirring. Decomposition of the aqueous solution from successful nitrosations appeared to be rapid, but neutralisation did not precipitate an azo-coupled product.

An attempt to perform the Sandmeyer reaction by addition of the solution to cuprous bromide (2·5 g.) in hydrobromic acid (25 ml.), as described above, produced no intermediate complex, and working up yielded a colourless liquid (0·80 g.), b. p. 68°/9 mm., n_D^{25} 1·5400 (Found: C, 60·2; H, 6·2%), and a yellow oil (0·30 g.), b. p. 54°/0·01 mm. (Found: C, 56·7; H, 6·3; Br, 28·5%). Neither fraction had the properties of 1-bromo-2-ethylbenzene,[21] and they were not identified.

(iv) *Ethyl* N,N′-*diphenylphosphorodiamidate.* Nitrosation of the diamidate (2·05 g.) occurred readily and completely on addition of nitrosylsulphuric acid (2·3 g.) in the normal manner; a green solution resulted on addition of water (100 ml.). Decomposition occurred with the deposition of a brown tar, and neutralisation of 20-ml. aliquot parts as above at intervals from 19 to 44 hr. yielded very impure precipitates of 4-hydroxyazobenzene. No decomposition rate could be obtained from the weights of these precipitates.

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[20] Hodgson and Marsden, *J.*, 1943, 379.
[21] Dreisbach and Martin, *Ind. Eng. Chem.*, 1949, **41**, 2875.