7. *The Reactivity of Organophosphorus Compounds. Part XIV.*[1] *Deoxygenation of Aromatic C-Nitroso-compounds by Triethyl Phosphite and Triphenylphosphine: a New Cyclisation Reaction.*

By P. J. BUNYAN and J. I. G. CADOGAN.

Triethyl phosphite and triphenylphosphine readily deoxygenate aromatic *C*-nitroso-compounds. Thus, nitrosobenzene and *o*-ethylnitrosobenzene give the corresponding azoxybenzenes; *p*-dimethylaminonitrosobenzene gives 4,4′-bisdimethylaminoazoxybenzene and triethyl *N*-*p*-dimethylaminophenylphosphorimidate; 2-nitrosobiphenyl and related compounds undergo ring closure to the corresponding carbazoles. These reactions are considered to proceed by way of electron-deficient nitrogen intermediates (azenes).

THERMAL or photo-induced decompositions of aryl azides which involve intramolecular cyclisation with an adjacent aromatic ring are well known,[2] Smith and Brown [2a] having

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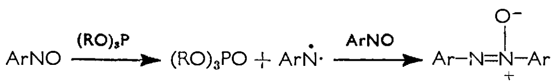
[1] Part XIII, Bunyan and Cadogan, *J.*, 1962, 2593.

[2] (*a*) Smith and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2435; (*b*) Smith and Boyer, *ibid.*, p. 2626; Smith, Brown, Putney, and Reinisch, *ibid.*, 1935, **75**, 6335; Smith, Clegg, and Hall, *J. Org. Chem.*, 1958, **23**, 524.

shown, for example, that 2-azidobiphenyl can be converted into carbazole in this way. Smolinsky [3] interpreted these reactions by assuming the formation of discrete azene (electron-deficient nitrogen) intermediates which were assumed to exist in the diradical form rather than as electrophiles having paired electrons. This interpretation has recently been supported by Walker and Waters.[4] Azenes have also been invoked as intermediates

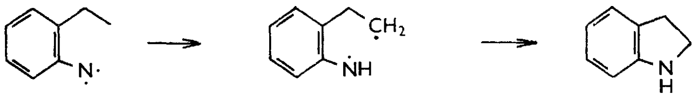
in the conversion, under the influence of ferrous oxalate, of 2-nitrobiphenyl into carbazole,[5] and in cyclisations effected by photolysis of aliphatic azides.[6] In view of the ease with which both organic and inorganic tervalent phosphorus compounds enter into deoxygenation reactions,[7] it seemed reasonable to expect that such reduction of *C*-nitroso-compounds might lead to the corresponding azenes. The experimental realisation of this is described in this paper.

Few reactions of *C*-nitroso-derivatives with tervalent phosphorus compounds have been previously recorded. Horner and Hoffmann [8] stated, in a reference to unpublished work, that substituted nitrosobenzenes, but not nitrosobenzene itself, reacted with triphenylphosphine to give the corresponding azoxybenzenes. It has now been shown that reaction of equimolar quantities of nitrosobenzene and triphenylphosphine in a solvent also gives azoxybenzene, in low yield, together with higher yields of triphenylphosphine oxide. A more satisfactory conversion of nitroso- into azoxy-benzene was achieved by the use of a one molar excess of nitrosobenzene over triethyl phosphite, but in this case an unidentified high-melting amorphous solid was also formed. *o*-Ethylnitrosobenzene similarly gave the corresponding azoxy-compound, identified by conversion into 2,2′-diethylhydrazobenzene. These observations can be explained by invoking attack of the tervalent phosphorus compounds on the oxygen of the nitroso-group with the formation of an azene which then combines with an unchanged nitroso-group:



$$\mathrm{ArNO}\xrightarrow{(\mathrm{RO})_3\mathrm{P}}(\mathrm{RO})_3\mathrm{PO}+\mathrm{Ar\dot{N}}\cdot\xrightarrow{\mathrm{ArNO}}\mathrm{Ar{-}N{=}}\underset{+}{\overset{\overset{\mathrm{O}^-}{|}}{\mathrm{N}}}\mathrm{{-}Ar}$$

By comparison with reactions [3] of related azides, however, the azene derived from *o*-ethylnitrosobenzene might be expected to rearrange to give dihydroindole:



That this did not occur to an observable extent even under conditions designed to minimise formation of the azoxy-compound is attributed at least in part to the preferred reaction of the azene with unchanged nitroso-compound.

In an attempt to produce a more stable azene intermediate, and thus reduce the possibility of reaction with unchanged nitroso-compound, the reaction of triethyl phosphite with *NN*-dimethyl-*p*-nitrosoaniline was investigated. The fundamental alteration in the properties of this nitroso-compound induced by the dimethylamino-group [9] can be

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[3] Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4717; 1961, **83**, 2489; *J. Org. Chem.*, 1961, **26**, 4108.

[4] Walker and Waters, *J.*, 1962, 1632.

[5] Abramovitch, Ahmad, and Newman, *Tetrahedron Letters*, 1961, 752.

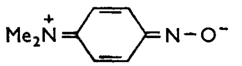
[6] Barton and Morgan, *J.*, 1962, 622.

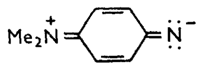
[7] Cadogan, *Quart. Rev.*, 1962, **16**, 208.

[8] Horner and Hoffmann, *Angew. Chem.*, 1956, **68**, 473.

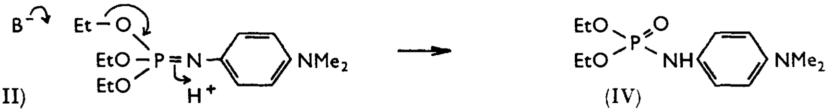
[9] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.

attributed to the contribution of the quinonoid structure (I) to the resonance hybrid. Thus reaction with triethyl phosphite would be expected to be slow, and the azene, if


(I)


(II)

formed, would be stabilised as a result of contributions of the form (II).[10] In accord with this, deoxygenation of *p*-dimethylaminonitrosobenzene (1 mol.) with triethyl phosphite (1 mol.) in benzene slowly gave 4,4′-bisdimethylaminoazoxybenzene (63·5%) and a compound formulated as triethyl *N*-*p*-dimethylaminophenylphosphorimidate (III) (13%) which was isolated, after hydrolysis during separation on alumina, as diethyl *N*-*p*-dimethylaminophenylphosphoramidate (IV). A similar hydrolysis on alumina of triphenyl *N*-toluene-*p*-sulphonylphosphorimidate has previously been reported.[11] The use of a molar excess of triethyl phosphite gave a lower yield of the azoxy-compound (50%) with a correspondingly higher yield of the phosphoramidate (IV) (25%). Reaction of a ten-molar excess of phosphite in the absence of solvent gave the azoxy-compound (23%), the phosphorimidate (58·5%), and diethyl *N*-*p*-dimethylaminophenylphosphoramidate (IV) (5%; presumably formed by fortuitous hydrolysis during working-up). These results suggest the participation of azenes which react with triethyl phosphite to give the phosphorimidate (III) as well as with unchanged nitroso-compound to give 4,4′-bisdimethylaminoazoxybenzene. The absence of 4,4′-bisdimethylaminoazobenzene indicates that dimerisation of *p*-dimethylaminophenylazene did not occur. Horner and Hoffmann,[8] in a reference to unpublished work, state that triphenylphosphine and *p*-dimethylaminonitrosobenzene give only the corresponding azoxy-compound.

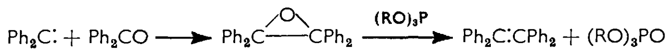

(III) (IV)

The reaction of *p*-dimethylaminophenylazene with triethyl phosphite is analogous to those of carbenes with triphenylphosphine, which give the corresponding methylenephosphoranes (V):[12]

$$X_2C\colon + Ph_3P \longrightarrow Ph_3P\colon CX_2 \quad (V)$$

A further parallel is that tri-isopropyl phosphite deoxygenates benzophenone to give ultimately tetraphenylethylene.[13] The suggested mechanism is:

$$(RO)_3P + Ph_2CO \longrightarrow (RO)_3PO + Ph_2C\colon \xrightarrow{Ph_2C\colon} Ph_2C\colon CPh_2$$



$$Ph_2C\colon + Ph_2CO \longrightarrow Ph_2C\overset{O}{\text{——}}CPh_2 \xrightarrow{(RO)_3P} Ph_2C\colon CPh_2 + (RO)_3PO$$

However, since tetraphenylethylene oxide, which is analogous to azoxybenzene isolated from reactions with nitrosobenzene, is not isolated, intermediate formation of a methylenephosphorane, followed by a Wittig-type reaction with benzophenone, cannot be excluded:

$$(RO)_3P + Ph_2C\colon \longrightarrow (RO)_3P\colon CPh_2 \xrightarrow{Ph_2CO} (RO)_3PO + Ph_2C\colon CPh_2$$

It is noteworthy that whereas Schönberg and Brosowski[14] have extended the Wittig reaction by the use of nitrosobenzene instead of a carbonyl compound [reaction (i)],

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[10] Cf. Smith and Hall, *J. Amer. Chem. Soc.*, 1962, **84**, 480.

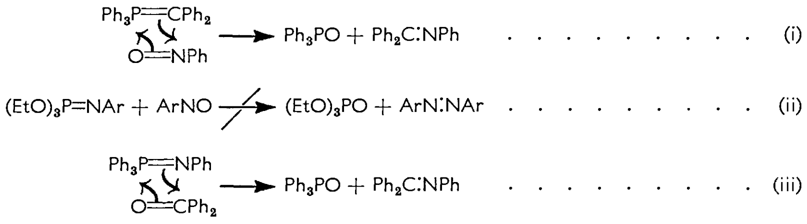
[11] Cadogan and Moulden, *J.*, 1961, 3079.

[12] Seyferth, Grim, and Read, *J. Amer. Chem. Soc.*, 1960, **82**, 1510.

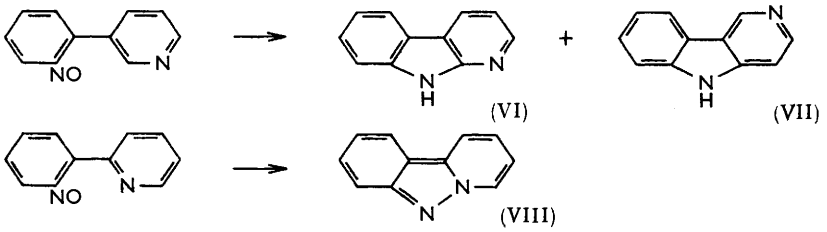
[13] Poshkus and Herweh, Amer. Chem. Soc. 141st Meeting, 1962, Abs., p. 17-O.

[14] Schönberg and Brosowski, *Chem. Ber.*, 1959, **92**, 2602.

attempts to effect a similar reaction between the analogous triethyl *N*-*p*-dimethylaminophenylphosphorimidate (III) and *p*-dimethylaminonitrosobenzene to give 4,4′-bisdimethylaminoazobenzene, were not successful [reaction (ii)]. The analogous reaction between triphenyl *N*-phenylphosphorimidate and benzophenone, on the other hand, gives triphenylphosphine oxide and the corresponding anil [reaction (iii)].[15]



The reduction, by triethyl phosphite or triphenylphosphine, of 2-nitrosobiphenyl and its 2′-chloro- and 4′-bromo-derivatives to the corresponding carbazoles is considered to be further evidence of the mediation of azenes in the deoxygenation. Addition of a benzene solution of triethyl phosphite to an equivalent of 2-nitrosobiphenyl in benzene at 0—5° led within a few minutes to carbazole (76%) and triethyl phosphate (84%). Similarly 3-*o*-nitrosophenylpyridine gave a mixture (64%) of α- (81·5%) (VI) and γ-carboline (18·5%) (VII), and 2-*o*-nitrosophenylpyridine gave an almost quantitative yield of pyrid[1,2-*b*]indazole (VIII). δ-Carboline was not detected.



The latter observation is in accord with the concept of an electron-deficient intermediate, possibly in the singlet (electrophilic) state, which would react preferentially at the electron-rich ring-nitrogen atom. Further, pyrid[1,2-*b*]indazole has been isolated on reaction of ferrous oxalate with 2-*o*-nitrophenylpyridine,[5,16] and a mixture of α- and γ-carboline of composition similar to that obtained by us has been isolated on decomposition of 3-*o*-azidophenylpyridine.[2b] Both these reactions are considered to proceed by way of azene intermediates.

The reduction of 2-nitrosobiphenyl to carbazole was investigated under various conditions. Triethyl phosphite and triphenylphosphine reacted readily in benzene or, more slowly, in ether. Phosphorus trichloride however, did not give carbazole, which is in accord with the higher electrophilicity of the phosphorus atom in this case. It is noteworthy that reduction of pyridine *N*-oxides by tervalent phosphorus compounds, which involves electrophilic attack of phosphorus on oxygen, proceeds more readily with phosphorus trichloride than with triethyl phosphite or triphenylphosphine.[7]

After completion of our experiments,* Boyer and Ellzey reported [17] the reduction of

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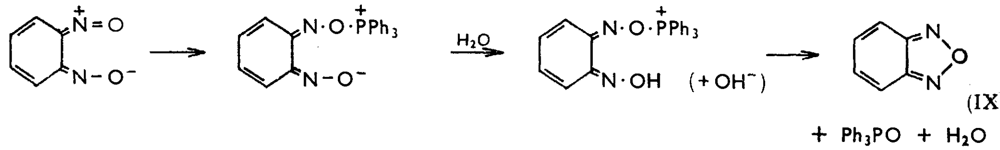
* For a preliminary account see Bunyan and Cadogan, *Proc. Chem. Soc.*, 1962, 78.

[15] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.
[16] Abramovitch and Adams, *Canad. J. Chem.*, 1961, **39**, 2516.
[17] Boyer and Ellzey, *J. Org. Chem.*, 1961, **26**, 4684.

o-dinitrosobenzene to benzofurazan (IX) by triphenylphosphine, and considered that the reaction involved intervention of water as follows:



(IX)

In view of our results it is tempting to regard this reduction as another example of azene participation:

Since the production of azenes by phosphite reduction of nitroso-compounds is so readily achieved, an attempt to investigate the electronic state of the azene-nitrogen atom by an examination of its electron-spin resonance has been made by Dr. G. Wilkinson and Mr. Allen of the Physics Department of this College. The only signal which could be detected, however, was attributed to the nitroso-compound.

EXPERIMENTAL

Preparations.—4-Bromo-2′-nitrobiphenyl, m. p. 65°, was prepared as described by Hey, Shih, and Williams,[18] who reported the same m. p. 2-Chloro-2′-nitrobiphenyl, m. p. 69·5—70·5°, was kindly provided by Professor D. H. Hey, F.R.S. *o*-Nitrophenylation of pyridine by Haworth, Heilbron, and Hey's method [19] gave 2-, m. p. 58° (picrate, m. p. 152°), and 3-*o*-nitrophenylpyridine, b. p. 170°/0·05 mm., m. p. 25° (picrate, m. p. 188°). Haworth *et al.* reported the same constants for the 2-isomer, and described the 3-isomer as an oil (picrate, m. p. 182°). α-Carboline and pyrid[1,2-*b*]indazole were kindly provided by Dr. R. A. Abramovitch, and γ-carboline by Dr. T. M. Moynehan. Triethyl phosphite, redistilled under nitrogen, had b. p. 57°/13 mm., n_D^{25} 1·4100. Triphenylphosphine had m. p. 79—80° after recrystallisation from ethanol–ether. Benzene and ether were dried over sodium and saturated with nitrogen before use.

o-Ethylnitrosobenzene, m. p. 60—61°, was prepared as described by Lutz and Lytton,[20] who reported m. p. 61°. Nitrosobenzene had m. p. 67—68°, and *NN*-dimethyl-*p*-nitrosoaniline had m. p. 86°. 2-Nitrosobiphenyl, m. p. 101°, was prepared by the method of Mijs *et al.*[21] who reported m. p. 101° (Found: C, 78·95; H, 5·1. Calc. for $C_{12}H_9NO$: C, 78·7; H, 4·9%).

3-o-*Nitrosophenylpyridine.*—Powdered zinc (3 g.) was added during 30 min. to a boiling solution of 3-*o*-nitrophenylpyridine (4·0 g.) and ammonium chloride (0·3 g.) in ethanol (15 ml.), water (2 ml.), and 2-methoxyethanol (7 ml.). The suspension was filtered, and the residue washed with hot ethanol. 10% Aqueous chromium trioxide (25 ml.) was then added during 15 min. to the stirred filtrate at 0°. After basification with sodium carbonate (3 g.), the mixture was exhaustively extracted with ether, and the extracts were washed and dried ($MgSO_4$). Removal of the solvent at <35°, since higher temperatures led to decomposition, left a brown oil, which after addition of methanol (10 ml.) slowly deposited a yellow solid at 0°. The solid was recrystallised from methanol and dried *in vacuo* over calcium chloride to give colourless 3-o-*nitrosophenylpyridine* (1·3 g., 35%), m. p. 97—98° (green liquid) (Found: C, 71·9; H, 4·6; N, 14·9. $C_{11}H_8N_2O$ requires C, 71·8; H, 4·4; N, 15·2%).

2-o-*Nitrosophenylpyridine* was similarly prepared in 18% yield from the corresponding nitro-compound, 50% of which was recovered from the methanolic mother-liquor. It was a buff solid, m. p. 142—143° (transient green liquid), after recrystallisation from methanol (Found: C, 71·5; H, 4·75; N, 15·1%).

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[18] Hey, Shih, and Williams, *J.*, 1958, 1885.

[19] Haworth, Heilbron, and Hey, *J.*, 1940, 349.

[20] Lutz and Lytton, *J. Org. Chem.*, 1937, **2**, 68.

[21] Mijs, Hoekstra, Ulmann, and Havinga, *Rec. Trav. chim.*, 1958, **77**, 746.

Diethyl N-p-*Dimethylaminophenylphosphoramidate*.—*NN*-Dimethyl-*p*-phenylenediamine (4 g.), obtained by the reduction of *NN*-dimethyl-*p*-nitrosoaniline with tin and hydrochloric acid, was allowed to react with bromotrichloromethane (12 g.) and diethyl phosphite (4 g.). When the vigorous reaction had subsided the mixture was extracted with 2N-hydrochloric acid (50 ml.), the extract basified, and the product isolated by extraction with ether. Recrystallisation from benzene–light petroleum [b. p. 40—60°] gave diethyl *N*-*p*-dimethylaminophenylphosphoramidate as pale yellow plates, m. p. 96° (lit.,[22] 94°) (Found: C, 52·9; H, 8·1; N, 10·4. Calc. for $C_{12}H_{21}N_2O_3P$: C, 52·9; H, 7·8; N, 10·3%).

4,4′-*Bisdimethylaminoazobenzene*.—*NN*-Dimethyl-*p*-phenylenediamine was diazotised and coupled with *NN*-dimethylaniline, to give 4,4′-bisdimethylaminoazobenzene, which when purified by chromatography on alumina, had m. p. 271—273° (lit.,[23] 262—265°) (Found: C, 71·4; H, 7·6; N, 20·9. Calc. for $C_{16}H_{20}N_4$: C, 71·6; H, 7·5; N, 20·9%).

Reactions of Nitrosobenzene.—(i) *With triethyl phosphite*. Triethyl phosphite (0·83 g., 0·005 mole) in benzene (10 ml.) was added during 15 min. to nitrosobenzene (1·08 g., 0·01 mole) in benzene (15 ml.) under nitrogen at 0°. After 3 hr. the green solution had become brown. After 18 hr. the solvent was removed and the residue was chromatographed on alumina (10″ × 1″). Elution with 1 : 1 benzene–light petroleum (b. p. 60—80°) gave azoxybenzene (0·214 g., 21·4%), m. p. and mixed m. p. 30—36° (correct infrared spectrum). Elution with 1 : 1 benzene–chloroform gave triethyl phosphate (0·462 g., 51%), b. p. 38°/0·03 mm., n_D^{25} 1·4050 (correct infrared spectrum). Elution with ethanol gave an intractable glass. Azoxybenzene did not react with triethyl phosphite under the above conditions.

Similar reactions, carried out by addition of nitrosobenzene (0·01 mole) to triethyl phosphite (0·01 mole) in benzene or in ether, gave triethyl phosphate (77—82%), b. p. 99°/14 mm. (correct infrared spectrum), and a brown amorphous ether-insoluble solid (0·20 g.), m. p. >360°, which was precipitated from the benzene solution by addition of ether. The solid did not contain phosphorus (Found: C, 64·8; H, 5·9%). Azoxybenzene was not isolated.

(ii) *With triphenylphosphine*. Nitrosobenzene (1·08 g., 0·01 mole) in benzene (14 ml.) was added during 10 min. to triphenylphosphine (2·62 g.; 0·01 mole) in benzene (14 ml.) under nitrogen at room temperature. The reaction was exothermic. After 2 hr. a brown solid was precipitated and the mixture was then heated at 80° for 2 hr. The solid (0·30 g.; m. p. 180—220°) was collected, the filtrate was evaporated, and the residue was chromatographed on alumina. Elution with 1 : 3 benzene–light petroleum (b. p. 60—80°) gave triphenylphosphine (0·415 g.), m. p. and mixed m. p. 77—79°. Elution with benzene gave azoxybenzene (0·07 g.), m. p. and mixed m. p. 32—36° (infrared spectrum). Elution with 1 : 1 benzene–chloroform gave triphenylphosphine oxide (1·18 g.; 42·5%), m. p. and mixed m. p. 147—157°.

Reaction of o-*Ethylnitrosobenzene with Triethyl Phosphite*.—*o*-Ethylnitrosobenzene (1·35 g., 0·01 mole) in benzene (15 ml.) was added during 15 min. to triethyl phosphite (1·66 g., 0·01 mole) in benzene (20 ml.) under nitrogen at 0°. The green solution became brown. After 1 hr. the solvent was removed and the residue was subjected to chromatography on alumina (10″ × 1″). Elution with 1 : 1 benzene–light petroleum (b. p. 60—80°) yielded a red oil (0·686 g.) which was further separated, by acid-extraction from an ether solution, into a neutral fraction (0·60 g.) and an unidentified basic fraction (0·085 g.). The neutral fraction was identified as 2,2′-diethylazoxybenzene (47%), by comparison of the infrared spectrum with that of azoxybenzene, and by quantitative reduction with zinc in sodium hydroxide to 2,2′-diethylhydrazobenzene which recrystallised from aqueous ethanol in needles, m. p. 109—110° (lit.,[24] 103—104°) (Found: C, 79·5; H, 8·2. Calc. for $C_{16}H_{20}N_2$: C, 79·9; H, 8·4%). Elution with 1 : 1 benzene–chloroform gave triethyl phosphate (1·056 g., 58%), n_D^{25} 1·4050.

In a similar reaction carried out in dilute ether (200 ml.) solution to facilitate a possible intramolecular reaction, the mixture had to be boiled under reflux for 3 hr. to obtain the desired colour change. 2,2′-Diethylazoxybenzene (57·5%) and triethyl phosphate (63%) were the only products isolated.

Reactions of NN-*Dimethyl*-p-*nitrosoaniline with Triethyl Phosphite*.—(i) *In solution*. The base (1·5 g., 0·01 mole) and triethyl phosphite (1·66 g., 0·01 mole) were boiled under reflux in benzene (30 ml.) under nitrogen, until the colour was deep red (3 hr.). Red crystals (0·90 g., 63·5%) which were deposited on storage, were filtered off and had m. p. 255—260°.

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[22] Cook, Ilett, Saunders, Stacey, Watson, Wilding, and Woodcock, *J.*, 1949, 2921.
[23] Noelting, *Ber.*, 1885, **18**, 1143.
[24] Smith, Schwartz, and Wheland, *J. Amer. Chem. Soc.*, 1952, **74**, 2282.

Chromatography on alumina and elution with 9 : 1 benzene–chloroform did not reveal any impurity, and recrystallisation from benzene yielded 4,4′-bisdimethylaminoazoxybenzene as dark red needles, m. p. 257—259° (Found: C, 67·2; H, 7·4; N, 19·8%; *M*, 294. Calc. for $C_{16}H_{20}N_4O$: C, 67·5; H, 7·1; N, 19·7%; *M*, 284). This m. p. was not depressed on admixture with 4,4′-bisdimethylaminoazobenzene, but the infrared spectra (Nujol mull) had an extra peak at 815 cm.$^{-1}$ (azoxy N–O).

The filtrate was also chromatographed on alumina. Elution with benzene, and various mixtures of benzene and chloroform, yielded a number of highly coloured liquid fractions (total wt. 0·91 g.) which had an odour of triethyl phosphate and were not characterised. Elution with ethanol yielded a brown metallic salt, which was insoluble in most common organic solvents. It was dissolved in 2N-hydrochloric acid to yield a pink solution, which was neutralised by sodium hydrogen carbonate, and the resulting mixture was extracted with ether. Evaporation of the extracts, followed by recrystallisation from light petroleum [b. p. 40—60°] (charcoal), gave diethyl *N-p*-dimethylaminophenylphosphoramidate (0·35 g., 13%) in plates, m. p. and mixed m. p. 96°. A purple band left at the head of the column was not eluted by ethanol.

In a parallel experiment with one molar excess of triethyl phosphite (3·28 g.), 4,4′-bisdimethylaminoazoxybenzene (0·71 g., 50%) was filtered from the reaction mixture, and highly coloured liquid fractions (total 2·2 g.) with an odour of triethyl phosphite, and diethyl *N-p*-dimethylaminophenylphosphoramidate (0·67 g., 24·6%) were obtained from the filtrate by chromatography on alumina.

(ii) *In the absence of solvent.* *NN*-Dimethyl-*p*-nitrosoaniline (2·5 g.) and triethyl phosphite (27·5 g.) were heated on a boiling water-bath for 1 hr. under a calcium chloride guard tube. The red solution was allowed to cool overnight, and 4,4′-bisdimethylaminoazoxybenzene (0·54 g., 22·8%), m. p. 252—260°, was filtered off. After removal of the excess of triethyl phosphite by distillation, triethyl phosphate (3·5 g.), b. p. 38°/0·03 mm., n_D^{25} 1·4050, was obtained, followed by a red liquid (2·92 g.), b. p. 122—123°/0·03 mm. The colour became deeper with time; when the material was then fractionated, the large golden-yellow middle fraction was stable and was identified as *triethyl* N-p-*dimethylaminophenylphosphorimidate* (58·5%) (Found: C, 56·2; H, 8·7; N, 9·5. $C_{14}H_{25}N_2O_3P$ requires C, 56·1; H, 8·4; N, 9·3%). The infrared spectrum was consistent with this structure [1163, 1030, 965 cm.$^{-1}$ (P·OEt); 1375, 1350, 1319 cm.$^{-1}$ (P=N)]. The residue from the distillation (0·71 g.) was extracted with light petroleum (b. p. 40—60°) and, after treatment with charcoal, yielded diethyl *N-p*-dimethylaminophenylphosphoramidate (0·25 g., 5·5%) as pale yellow plates, m. p. and mixed m. p. 94—96°.

Reactions of Triethyl N-p-*Dimethylaminophenylphosphorimidate.*—(i) Triethyl *N-p*-dimethylaminophenylphosphorimidate (0·24 g.) was washed on to an alumina column (10″ × 1″) packed in light petroleum (b. p. 60—80°), and set aside for 3 days. A purple colour developed. Elution of the column with benzene, and chloroform–benzene yielded nothing, but alcohol (200 ml.) yielded a pale brown solid which, on treatment as previously described, afforded diethyl *N-p*-dimethylaminophenylphosphoramidate (1·5 g., 69%). The purple colour remained at the head of the column.

(ii) Triethyl *N-p*-dimethylaminophenylphosphorimidate (0·5 g.) and *NN*-dimethyl-*p*-nitrosoaniline (0·25 g.) were boiled under reflux in benzene for 3 hr. The green colour was not discharged. Chromatography on alumina and elution with 9 : 1 benzene–chloroform yielded a small amount of an unidentified red solid (0·03 g.). Further elution with benzene–chloroform afforded only the starting materials.

Reactions of 2-Nitrosobiphenyl.—(i) *With triethyl phosphite.* Triethyl phosphite (1·26 g., 0·0075 mole) in benzene (10 ml.) was added during 5 min. to 2-nitrosobiphenyl (1·38 g., 0·0075 mole) in benzene (20 ml.) at 0° under nitrogen; during this time the colour of the solution changed from green through yellow to brown. After a further 5 min. the mixture was allowed to attain room temperature, carbazole (0·45 g.), m. p. and mixed m. p. 244—246°, being precipitated. Evaporation of the mother-liquors gave more carbazole (0·25 g.; total 75·5%). Distillation of the residue gave triethyl phosphate (1·12 g., 83·5%), b. p. 38°/0·05 mm., n_D^{25} 1·4040 (correct infrared spectrum). Yields of both products were depressed by 10% when the addition was carried out in the reverse order.

The corresponding reaction in ether was much slower, possibly because of the insolubility of 2-nitrosobiphenyl, colour changes occurring after 20 min. at the b. p. Carbazole (82%),

m. p. and mixed m. p. 248—249°, and triethyl phosphate (88%), n_D^{25} 1·4040 (correct infrared spectrum), were obtained as described above.

(ii) *With triphenylphosphine.* Triphenylphosphine (1·31 g., 0·005 mole) in benzene (8 ml.) was added during 5 min. to 2-nitrosobiphenyl (0·92 g., 0·005 mole) in benzene (8 ml.) at 0°. After a further 5 min. the mixture was allowed to attain room temperature. Carbazole (0·157 g.), mixed m. p. 247—249°, which separated was collected and the red filtrate evaporated. The residue was chromatographed on alumina; elution with light petroleum (b. p. 60—80°) gave triphenylphosphine (0·10 g.), mixed m. p. 67—75°; 1 : 1 benzene–light petroleum gave an orange solid (0·53 g.), m. p. 110—245°, from which carbazole (0·425 g.) sublimed at 200°/0·03 mm. The total yield of carbazole was 69%. The residue from sublimation, which yielded a small quantity of tan needles, m. p. 150—170° (from acetone), was not identified. Further elution with benzene gave triphenylphosphine oxide (1·265 g., 91%), m. p. 155—157°, undepressed on admixture with an authentic specimen after one crystallisation from light petroleum (b. p. 100—120°)–ethanol.

(iii) *With phosphorus trichloride.* Phosphorus trichloride (0·69 g., 0·005 mole) in benzene (10 ml.) was added to 2-nitrosobiphenyl (0·92 g., 0·005 mole) in benzene (8 ml.) at 0° under nitrogen. No colour change occurred after 1 hr. at room temperature. The mixture was boiled under reflux for 5 hr. (red colour), set aside overnight, and extracted with 2N-sodium hydroxide; an immiscible brown oil separated. The benzene layer and the oil were separated, homogenised by addition of acetone and benzene, washed with water (25 ml.), dried ($MgSO_4$), and recovered. The residue, on chromatography, gave unchanged 2-nitrosobiphenyl (0·28 g.), mixed m. p. 101—106°, and a yellow solid (0·07 g.), m. p. 137—145°. Carbazole was not detected.

Reaction of 2-o-*Nitrosophenylpyridine with Triethyl Phosphite.*—Triethyl phosphite (0·63 g.) and the nitroso-compound (0·71 g.) were allowed to react in benzene at 0° for 5 min. in the usual way. After a further 1 hr. at 80°, benzene was removed and the residue was chromatographed on neutral alumina, prepared by the addition of 5% (w/w) of 10% (v/v) acetic acid. Elution with 3 : 1 benzene–light petroleum (b. p. 60—80°) gave crude pyrid[1,2-*b*]indazole (98%) which on recrystallisation from ethanol–light petroleum (b. p. 60—80°) had m. p. and mixed m. p. 84—86° (0·63 g.).

Reaction of 3-o-*Nitrosophenylpyridine with Triethyl Phosphite.*—Reaction of triethyl phosphite (0·84 g., 0·005 mole) with the nitroso-compound (0·94 g., 0·005 mole) as described above gave, on chromatography, α-carboline (0·44 g.; eluted with 4 : 1 benzene–light petroleum), m. p. and mixed m. p. 224—225° [from benzene–light petroleum (b. p. 60—80°)], and γ-carboline (0·1 g.; eluted with 1 : 1 benzene–ether), m. p. and mixed m. p. 242°.

Reaction of 4-*Bromo-2′-nitrosobiphenyl with Triethyl Phosphite.*—Treatment of 4-bromo-2′-nitrobiphenyl as described by Mijs *et al.*[21] gave the impure nitroso-compound, as a pale green solid, m. p. 104—110° (1·98 g.), which was allowed to react without further purification with triethyl phosphite (1 equiv.) in the normal manner. Chromatography of the products on active alumina yielded unchanged 4-bromo-2′-nitrobiphenyl (1·13 g.), m. p. and mixed m. p. 63—65°, followed by an orange solid (0·1 g.), m. p. 173—175° (Found: C, 52·9; H, 3·85; Br, 27·95%), on elution with light petroleum. Elution with 1 : 1 benzene–light petroleum yielded 2-bromocarbazole (0·40 g., 51%), m. p. 252—253° (lit.,[25] 250—251°) (needles from xylene) (Found: C, 58·1; H, 3·3. Calc. for $C_{12}H_8BrN$: C, 58·5; H, 3·25%). Triethyl phosphate (0·45 g., 32·6%), n_D^{24} 1·4040 (correct infrared spectrum), was eluted with benzene–chloroform.

Reaction of 2-*Chloro-2′-nitrosobiphenyl with Triethyl Phosphite.*—Treatment of 2-chloro-2′-nitrobiphenyl as described by Mijs *et al.*[21] gave the impure nitroso-compound, m. p. 60—70° (green liquid). This solid (1·2 g., 0·005 mole) was allowed to react with triethyl phosphite (0·84 g., 0·005 mole) in benzene as previously described. Chromatography of the products yielded unchanged 2-chloro-2′-nitrobiphenyl (0·88 g.), m. p. and mixed m. p. 67—70°, by elution with light petroleum, and 4-chlorocarbazole (0·30 g., 30%; 100% based on nitroso-compound used) as needles [from light petroleum (b. p. 60—80°)], m. p. 96—97° (lit.,[26] 96°) (Found: C, 71·9; H, 4·4. Calc. for $C_{12}H_8ClN$: C, 71·6; H, 4·0%), by elution with 1 : 1 benzene–light petroleum. Triethyl phosphate (33%) was also recovered.

The authors are grateful to Professor D. H. Hey, F.R.S., for his interest.

King's College, Strand, London, W.C.2. [*Received, July 11th,* 1962.]

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[25] Barclay and Campbell, *J.*, 1945, 530.

[26] Moggridge and Plant, *J.*, 1937, 1125.