896. *The Reactivity of Organophosphorus Compounds. Part XIX.*[1] *Reduction of Nitro-compounds by Triethyl Phosphite: a Convenient New Route to Carbazoles, Indoles, Indazoles, Triazoles, and Related Compounds* *

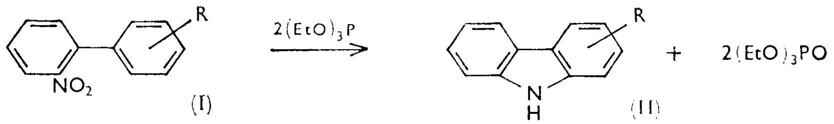
By J. I. G. CADOGAN, M. CAMERON-WOOD, R. K. MACKIE, and R. J. G. SEARLE

Reduction of nitro-compounds by triethyl phosphite or triphenylphosphine has been examined. Thus, 2-nitrobiaryls are readily reduced to carbazoles in high yields in boiling triethyl phosphite after 8 hr. 2-*o*-Nitrophenylpyridine similarly gives pyrido[1,2-*b*]indazole in almost quantitative yield; anils such as *o*-nitrobenzylideneaniline give 2-arylindazoles, 2-nitroazobenzenes give 2-aryltriazoles, and α-nitrostilbene and *cis*- or *trans*-2-nitrostilbene give 2-phenylindole. Other related deoxygenations have been carried out and the scope of the reduction is indicated.

BUNYAN and CADOGAN[2] recently demonstrated that aromatic *C*-nitroso-compounds are readily deoxygenated by triethyl phosphite or triphenylphosphine to give a variety of products dependent on the nature of the nitroso-compound: carbazoles, for example, being readily formed from the corresponding 2-nitrosobiaryls. The preparative significance of this reaction is reduced, however, by the difficulties sometimes encountered in the preparation of the nitroso-compound from the corresponding nitrobiaryl. It was therefore of interest to investigate the possibility of *in situ* preparation and subsequent reduction of the nitroso-compound by reaction of the parent nitro-compound with an excess of triethyl phosphite.

At the outset of this investigation, very few reactions of nitro-compounds with tervalent organic compounds of phosphorus had been reported and in many of these the nitro-group remains intact. Thus, Horner and Klupfel[3] showed that *o*-dinitrobenzene and *o*-nitrobenzaldehyde react reversibly with triethylphosphine to give unstable 1 : 1-adducts, *o*- and *p*-nitrobenzaldehyde undergo apparently irreversible additions with trialkyl phosphites,[4] while nitrobenzene was recovered unchanged from a similar reaction.[3] The reaction of triphenylphosphine with 4-nitropyridine 1-oxide at 200°, on the other hand, led to the evolution of nitrous fumes, the fate of the remainder of the molecule being undetermined.[5]

It has now been shown that 2-nitrobiaryls (I; R = H, 2′-Cl, 2′-Br, 4′-Br, 2′-Me, 4′-Me) react with triethyl phosphite at the boiling point to give good yields of the corresponding



carbazoles (II) and triethyl phosphate; *i.e.*, under much more vigorous conditions than those necessary to effect the corresponding reduction of 2-nitrosobiaryls. 1-*o*-Nitrophenylnaphthalene, which presents two possible points of ring closure, also reacted to give a

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* Preliminary accounts of this work have appeared: J. I. G. Cadogan and M. Cameron-Wood, *Proc. Chem. Soc.*, 1962, 361; J. I. G. Cadogan and R. J. G. Searle, *Chem. and Ind.*, 1963, 1282.

[1] Part XVIII, A. J. Burn, J. I. G. Cadogan, and P. J. Bunyan, *J.*, 1964, 4369.

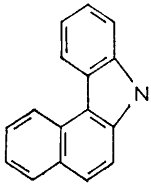
[2] P. J. Bunyan and J. I. G. Cadogan, *J.*, 1963, 42.

[3] L. Horner and K. Kupfel, *Annalen*, 1955, **591**, 69.

[4] V. A. Kukhtin and K. M. Kirillova, *J. Gen. Chem.* (*U.S.S.R.*), 1961, **31**, 2078 (*Chem. Abs.*, 1962, **56**, 3507).

[5] E. Howard, jun., and W. F. Olszewski, *J. Amer. Chem. Soc.*, 1959, **81**, 1483.

product containing a pyrrole ring, 3,4-benzcarbazole (III) rather than the isomeric meso-benzacridine (IV), while 2-*o*-nitrophenylpyridine under similar conditions gave pyrido[1,2-*b*]indazole (V) (>90%) rather than the alternative product of ring closure, δ-carboline, *i.e.*, reaction occurred exclusively at the relatively electron-rich pyridine nitrogen atom. This cyclisation has been effected previously in lower yield by ferrous oxalate,[6] whilst pyrido[1,2-*b*]indazole has also been isolated from the reduction of 2-*o*-nitrosophenylpyridine by triethyl phosphite.[2] Such ring-closure at nitrogen in a conjugated δ-position has now been exploited as a convenient new route to indazoles and triazoles. Thus *o*-nitroanils (VI; Ar = Ph, *p*-C_6H_4·Me, *o*-C_6H_4·Me, *p*-C_6H_4·OMe, *o*-C_6H_4Br, α-$C_{10}H_7$) are readily converted by triethyl phosphite into the corresponding indazoles (VII), while 2-nitroazobenzenes (VIII; Ar = Ph, *p*-C_6H_4Br, *p*-C_6H_4·OMe, *p*-C_6H_4Cl, *p*-C_6H_4·Me) similarly undergo reduction to the corresponding benzotriazoles (IX), as does bis-(*o*-nitrobenzylidene)-*p*-phenylenediamine to *p*-di-2*H*-indazol-2-ylbenzene (X).



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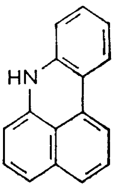

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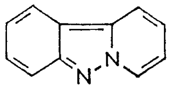

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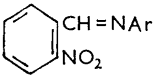

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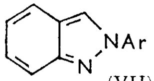

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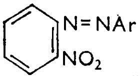

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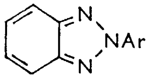

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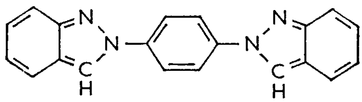

(X)

2-Nitro-4′-hydroxyazobenzene, on the other hand, gave 2-*p*-ethoxyphenyl-2*H*-benzotriazole indicating that ethylation by triethyl phosphate, which is a known alkylating agent,[7] had occurred.

In a closely related reduction, 2-nitrostilbene afforded 2-phenylindole, and it is of interest that whilst both the *cis*- and *trans*-isomers reacted, a higher yield was unexpectedly obtained from the former (85% cf. 58%): a lower yield (16%) was obtained from the isomeric α-nitrostilbene. That such reductions are very sensitive to steric environment also follows from the observations that *o*-nitrostyrene gave only a trace of indole whilst β-nitrostyrene gave none, and *o*-nitrocinnamic acid was reduced and esterified to give a low yield of indole-2-carboxylic ester. Despite this it is clear that the reduction affords a good route to certain five-membered rings containing nitrogen and that many extensions of the reaction are possible. Thus, reaction of triethyl phosphite with suitable dinitro-compounds leads to polycyclic compounds containing fused five-membered rings, dibenzo-[*b,f*]-1,3a,4,6a-tetra-azapentalene (XI), 2,2′-bi-2*H*-indazolyl (XII) and indolo[3,2-*b*] indole (XIII) being obtained from 2,2′-dinitroazobenzene, *o*-nitrobenzaldehyde azine, and 2,2′-dinitrostilbene, respectively.

The mechanisms of these reactions have not been established, and it may be that there is not a common mechanistic pathway. A notable feature of the reduction is its success when applied to the synthesis of five-membered rings containing nitrogen, though 2-nitrodiphenylamine and 2-nitrodiphenyl ether, for example, gave a very low yield of phenazine

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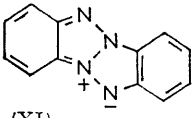
[6] R. A. Abramovitch, Y. Ahmad, and D. Newman, *Tetrahedron Letters*, **1961**, 752.
[7] J. I. G. Cadogan, *J.*, **1957**, 1079.

and a tar, respectively. Other nitro-compounds which gave tars on treatment with triethyl phosphite included nitrobenzene, *p*-chloronitrobenzene, *NN*-dimethyl-*p*-nitroaniline, 2-nitrobenz-*p*-toluidine, *N*-benzoyl-*o*-nitroaniline, *o*-nitrobenzaldehyde phenylhydrazone, 1-nitrobutane, *o*-nitro-t-butylbenzene, and 1-furyl- and 1-thiophenyl-2-phenyl-2-nitroethylene, 2-nitrochalcone, and *o*-nitrophenylhydrazine.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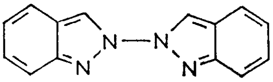
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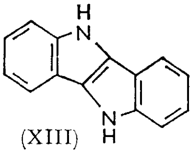
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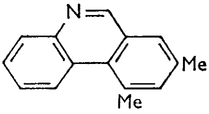
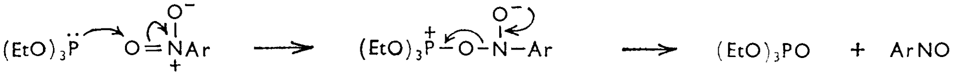
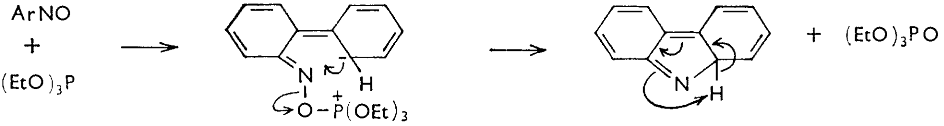

(XIV)

A study of the reduction of 2-nitrobiphenyl to carbazole under a variety of conditions has shown that triethyl phosphite and triphenylphosphine have similar reactivities at 130° ($t_{\frac{1}{2}}$ *ca.* 4—6 hr.) whereas phosphorus trichloride does not react with 2-nitrobiphenyl at this temperature. Similar relative reactivities were noted during the corresponding conversions of 2-nitrosobiphenyl with carbazole. These results point to nucleophilic attack by the tervalent phosphorus atom on both nitro- and nitroso-oxygen and it is likely that the former reduction proceeds *via* the nitroso-compound which, in turn, is reduced very rapidly.



The earlier suggestion [2] that reduction of the nitroso-compound proceeds *via* an electron-deficient nitrene intermediate is supported on the one hand by the similarity in behaviour of simple 2-nitrobiaryls and 2-*o*-nitrophenylpyridine when compared with that of the corresponding azides, which are known to give nitrenes on thermal decomposition.[8] Against the nitrene hypothesis however is the fact that the nitrene obtained from 2-azido-2′,4′,6′-trimethylbiphenyl undergoes a C–H insertion reaction at an *ortho*-methyl group to give 8,10-dimethylphenanthridine (XIV),[9] whereas the corresponding reduction by triethyl phosphite gave only a tar. It is possible therefore that these reductions may proceed without the intermediacy of a discrete nitrene, *e.g.*,



The results of current experiments designed to establish the mechanism of these and related reactions will be reported later.

The deoxygenation of *o*-nitrosonitrobenzene has also been studied, since this molecule contains two groups which in theory are susceptible to attack by triethyl phosphite. Smooth reduction to benzofurazan oxide (19%) took place at room temperature, whilst further reduction of benzofurazan oxide with triethyl phosphite at 150° then gave benzofurazan, which has also been obtained by deoxygenation of *o*-dinitrosobenzene by triethyl phosphite.[10]

[8] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, **64**, 149.
[9] G. Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4717.
[10] J. H. Boyer and S. E. Ellzey, jun., *J. Org. Chem.*, 1961, **26**, 4684.

It has previously been noted [11] that whereas pyridine *N*-oxide and related compounds are readily reduced by phosphorus trichloride, benzo[*c*]cinnoline mono- and di-*N*-oxide and azoxybenzene are not. It has now been shown that reaction with an excess of triethyl phosphite at 160° gives a good yield (86%) of benzo[*c*]cinnoline, which is also obtained in 1·5% yield by similar reduction of 2,2′-dinitrobiphenyl. Such forcing conditions also lead to the reduction of azoxybenzene to azobenzene (82%). A similar reduction has been reported by Horner and Hoffmann, who used triethylphosphine.[12] Since no comparable data for these reactions involving phosphorus trichloride and triethyl phosphite so far exist, it is not possible to say whether they proceed by attack by electrophilic or nucleophilic phosphorus on the oxygen atom.

Since this work was completed and a preliminary account published, it has been reported [13] that diphenylfurazan oxide and azoxybenzene can be reduced by triethyl phosphite at 160° to diphenylfurazan and azobenzene, respectively.

EXPERIMENTAL

Reagents.—The following compounds were prepared by standard routes and recrystallised to constant m. p.s which, in each case, corresponded with the literature value: 2-nitrobiphenyl (m. p. 36—37°), 2-chloro-2′-nitrobiphenyl (69·5—70·5°), 4-bromo-2′-nitrobiphenyl (65°) 2-methyl-2′-nitrobiphenyl (64—65°) 4-methyl-2′-nitrobiphenyl (37—37·5°), 2-bromo-2′-nitrobiphenyl (71—72°), 1-*o*-nitrophenylnaphthalene (91°), 2-*o*-nitrophenylpyridine (58°), *cis*- (66°) and *trans*-2-nitrostilbene (70°), 2,2′-dinitrobiphenyl (125—126°), 2-ethoxycarbonylindole (116—118°).

α-Nitrostilbene (m. p. 73—74°) and 1-2′-furyl-2-nitro-2-phenylethylene (m. p. 85—87°) were prepared as described by Robertson, who reported m. p.s 75° and 87—87·5°, respectively.[14] *o*-Nitrobenzylidene derivatives of the following amines were prepared by Senier and Clarke's method: [15] aniline (m. p. 67—69°), *o*-toluidine (81—82°), *p*-toluidine (72—73°), *p*-bromoaniline (97—98°), *p*-anisidine (79—80°), α-naphthylamine (50°), *p*-phenylenediamine (140°). The products were converted into the dimorphic forms by sunlight. *o*-Nitronitrosobenzene (m. p. 124—126°), 2-nitroazobenzene (m. p. 70—71°), 2-nitro-4′-bromoazobenzene (m. p. 155—157°), 2-nitro-4′-methoxyazobenzene (72—73°), 2-nitro-4′-chloroazobenzene (144—145°), 2-nitro-4′-methylazobenzene (85—87°), and 2-nitro-4′-hydroxyazobenzene (162—163°), were prepared by standard methods.[16] 2,2′-Dinitroazobenzene (m. p. 216°; 15% yield, lit., m. p. 210°) was prepared by phenyl iodosoacetate oxidation of *o*-nitroaniline in acetic acid.[17]

Authentic samples were kindly donated as follows: benzo[*c*]cinnoline and its di-*N*-oxide (Dr. C. W. Rees), 3,4-benzocarbazole (Drs. J. F. Corbett and P. Holt), 2-phenylindole (Dr. C. Sabet), 2- and 4-methylcarbazole (Drs. Campaigne and Lake), pyrido[1,2-*b*]indazole (Dr. R. A. Abramovitch). 2-*p*-Hydroxyphenyl-2*H*-benzotriazole (m. p. 219—220°; lit.,[18] 219—220°) (Found: C, 67·8; H, 4·4. Calc. for $C_{12}H_9N_3O$: C, 68·2; *H*, 4·3%), was obtained in 26% yield by zinc dust reduction of 2-nitro-4′-hydroxyazobenzene.[16] Ethylation of the product using diethyl sulphate gave 2-p-*ethoxyphenyl*-2H-*benzotriazole* m. p. 101—102° (Found: C, 70·1; H, 5·4; N, 17·9. $C_{14}H_{13}N_3O$ requires C, 70·3; H, 5·4; N, 17·6%)

2-Phenyl-2*H*-benzotriazole was prepared by the reduction of 2-nitroazobenzene (1·5 g.) with ferrous oxalate (1·75 g.) in the presence of lead (15 g.) at 300° for 1 hr. Work-up gave the product (20%); m. p. 104—106° (from ethanol).

1-Nitrobutane had b. p. 151—152°, and *o*-t-butylnitrobenzene, prepared by Brown and Nelson's method,[19] had b. p. 127—128°/17 mm.; n_D^{26} 1·5150, and was free fom isomers (gas-liquid chromatography).

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[11] T. R. Emerson and C. W. Rees, *J.*, 1964, 2319.

[12] L. Horner and H. Hoffmann, *Angew. Chem.*, 1956, **68**, 473.

[13] T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, 1962, **27**, 3651.

[14] D. N. Robertson, *J. Org. Chem.*, 1960, **25**, 47.

[15] A. Senier and R. Clarke, *J.*, 1914, **105**, 1917.

[16] E. Bamberger and R. Hübner, *Ber.*, 1903, **36**, 3803, 3822.

[17] G. B. Barlin, K. H. Pausaker, and N. V. Riggs, *J.*, 1954, 3123.

[18] K. Elbs, *J. prakt. Chem.*, 1924, **108**, 208.

[19] K. L. Nelson and H. C. Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 5605.

Reactions of 2-Nitrobiphenyl.—(i) *With triethyl phosphite.* 2-Nitrobiphenyl (3·98 g., 0·02 mole) and triethyl phosphite (13·28 g., 0·08 mole) were boiled under reflux under nitrogen for 9 hr. Distillation of the red solution gave triethyl phosphite (6·7 g.), b. p. 41°/0·2 mm., n_D^{25} 1·4102 and triethyl phosphate (6·66 g.), b. p. 51°/0·2 mm., n_D^{25} 1·4049. The solid residue was treated with hot acetone, the solution evaporated and the resulting pale yellow solid stirred with light petroleum (b. p. 60—80°) and filtered to give carbazole (2·77 g., 82·5%) as a white solid, m. p. and mixed m. p. 247—248°.

In a similar experiment carried out at 130° for 9 hr. the yield of carbazole was 48%.

(ii) *With triphenylphosphine.* 2-Nitrobiphenyl (4 g., 0·021 mole) and triphenylphosphine (10·48 g., 0·04 mole) were heated in a sealed tube at 130° for 9 hr. The solid reaction mixture was stirred with hot ethanol (100 ml.), cooled and filtered to give carbazole (1·4 g.) m. p. and mixed m. p. 246—248°. Evaporation of the filtrate followed by chromatography on alumina as described by Bunyan and Cadogan [2] gave triphenylphosphine (4·8 g.), m. p. 69—72°, 2-nitrobiphenyl (1·6 g.), m. p. and mixed m. p. 36—37°, carbazole (0·05 g.), triphenylphosphine oxide (5·1 g.), m. p. and mixed m. p. 154—156°, and a small quantity of bown oil. The total yield of carbazole was 43%.

(iii) *With phosphorus trichloride.* 2-Nitrobiphenyl (4 g.; 0·021 mole) in phosphorus trichloride (5·6 g.; 0·041 mole) was heated at 130° for 9 hr. in a sealed tube. The yellow solution was poured into ether (150 ml.) and water (100 ml.) was added slowly. The ether layer was separated, washed with water and dried ($MgSO_4$). Removal of the ether gave a yellow oil (3·86 g.) which on chromatography gave 2-nitrobiphenyl (3·7 g., 93%) m. p. and mixed m. p. 36—37°. Carbazole was not detected.

Reaction of 2-Methyl-2′-nitrobiphenyl and Related Compounds with Triethyl Phosphite.—A mixture of triethyl phosphite (1·66 g.; 0·01 mole) and 2-methyl-2′-nitrobiphenyl (1·06 g.; 0·005 mole) was boiled under reflux under nitrogen for 14 hr. Triethyl phosphate (2·1 g.) b. p. 65°/2 mm. (correct infrared spectrum) was distilled from the dark brown reaction mixture and the residue was extracted with benzene and chromatographed on active alumina; elution with 2 : 1 light petroleum (b. p. 60—80°)–benzene gave crude 4-methylcarbazole (0·68 g.) which crystallised from ethanol as white needles m. p. 128—129° (lit.,[20] 129·5—130°). (Found: N, 8·0. Calc. for $C_{13}H_{11}N$: N, 7·7%). Using the general procedure described above the following substituted biphenyls were deoxygenated to carbazoles: 2-Chloro-2′-nitrobiphenyl gave 4-chlorocarbazole (36%), m. p. and mixed m. p. 92—93°; 2-bromo-2′-nitrobiphenyl gave 4-bromocarbazole (42%), m. p. 104—105° (lit.,[21] 104—105°) (Found: C, 58·4; H, 3·5. Calc. for $C_{12}H_8BrN$: C, 58·5; H, 3·25%); 4-bromo-2′-nitrobiphenyl gave 2-bromocarbazole (77%), m. p. and mixed m. p. 251—252°; 4-methyl-2′-nitrobiphenyl gave 2-methylcarbazole (83%), m. p. and mixed m. p. 260° (lit.,[20] 261—262°) (Found: N, 8·4. Calc. for $C_{13}H_{14}N$: N, 7·7%); 2,4,6-trimethyl-2′-nitrobiphenyl gave triethyl phosphate and irresolvable tar; 1-*o*-nitrophenylnaphthalene gave 3,4-benzocarbazole (62%), m. p. and mixed m. p. 132—133° (lit.,[22] 134—135°).

Reaction of cis- *and* trans-*2-Nitrostilbene and of α-Nitrostilbene with Triethyl Phosphite.*—Triethyl phosphite (2·78 g.; 0·017 mole) and *trans*-2-nitrostilbene (1·25 g., 0·0051 mole) were boiled under reflux under nitrogen for 18 hr. Triethyl phosphite and triethyl phosphate were distilled from the resulting red solution at 40—60°/0·02 mm., and the solid residue was crystallised from 60% aqueous ethanol to give 2-phenylindole (0·63 g., 58%) m. p. and mixed m. p. 188—189° (expected infrared spectrum). A similar reaction with *cis*-2-nitrostilbene gave 2-phenylindole in 85% yield; this was also obtained in 16% yield from α-nitrostilbene.

Reaction of o-Nitrocinnamic Acid with Triethyl Phosphite.—Reaction of triethyl phosphite (4·85 g., 0·029 moles) and *o*-nitrocinnamic acid (1·7 g., 0·011 moles) under nitrogen for 24 hr. at the boil gave a dark brown solution from which triethyl phosphite and phosphate were recovered by distillation. The gummy residue was extracted with hot benzene and chromatographed on neutral alumina. Elution with benzene gave a white solid (0·13 g.) which yielded white needles, m. p. 115—117° (0·1 g., 7·5%) (from ethanol) identified as ethyl indole-2-carboxylate by mixed m. p. and infrared spectrum.

o-Nitrostyrene prepared from *o*-nitrocinnamic acid by the method of Wiley and Smith,[23]

[20] E. Campaigne and R. D. Lake, *J. Org. Chem.*, 1959, **24**, 478.

[21] B. M. Barclay and N. Campbell, *J.*, 1945, 530.

[22] J. F. Corbett and P. Holt, *J.*, 1960, 3646.

[23] R. H. Wiley and N. R. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 5198.

was allowed to react with triethyl phosphite in the usual way. Gas–liquid chromatography of the reaction mixture revealed that only a trace of indole had been produced.

Reaction of N-o-*Nitrobenzylideneaniline and Related Compounds with Triethyl Phosphite.*—A mixture of triethyl phosphite (3·88 g., 0·023 mole) and *N*-*o*-nitrobenzylideneaniline (2·26 g., 0·01 mole) was boiled under reflux under nitrogen for 6 hr. Distillation of the resulting brown solution gave a small quantity of triethyl phosphite and then triethyl phosphate (3·1 g.; b. p. 51°/0·2 mm.; n_D^{25} 1·4046). Extraction of the residue with chloroform followed by chromatography on alumina gave a pale yellow solid (1·3 g.) eluted with 4 : 1 benzene–chloroform. Recrystallisations from 70% ethanol gave 2-phenylindazole (1·12 g., 60%) as white needles, m. p. 80—81° undepressed on admixture with authentic specimen prepared as described by Paal (lit.,[24] 83—84°). Using a similar procedure to that described above, the following indazoles have been prepared from the *N*-*o*-nitrobenzylidene derivative of the corresponding amine: 2-*o*-tolylindazole (34%), yellow needles from ethanol, m. p. 75—76° (lit.,[25] 80°) (Found: C, 80·8; H, 6·1; N, 13·0. Calc. for $C_{14}H_{12}N_2$: C, 80·8; H, 5·8; N, 13·5%); 2-*p*-tolylindazole (55%), colourless needles from ethanol, m. p. 99—100° (lit.,[26] 102—103°) (Found: N, 13·5. Calc. for $C_{14}H_{12}N_2$: N, 13·5%); 2-*p*-bromophenylindazole (38%), cream plates from ethanol, m. p. 147—148° (lit.,[24] 147°) (Found: N, 10·2. Calc. for $C_{13}H_9BrN_2$: N, 10·3%); 2-*p*-methoxyphenylindazole (83·5%), pale yellow plates from ethanol, m. p. 130—131° (Found: N, 12·6. Calc. for $C_{14}H_{12}N_2O$: N, 12·5%); *2-α-naphthylindazole* (51%), m. p. 97·5—98·5° (from ethanol) (Found: C, 83·4; H, 5·1. $C_{17}H_{12}N_2$ requires: C, 83·6; H, 4·9%); p-*di*-2H-*indazol*-2-*yl*-*benzene* (38%), m. p. 280—282° (from *NN*-dimethylformamide) (Found: C, 77·15; H, 4·8; N, 18·2. $C_{20}H_{14}N_4$ requires: C, 77·4; H, 4·5; N, 18·0%).

Reaction of 2-Nitroazobenzene with Triethyl Phosphite.—Triethyl phosphite (4·85 g., 0·029 moles) and the azo-compound (1·3 g., 0·0057 moles) were boiled under reflux under nitrogen for 24 hr. The excess of triethyl phosphite and the triethyl phosphate produced were removed by distillation, and the residue extracted with chloroform. Chromatography on active alumina and elution with benzene gave crude 2-phenyl-2*H*-benzotriazole (0·92 g.) which crystallised from light petroleum (b. p. 60—80°) as needles (0·81 g., 72·5%), m. p. and mixed m. p. 108—109° (lit.,[23] 109°) (Found: C, 74·0; H, 4·2; N, 21·8. Calc. for $C_{12}H_9N_3$: C, 73·9; H, 4·6; N, 21·5%.

Similar procedures applied to related 2-nitroazobenzenes gave the corresponding 2*H*-benzotriazoles as summarised in Table 1.

TABLE 1

Preparation of 2*H*-benzotriazoles ($C_6H_4N_3{\cdot}C_6H_3X$)

X	Yield (%)	M. p.	Lit. (ref.)	Found (%) C	Found (%) H	Found (%) N	Formula	Calc. (%) C	Calc. (%) H	Calc. (%) N
4-Br	68	176—177°	174 (18, 23)	52·9	2·9	15·3	$C_{12}H_8BrN_3$	52·7	2·6	15·4
4-MeO ...	31	108—110	136—138 (18, 27)	69·3	4·8	18·85	$C_{13}H_{11}N_3O$	69·4	4·9	18·6
4-Cl	68	170—171	167—168 (16)	62·4	3·7		$C_{12}H_8ClN_3$	62·8	3·5	
4-Me ...	54	120—121	114 (28)	74·2	5·3		$C_{13}H_{11}N_3$	74·6	5·3	

As a result of the discrepancy between the observed and literature m. p. of 2-*p*-methoxyphenyl-1*H*-benzotriazole the ultraviolet spectrum of the material obtained from our experiments was recorded and compared with those of other 2*H*-benzotriazoles (Table 2).

Reaction of 4-hydroxy-2′-nitroazobenzene with triethyl phosphite under the standard conditions gave 2-*p*-ethoxyphenyl-2*H*-benzotriazole (52%) m. p. and mixed m. p. 100—101° (Found: C, 69·9; H, 5·1. Calc. for $C_{14}H_{13}N_3O$: C, 70·3; H, 5·4%).

Reduction of Dinitro-compounds with Triethyl Phosphite.—(i) *2,2′-Dinitroazobenzene.* Reaction with triethyl phosphite (5 mol.) at 150° under nitrogen for 12 hr. gave dibenzo-[*b,f*]-1,3a,4,6a-tetra-azapentalene (63%) as yellow needles from ethanol, m. p. 238—239° (lit.,[29] 237—238°) (Found: C, 69·0; H, 3·9; N, 26·8. Calc. for $C_{12}H_8N_4$: C, 69·2; H, 3·9; N, 26·9).

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TABLE 2

Ultraviolet spectra of 2-aryl-2*H*-benzotriazoles

Aryl group	$\lambda_{max.}$ (mμ) ($\varepsilon_{max.} \times 10^{-4}$)					
Ph	219(1·45)	237(1·03)	241(0·88)	251(0·45)	305(2·80)	310(2·46)
p-C_6H_4·Me	221(1·20)	238(0·65)	242(0·65)	253(0·44)	309(2·83)	314(2·41)
p-C_6H_4Cl	219(1·06)	240(0·87)	243(0·81)	253(0·47)	308(3·10)	315(2·70)
p-C_6H_4Br	220(1·50)	240(1·17)	245(1·20)	253(0·68)	309(2·79)	313(2·78)
p-C_6H_4·OMe	220(0·99)	250(0·54)	252(0·54)	259(0·56)		317(2·44)
p-C_6H_4·OEt	220(1·26)	249(0·93)	251(0·96)	257(1·00)		316(2·37)
p-C_6H_4·OH	220(1·28)	248(0·99)	252(1·00)	259(1·03)		316(2·74)

(ii) o-*Nitrobenzaldehyde azine.* This gave under similar conditions, 2,2′-bi-2*H*-indazolyl (22%), m. p. 268—269° (lit.,[30] 268°) (Found: C, 71·9; H, 4·3; N, 23·35. Calc. for $C_{14}H_{10}N_4$: C, 71·8; H, 4·3; N, 23·9%).

(iii) 2,2′-*Dinitrostilbene.* The starting material, which contained both *cis*- and *trans*-isomers, was prepared by the reaction of *o*-nitrobenzyl chloride and potassium hydroxide. Reaction in the usual way gave a very low yield (2%) of indolo[3,2-*b*]indole, m. p. 370—372° (decomp.) (lit.,[31] 375°) (Found: C, 81·4; H, 4·9; N, 13·5. Calc. for $C_{14}H_{10}N_2$: C, 81·5; H, 4·9; N, 13·6%).

Reaction of Azoxybenzene and Related Compounds with Triethyl Phosphite.—Triethyl phosphite (3·02 g., 0·019 moles) and azoxybenzene (1·98 g., 0·01 moles) boiled under reflux under nitrogen for 5 hr. gave, after removal of triethyl phosphite and phosphate, crude azobenzene (1·62 g.). Crystallisation from aqueous ethanol produced orange-red prisms (1·5 g., 82%), m. p. and mixed m. p. 66°.

In a similar reaction benzo[*c*]cinnoline di-*N*-oxide gave, after chromatography on alumina, benzo[*c*]cinnoline (86%), m. p. and mixed m. p. 156°.

The deoxygenation of benzofurazan *N*-oxide with triethyl phosphite yielded benzofurazan (19%), m. p. and mixed m. p. 47—48° and an unidentified white gum.

Reaction of o-*Nitronitrosobenzene with Triethyl Phosphite.*—A solution of triethyl phosphite (6·8 g., 0·041 moles) in dry benzene (50 ml.) was slowly added under nitrogen to a stirred suspension of *o*-nitronitrosobenzene (3 g., 0·02 moles) in benzene (30 ml.) at 0°. The nitroso-compound slowly dissolved and, after 24 hr. stirring at room temperature, the reaction mixture had become brown in colour. Evaporation of the benzene followed by distillation of triethyl phosphite and phosphate gave a brown residue which was chromatographed on alumina. Elution with 1 : 1 benzene–light petroleum (b. p. 60—80°) and crystallisation from ethanol gave benzofurazan *N*-oxide (0·51 g., 18%), m. p. and mixed m. p. 67—68° (expected infrared spectrum).

Reaction of 2,2′-Dinitrobiphenyl with Triethyl Phosphite.—Reaction of triethyl phosphite (8·5 g., 0·051 moles) and 2,2′-dinitrobiphenyl (2·44 g.; 0·01 mole) gave, after the usual work-up, benzo[*c*]cinnoline (0·024 g., 1·4%), m. p. and mixed m. p. 156°.

Reaction of 2-Nitrodiphenylamine with Triethyl Phosphite.—2-Nitrodiphenylamine (3·18 g., 0·01 mole) and triethyl phosphite (5·3 g., 0·032 mole) gave phenazine (0·0344 g.; 1·4%) as yellow needles, m. p. and mixed m. p. 172—173·5°.

*Reaction of 2-*o*-Nitrophenylpyridine with Triethyl Phosphite.*—Reaction of triethyl phosphite (3·0 g., 0·019 mole) with 2-*o*-nitrophenylpyridine (0·85 g., 0·0042 mole) gave after 16 hr. a brown solution which was distilled and chromatographed in the usual manner. Elution with 3 : 1 benzene–light petroleum (b. p. 60—80°) gave crude pyrido[1,2-*b*]indazole (0·7 g.) which on recrystallisation from light petroleum (b. p. 60—80°) had m. p. and mixed m. p. 78—79° (0·68 g., 95%).

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