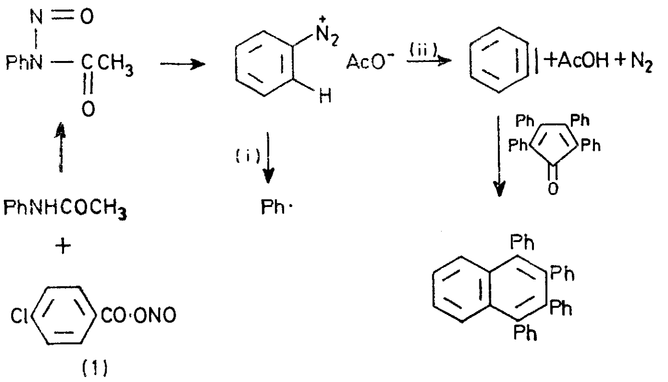
Acylarylnitrosamines. Part VIII.[1] ^{15}N-Labelling Experiments and their Relevance to the Mechanisms of Formation of Benzyne from Benzenediazonium Acetate and of the Benzenediazonium Ion from Hydroxyazo-compounds

By **J. I. G. Cadogan,* Charles D. Murray,** and **John T. Sharp,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Experiments using ^{15}N-labelled *N*-nitrosoacetanilide and related compounds have shown that the complex reaction leading to benzyne and/or phenyl radicals does not involve the reversible extrusion of nitrogen. The contrasting observation that nitrogen exchange did occur in the formation of benzenediazonium ions by the *in situ* nitrosation of ^{15}N-labelled acetanilide is attributed to the generation of unlabelled benzenediazonium ions by the reaction of phenyl radicals with the nitrosating agent. The reactions of nitrosating reagents such as *p*-chlorobenzoyl nitrite with 1-phenylazo-2-naphthol and related hydroxyazo-compounds to give benzenediazonium ions have been investigated, and it is suggested that nitrosation of the hydrazone form of the hydroxyazo-compound followed by rearrangement and cleavage provides the primary source of the diazonium ions but that these are again regenerated in the system from phenyl radicals and the nitrosating reagent. In accord with this, azobenzene and 4-phenylazo-1-methoxynaphthalene, which cannot exist as hydrazones do not so react, in contrast to phenylazotetrachlorocyclopentadiene, which does exist in the hydrazone form. Reactions of *p*-chlorobenzoyl nitrite or pentyl nitrite with 1-phenylazo-2-naphthol in benzene at 50° lead to biphenyl, *via* phenyl radicals, in 30 and 41% yield (82% based on azo-compound consumed).

THAT decomposition of *N*-nitrosoacetanilide (NNA) and hence benzenediazonium acetate, proceeds *via* two competing routes to give phenyl radicals [Scheme 1, route (i)] or benzyne [Scheme 1, route (ii)] is now well established.[2]



SCHEME 1

A major puzzling feature of the reaction lies in the observations that while yields of up to 80% of biphenyl have been recorded on decomposition of NNA alone in benzene, decomposition in the presence of added tetraphenylcyclopentadienone (tetracyclone), as a benzyne trap, led to equally high yields of the benzyne adduct 1,2,3,4-tetraphenylnaphthalene. There are two possible explanations of these observations. First, that the decomposition of the benzenediazonium ion to benzyne [route (ii)] is reversible, *i.e.* that benzyne is capable of fixing nitrogen under these conditions, tetracyclone merely acting by displacing the equilibrium in favour of benzyne formation. Alternatively, tetracyclone could have a dual function by inhibiting the competing radical chain reaction [route (i)] as well as acting as a trap for benzyne. On intuitive and energetic grounds we preferred the latter explanation but it was necessary to investigate the former possibility.

We now report the results of such experiments which not only clearly establish that benzyne formation is not reversible under our conditions, but also shed light on the mechanism of the conversion of 1-phenylazo-2-naphthol into the benzenediazonium ion [3a] and further lead to new chemistry of the former.

The basis of our experiments was to allow ^{15}N-labelled *N*-nitroacetanilide to decompose to *ca.* 50% in benzene in an atmosphere of $^{14}N_2$. The unchanged benzenediazonium ion would be isolated as 1-phenylazo-2-naphthol, by reaction with aqueous alkaline 2-naphthol, which would then be analysed for ^{15}N/^{14}N content by mass spectroscopy. The first experiment, which used [^{15}N]nitrosoacetanilide generated *in situ* by reaction of *p*-chlorobenzoyl nitrite [2c] with [^{15}N]acetanilide (96% ^{15}N), in benzene at 65° led to the surprising result that the derived 1-phenylazo-2-naphthol contained only 57% of the original ^{15}N label. At first sight this result pointed to reversibility of step (ii) (Scheme 1). On the other hand, corresponding reactions performed under a wide variety of conditions, of preformed [^{15}N]nitrosoacetanilide (96% ^{15}N), or [^{15}N]-benzenediazonium fluoroborate (99% ^{15}N) in the presence of potassium acetate, all led to the isolation of 1-phenylazo-2-naphthol with no loss of the ^{15}N-label. These observations clearly suggested that the ^{15}N–^{14}N exchange observed in the first experiment was due to intervention of the nitrosating agent, *p*-chlorobenzoyl nitrite, rather than atmospheric nitrogen *via* the reverse of route (ii). Compelling evidence that this was so, came from the observation that substantial loss of the

---

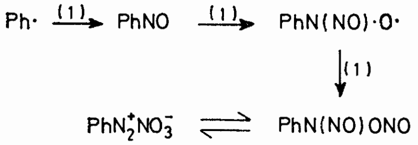
[1] Part VII, J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1974, 1321.

[2] (*a*) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727; (*b*) J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186; (*c*) B. D. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

[3] (*a*) R. Huisgen, *Annalen*, 1951, **574**, 184; (*b*) R. Huisgen and G. Horeld, *ibid.*, 1949, **562**, 137.

^{15}N-label resulted from reaction of [^{15}N]acetanilide with *p*-chlorobenzoyl nitrite in an atmosphere of argon.

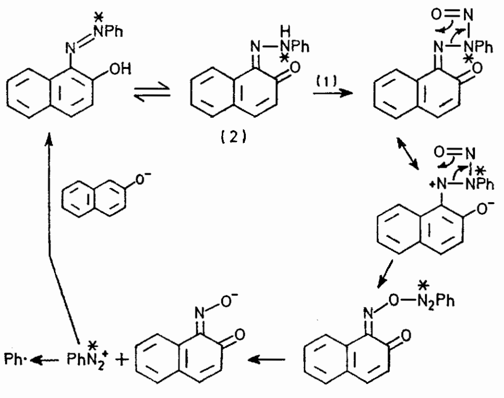
Almost 80 years ago Bamberger[4] showed that nitric oxide will convert nitrosobenzene into benzenediazonium nitrate and much more recently Tedder and Theaker[5] similarly showed that nitrosation of nitroso-compounds could lead directly to diazonium cations. Our nitrogen exchange results can therefore be explained as in Scheme 2 whereby phenyl radicals formed in the usual manner, with concomitant loss of labelled nitrogen, react with the nitrosating agent to give nitrosobenzene. This in turn is further nitrosated as established earlier[4] to give a benzenediazonium cation, which is unlabelled, because both nitrogen atoms come from the nitrosating agent.



SCHEME 2

That such a mechanism was tenable followed from our observations that decomposition of phenylazotriphenylmethane, an authentic source of phenyl radicals, in benzene in the presence of *p*-chlorobenzoyl nitrite, followed by treatment with sodium 2-naphthoxide, gave 1-phenylazo-2-naphthol (27%). Moreover, reaction of *p*-chlorobenzoyl nitrite with nitrosobenzene and *p*-methylnitrosobenzene gave the corresponding diazonium cations (23 and 16%).

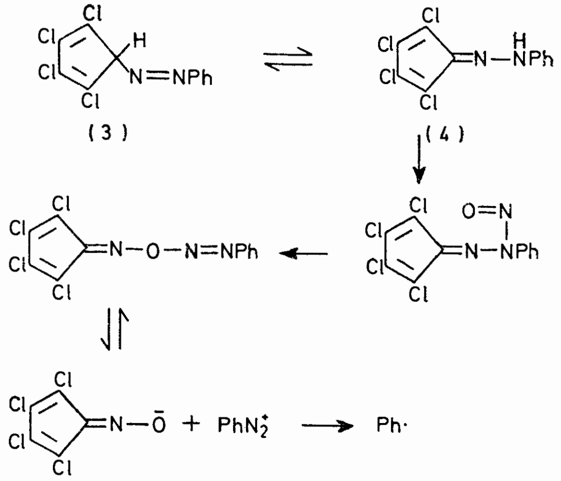
There remained however, the further possibility that the benzenediazonium cation could be generated by nitrosation of 1-phenylazo-2-naphthol, *via* its hydrazone form [(2); Scheme 3], into the nitroso-hydrazone and then by rearrangement through the diazo-ether to the diazonium salt, by analogy with the nitrosation and rearrangement of acetanilide.[2b,3b] This route is considered unlikely to be of great importance in this case, however, because 1-phenylazo-2-naphthol was formed only after drowning out in aqueous solution, which process rapidly decomposes the nitrosating agent. Further, Scheme 3 calls for complete retention of the ^{15}N-label, which was not observed in this case (see above).



SCHEME 3

It is noteworthy however, as an entirely separate issue, that 1-phenylazo-2-naphthol does react with *p*-chlorobenzoyl nitrite in benzene solution, in which the nitrosating agent is stable, to regenerate the benzenediazonium cation. Although we were not aware of it at the time, this observation was pre-empted by Huisgen[3a] during his searching investigations of the reaction of diazonium compounds when he observed that this azo-compound gave the benzenediazonium cation and 1-nitroso-2-naphthol on treatment with nitrous fumes in acetic acid.

The question of the mechanism of this reaction now arises. In theory this could proceed *via* Scheme 3, coupled to Scheme 2, or *via* direct displacement of the diazonium cation by the nitrosonium cation. Our experiments, summarised below, tend to point to the former. Thus 1-phenylazo-4-methoxynaphthalene and azobenzene, which cannot exist in hydrazone forms, were recovered unchanged from corresponding nitrosations, whereas 1-phenylazotetrachlorocyclopentadiene [(3); Scheme 4] which is known[6] to exist largely as the hydrazone (4) was rapidly converted to the benzenediazonium ion. Further, 4-phenylazo-1-naphthol, 2-phenylazo-1-naphthol, and 2-phenylazo-4-methylphenol all gave the benzenediazonium cation on nitrosation in benzene, using pentyl nitrite as well as *p*-chlorobenzoyl nitrite as shown by subsequent coupling with sodium 2-naphthoxide. Reaction of 1-phenylazo-2-naphthol with *p*-chlorobenzoyl nitrite followed by treatment with sodium 7-methoxy-2-naphthoxide gave 1-phenylazo-7-methoxy-2-naphthol, while similar reaction of 4-phenylazo-1-naphthol followed by coupling with sodium 2-naphthoxide gave 1-phenylazo-2-naphthol (Scheme 5).



SCHEME 4

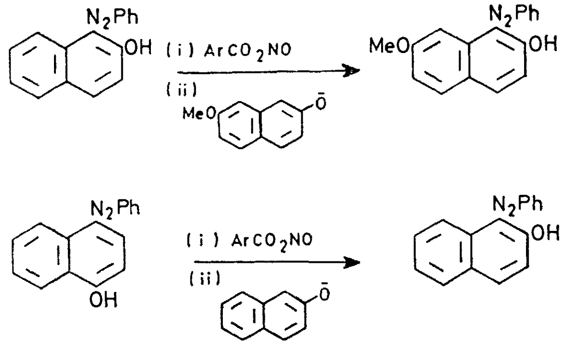
---

[4] E. Bamberger, *Ber.*, 1897, **30**, 506.

[5] J. M. Tedder and G. Theaker, *Tetrahedron*, 1959, 288.

[6] J. Griffiths and M. Lockwood, *J.C.S. Perkin II*, 1973, 1155.

All this is therefore in accord with Scheme 3. Further support for this was then sought using ^{15}N-labelled 1-phenylazo-2-naphthol which should react with retention of the label as shown by trapping of the resulting labelled diazonium cation with sodium 2-naphthoxide (Scheme 3). In the event, 70% of the resulting 1-phenylazo-2-naphthol had *lost* the ^{15}N-label. Scheme 3 is not therefore wholly satisfactory.



SCHEME 5 Ar = p-ClC$_6$H$_4$

Since it is known from the experiments of Holt and Bullock[7] that there is no interchange between the nitrogen atoms of a benzenediazonium cation during diazotisation and coupling to give 1-phenylazo-2-naphthol, a conclusion confirmed by our own observations based on ^{15}N resonance n.m.r. analysis, an additional route to regenerate the benzenediazonium cation was therefore required. Since it is known that phenyl radicals react with nitrosating agents to give the diazonium ion (Scheme 2) it follows that our results can be accommodated by the formation of the diazonium cation, as in Scheme 3, some of which survives to be captured by reaction with sodium naphthoxide, but the remainder decomposes with loss of ^{15}N-label to give phenyl radicals, which subsequently react with the nitrosating agent *via* Scheme 2 to give the unlabelled diazonium cation. In accord with this, nitrosation of 1-phenylazo-2-naphthol by p-chlorobenzoyl nitrite or pentyl nitrite in benzene gave biphenyl in 30 and 41% yields respectively, the latter figure translating to 82% on azo-compound consumed. That these were radical reactions were shown by the formation of a mixture of isomeric t-butylbiphenyls of the correct, *i.e.* radical derived, isomeric composition (2-, 20%; 3-, 57%; 4-, 23%),[8] when the reaction was carried out in t-butylbenzene rather than benzene.

Finally it is necessary to consider the alternative mechanism involving direct displacement of the diazonium cation by reaction of the nitrosonium ion at nuclear position 1 of 1-phenylazo-2-naphthol. Although our experiments do not rigorously exclude this possibility it is considered to be less satisfactory because it accommodates only some, but not all our observations.

Thus, while 4-phenylazo-1-naphthol, and all azo-compounds capable of tautomerism, which we studied, were instantly decolourised by nitrosating agent, the corresponding 4-phenylazo-1-methoxynaphthalene, which would also be expected to be strongly activated towards the direct displacement route, was completely inactive. Such inactivity is easily explained by a mechanism based on a hydrazone tautomer (Scheme 3). To support direct displacement, it would be necessary to argue that whereas the hydroxy-azo-compound was sufficiently activated for direct ring nitrosation, the methoxy-analogue was not. In which unlikely case it would then be difficult to explain the ease with which the heavily deactivated tetrachlorocyclopentadiene derivative (3) underwent the reaction.

In this connection it should be noted, however, that very recently Bunce[9] has reported examples of direct displacement of diazonium cations from o-arylazophenols by electrophiles stronger than the nitrosium cation, such as NO_2^+ and Br^+.

EXPERIMENTAL

Mass Spectrometry.—Exact mass measurements were conducted on an MS902 instrument. The isotope enrichment of compounds was calculated by Biemann's method,[10] the following assumptions being inherent in the technique. (1) The intensity of the isotope peaks at $M + 1$ and $M + 2$ is the same in both standard and labelled compound. (2) There is no '$M + 1$' peak due to ion–molecule collisions. (3) The electron energy does not change from one sample to another. (4) There are no background or other impurities present that contribute to the peaks being measured. While for some of the samples (both standard and labelled) an electron energy of 12 eV was used (at which the molecular ion peak is still intense enough to be measured accurately while the fragmentation resulting in the loss of one or more hydrogen atoms is negligible) it was found that identical results were obtained from spectra run at 70 eV.

Materials.—p-Chlorobenzoyl nitrite was prepared as described previously[2c] and was stored in benzene solution (16% w/v) at −15° under dry conditions. [^{15}N]Nitrosoacetanilide was prepared from ^{15}N-labelled acetanilide (96% ^{15}N) using the standard procedure for the preparation of the unlabelled compound, m.p. 49—51° (decomp.).

[^{15}N]*Aniline hydrochloride.* [^{15}N]Benzamide, prepared in 80% yield from labelled ammonium chloride (99% ^{15}N) by the method of Lewis,[11] was treated with chlorine and sodium hydroxide to give the labelled aniline *via* a Hoffman degradation. Steam distillation afforded a pale yellow oil which was extracted with ether. The aniline hydrochloride was precipitated by the introduction of anhydrous hydrogen chloride. The yield of product was 64%, m.p. 196—198° (lit.,[12] 198—200°).

[^{15}N]*Benzenediazonium fluoroborate.* This was prepared from the corresponding aniline hydrochloride by diazotisation in aqueous hydrochloric acid followed by treatment

---

[7] P. F. Holt and B. I. Bullock, *J. Chem. Soc.*, 1950, 2310.

[8] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 3352.

[9] N. J. Bunce, *J.C.S. Perkin I*, 1974, 942.

[10] R. Biemann, 'Mass Spectrometry: Organic Chemical Applications', McGraw-Hill, New York, 1971.

[11] E. S. Lewis and R. E. Holliday, *J. Amer. Chem. Soc.*, 1969, **91**, 426.

[12] A. I. Vogel, 'Practical Organic Chemistry', Longmans, London, 1956.

with aqueous sodium fluoroborate. Recrystallisation from acetone–ether (4 times) afforded colourless crystals, m.p. 96° (decomp.).

[^{15}N]-1-*Phenylazo-2-naphthol*. This was prepared by the coupling of ^{15}N-labelled benzenediazonium fluoroborate with an alkaline solution of β-naphthol. Recrystallisation of the filtered product from ethanol afforded the labelled compound in 90% yield, m.p. 133°. Analysis by m.s. showed a 99% enrichment of the nitrogen label in the product, δ ($CDCl_3$) +110·8 p.p.m. downfield relative to NO_3^- in NH_4NO_3).

Reactions of ^{15}*N-Labelled Compounds*. (a) *Partial decomposition of* ^{15}*N-labelled NNA formed* in situ *in benzene*. (i) *In the absence of a trap*. 4-Chlorobenzoyl nitrite (0·3 g, 1·6 mmol) in benzene (5 ml) was added dropwise to a solution of acetanilide (0·11 g, 0·8 mmol; 96% ^{15}N) in benzene (20 ml) at 45°, under an atmosphere of dry nitrogen, and stirring was continued for 15 min. A solution of sodium 2-naphthoxide (0·17 g, 1·0 mmol) in water (10 ml) was added to the mixture with vigorous stirring. Extraction with ether gave an orange solution, from which 1-phenylazo-2-naphthol (0·040 g, 20 mmol/100 mol) was isolated by dry column chromatography on alumina, eluting with carbon tetrachloride. Mass spectral analysis of the recrystallised product showed a nitrogen-15 isotope content of 93% indicating a 3% loss of the label. In a parallel experiment at 65°, 1-phenylazo-2-naphthol, isolated in 5% yield, showed a nitrogen-15 isotope content of 53% indicating 43% loss of the label. The origin of the peaks at *m/e* 248 and 249 was confirmed by exact mass measurements (Found: M^+, 249·092092. $C_{16}H_{12}{}^{14}N^{15}NO$ requires *M*, 249·091993. Found: M^+, 248·085645. $C_6H_{11}{}^{14}N^{15}NO$ requires *M*, 248·084168. Found: M^+, 248·092935. $C_{16}H_{12}{}^{14}N_2O$ requires *M*, 248·094958).

(ii) *In the presence of tetracyclone*. 4-Chlorobenzoyl nitrite (0·15 g, 0·80 mmol) in benzene (3 ml) was added to a solution of acetanilide (0·05 g, 0·37 mmol; 96% ^{15}N) and tetracyclone (0·014 g, 0·37 mmol) in benzene (10 ml) as described in the previous experiment. After 15 min sodium 2-naphthoxide (0·083 g, 0·5 mmol) in water (5 ml) was added with vigorous stirring. 1-Phenylazo-2-naphthol (0·014 g, 15 mol/100 mol) was isolated by dry column chromatography and showed a ^{15}N content of 90%.

(b) *Partial decomposition of* ^{15}*N-labelled benzenediazonium fluoroborate in various solvents*. ^{15}N-Labelled benzenediazonium fluoroborate (0·071 g, 0·37 mmol; 99% ^{15}N) was added to solvent (20 ml) with vigorous stirring under an atmosphere of nitrogen at 60°. After 15 min, sodium 2-naphthoxide (0·083 g, 0·50 mmol) in water (5 ml) was added. The organic layer was extracted with ether, washed with sodium hydroxide, and dried ($MgSO_4$). Dry column chromatography afforded 1-phenylazo-2-naphthol. Reactions were carried out in the following solvents and solvent mixture: benzene, water, acetone, methanol, and benzene–water (2 : 1). In all cases the ^{15}N content of the azo-product was 99%.

(c) *Partial decomposition of* ^{15}*N-labelled NNA in benzene*. (i) *Under nitrogen*. ^{15}N-Labelled *N*-nitrosoacetanilide (0·050 g, 0·30 mmol; 96% ^{15}N) was added to benzene (20 ml) under dry nitrogen and the reaction mixture stirred for 5 min at 50°. The reaction mixture was then flushed with a solution of sodium 2-naphthoxide (0·08 g, 0·50 mmol) in water (10 ml). Ethereal extraction of the organic products followed by dry column chromatography afforded 1-phenylazo-2-naphthol (0·025 g, 30 mol/100 mol; 96% ^{15}N).

(ii) *In the presence of* 4-*chlorobenzoyl nitrite*. ^{15}N-Labelled *N*-nitrosoacetanilide (0·050 g, 0·30 ml; 96% ^{15}N) was added to a solution of 4-chlorobenzoyl nitrite (0·15 g, 0·80 mmol) in benzene (20 ml). 1-Phenylazo-2-naphthol (0·027 g, 32 mol/100 mol), isolated as described above, showed a ^{15}N content of 88%.

(d) *Decomposition of* ^{15}*N-labelled NNA formed* in situ *in benzene under argon*. A solution of acetanilide (0·05 g, 0·37 mmol; 96% ^{15}N) in benzene (20 ml) was degassed (5 times) and the reaction vessel flushed out with argon. The mixture was stirred for 10 min at 50° and then 4-chlorobenzoyl nitrite (0·15 g, 0·80 mmol) added through a syringe, the reaction flask being fitted with a liquid paraffin bubbler. Stirring was continued for a further 5 min and the solution flushed with sodium 2-naphthoxide (0·08 g, 0·50 mmol) in water (5 ml). Extraction of 1-phenylazo-2-naphthol (0·014 g, 15 mol/100 mol) was as described before and m.s. showed the ^{15}N content to be 87%.

(e) *Reaction of* ^{15}*N-labelled* 1-*phenylazo*-2-*naphthol with* 4-*chlorobenzoyl nitrite*. 4-Chlorobenzoyl nitrite (0·10 g, 0·54 mmol) in benzene (1 ml) was added from a syringe to a well stirred solution of 1-phenylazo-2-naphthol (0·05 g, 0·20 mmol; 99% ^{15}N) in benzene (20 ml) at 50°. After 8 min, sodium 2-naphthoxide (0·07 g, 0·40 mmol) in benzene (10 ml) containing crown ether was added with vigorous stirring and the reaction quenched with water (20 ml). The regenerated zero compound (0·01 g, 20 mol/100 mol), was isolated by dry column chromatography and showed a ^{15}N content of 51%. In a parallel experiment carried out under argon using degassed solvents, the isolated 1-phenylazo-2-naphthol (0·015 g, 30 mol/100 mol) showed a ^{15}N content of 38%.

Nitrosation of Hydroxy-azo-compounds.—(i) 1-*Phenylazo*-2-*naphthol*. 4-Chlorobenzoyl nitrite (2·5 g, 13·6 mmol) in benzene (25 ml) was added dropwise to a well stirred solution of 1-phenylazo-2-naphthol (1·7 g, 6·8 mmol) in benzene (150 ml) over a period of 2 min, the reaction being carried out under dry nitrogen. The red colour due to the dissolved azo-compound was rapidly discharged. Stirring was continued for a further 1 h and the solvent removed by evaporation. Addition of ether (100 ml) to the residual oil induced the precipitation of a brown solid (0·3 g) which showed four spots on t.l.c. Successive recrystallisations of this solid from acetone–light petroleum failed to purify the sample. The remainder of the reaction mixture was chromatographed on alumina eluting with light petroleum–ether. Biphenyl (0·25 g, 24 mol/100 mol) was collected as the only major product and after recrystallisation from light petroleum it had m.p. and mixed m.p. 70—71° (i.r. spectrum). A parallel experiment carried out in boiling benzene gave biphenyl (30%).

(ii) 2-*Phenylazo*-1-*naphthol*. 4-Chlorobenzoyl nitrite (0·30 g, 1·6 mmol) in benzene (5 ml) was added dropwise to a well stirred solution of 2-phenylazo-1-naphthol (0·20 g, 0·8 mmol) in benzene (20 ml) at 50°, as above. Rapid decolourisation of the solution ensued, and g.l.c. investigation of the reaction mixture showed that the azo-compound had been completely consumed. Further examination of the reaction mixture by g.l.c. (1% SE30; 140°) showed the presence of biphenyl. Dry column chromatography on alumina, eluting with cyclohexane, afforded biphenyl (0·021 g, 17 mol/100 mol), m.p. 70—70·5°.

(iii) 4-*Phenylazo*-1-*naphthol*. This similarly gave biphenyl (27 mol/100 mol).

(iv) 1-*Phenylazo*-4-*methoxynaphthalene and azobenzene*.

4-Chlorobenzoyl nitrite (0·15 g, 0·80 mmol) in benzene (5 ml) was added to a well stirred solution of 1-phenylazo-4-methoxynaphthalene (0·10 g, 0·38 mmol) in benzene (20 ml), as described above, and the reaction was followed by g.l.c. over 48 h. The peak corresponding to the azo-compound persisted throughout the reaction while no trace of biphenyl was observed. A similar result was obtained for the reaction of 4-chlorobenzoyl nitrite with azobenzene.

Nitrosation of Hydroxy-azo-compounds followed by Treatment with Naphthoxide Salts.—(i) 2-*Phenylazo*-1-*naphthol*. A solution of 4-chlorobenzoyl nitrite (0·22 g, 1·20 mmol) in benzene (5 ml) was added dropwise over 2 min to a solution of 2-phenylazo-1-naphthol (0·10 g, 0·40 mmol) in benzene (20 ml) at 50°. Almost immediately, sodium 2-naphthoxide (0·10 g, 0·60 mmol) in water (15 ml) was added with vigorous stirring. The mixture was extracted with ether and the organic layer evaporated. Dry column chromatography of the residue on alumina, eluting with carbon tetrachloride, afforded 1-phenylazo-2-naphthol (0·053 g, 53 mol/100 mol), m.p. 133—134°. The i.r. (Nujol) spectrum was indistinguishable from that of an authentic sample.

(ii) 1-*Phenylazo*-2-*naphthol*. 4-Chlorobenzoyl nitrite (0·22 g, 1·20 mmol) in benzene (5 ml) was added to a solution of 1-phenylazo-2-naphthol (0·10 g, 0·38 mmol) in benzene (20 ml) at 50°. Sodium 7-methoxy-2-naphthoxide (0·13 g, 0·60 mmol) in water (15 ml) was then added as described in the previous experiment. Examination of the mixture by g.l.c. and g.l.c.–m.s. (1% SE30; 250°) showed 1-phenylazo-7-methoxy-2-naphthol to be present as a major product.

Nitrosation of Nitroso-compounds followed by Treatment with Sodium 2-*Naphthoxide*.—(i) o-*Methylnitrosobenzene*. 4-Chlorobenzoyl nitrite (0·19 g, 1·0 mmol) in benzene (3 ml) was added dropwise over 2 min to a solution of *o*-methylnitrosobenzene (0·06 g, 0·5 mmol) in benzene (30 ml) at 50°. The reaction mixture was stirred for a further 5 min before the addition of sodium 2-naphthoxide (0·08 g, 0·5 mmol), dissolved in benzene (5 ml) containing crown ether. The solution was then stirred for 1 h over which period the orange colour deepened. Chromatography of the reaction mixture on alumina afforded 1-(*o*-methylphenylazo)-2-naphthol (0·021 g, 16 mol/100 mol), m.p. 135° (lit.,[13] 135°), *m/e* 262 (M^+).

(ii) *Nitrosobenzene*. 4-Chlorobenzoyl nitrite (0·34 g, 1·86 mmol) in benzene (5 ml) was added to a solution of nitrosobenzene (0·10 g, 0·93 mmol) in benzene (30 ml) as described in the previous experiment. Treatment of the reaction mixture with a solution of sodium 2-naphthoxide afforded a red solution, chromatography of which gave 1-phenylazo-2-naphthol (0·056 g, 23 mol/100 mol), m.p. and mixed m.p. 134°.

Nitrosation of 1-*Phenylazo*-2,3,4,5-*tetrachlorocyclopentadiene*.—4-Chlorobenzoyl nitrite (0·28 g, 1·5 mmol) in benzene (5 ml) was added dropwise to a well-stirred solution of 1-phenylazo-2,3,4,5-tetrachlorocyclopentadiene (0·31 g, 1 mmol)[6] in benzene (30 ml) at 50°. Stirring was continued until t.l.c. showed the azo-compound to be consumed. Biphenyl (0·036 g, 17 mol/100 mol) was isolated by dry column chromatography and after recrystallisation from light petroleum had m.p. 70—70·5°. In a blank reaction in which the azo-compound was heated in benzene for 18 h at 50° no biphenyl was formed.

Nitrosation of 1-*Phenylazo*-2-*naphthol in t-Butylbenzene*.—1-Phenylazo-2-naphthol (0·20 g, 0·80 mmol) was dissolved in t-butylbenzene (20 ml) and the mixture heated with stirring to 50° under dry nitrogen. 4-Chlorobenzoyl nitrite (0·22 g, 1·20 mmol) in benzene (1 ml) was added dropwise over 1 min and the mixture stirred for a further 2 h. The ratios of the isomeric t-butylbiphenyls, established by g.l.c. comparison with authentic specimens (1% SE30; 138°)[8] were: 2- 20%; 3- 57%; 4- 23%. The total yield of t-butylbiphenyls was *ca*. 20%.

Decomposition of Phenylazotriphenylmethane in the Presence of 4-*Chlorobenzoyl Nitrite*.—Phenylazotriphenylmethane (0·24 g, 0·62 mmol) was added to a solution of 4-chlorobenzoyl nitrite (0·34 g, 1·86 mmol) in benzene (10 ml) at 50°, the reaction mixture being well stirred. After 1 h, sodium 2-naphthoxide (0·40 g, 2·48 mmol) in benzene containing crown ether was added. 1-Phenylazo-2-naphthol (0·021 g, 27 mol/100 mol) was isolated by dry column chromatography and had m.p. 133—134° (from ethanol).

Reaction of Pentyl Nitrite with 1-*Phenylazo*-2-*naphthol* (with Mr. R. LANDELLS).—Pentyl nitrite (0·88 g, 7·5 mmol) in benzene (10 ml) was added dropwise over 5 min to 1-phenylazo-2-naphthol (0·7 g, 2·8 mmol) in boiling benzene (90 ml). Boiling was continued under reflux for 22 h. Chromatography gave biphenyl (0·18 g), m.p. and mixed m.p. 70—71°, and unchanged azo-compound (0·35 g). The yield of biphenyl was therefore 41% (82% based on azo-compound consumed).

A control experiment using the azo-compound alone gave no biphenyl.

We are grateful to Mr. R. Landells for carrying out the last mentioned experiment and to the Carnegie Trust for the Universities of Scotland for financial support (to C. D. M.).

[4/2046 *Received, 4th October*, 1974]

---

[13] G. M. Norman, *J. Chem. Soc.*, 1912, **101**, 1913.