Trapping and Identification of Free Radicals in the Oxidation of Some Substituted Hydrazines

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Free radicals produced during treatment of substituted aroylhydrazines with sodium hydride in the presence of air have been scavenged with 2-methyl-2-nitrosopropane. The resulting stable nitroxides were examined by e.s.r. spectroscopy. A number of heterocyclic nitroxides were generated in this manner and by oxidation of heterocyclic amines with pentyl nitrite and also by oxidation of hydrazines by metallic oxides. Product analysis of some of these reactions carried out in the absence of nitrosobutane has shown a good correspondence between the structure of the trapped radical and the probable major reaction intermediates. The results provide further evidence for the versatility of the radical-scavenging (spin-trapping) technique. Phenylation by oxidation of phenylhydrazine with silver oxide in suitable solvents has been shown to be critically dependent on the concentration of phenylhydrazine in the reaction medium.

In a previous report,[1] we described how the radical-trapping technique [2] could be used to demonstrate the formation of aryl radicals during treatment of *N*-aroyl-*N'*-arylhydrazines (*N*-arylarenecarbohydrazides) with sodium hydride in the presence of oxygen. Analysis of the reaction products had previously led us to suspect a mechanism involving aryl radical intermediates. We have now extended this work to include *N*-aroyl-*N'*-methyl-, -*N'*-benzyl-, and -*N'*-pyridyl-hydrazines. The results are compared with those obtained by direct oxidation of hydrazines with inorganic reagents. The radical-trapping technique was then used to investigate the free radical intermediates in the oxidation of a variety of aryl and heterocyclic amines with pentyl nitrite.[3]

RESULTS AND DISCUSSION

Oxidation of N-*Aroyl*-N'-*arylhydrazines*.—Treatment of a solution of *N*-benzoyl-*N'*-phenylhydrazine in benzene with sodium hydride in the presence of air gave biphenyl and benzoic acid in 60—70% yields. Addition of 2-methyl-2-nitrosopropane (I) to the reaction mixture afforded an intense e.s.r. signal of phenyl t-butyl

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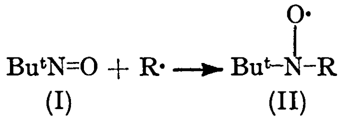
[1] R. A. W. Johnstone, A. F. Neville, and P. J. Russell, *J. Chem. Soc.* (*B*), 1971, 1183.

[2] For leading references see M. J. Perkins, ' Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.*, 1970, No. 24, ch. 5; E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

[3] Shu Huang, *Acta Chim. Sinica*, 1959, **25**, 171; J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

nitroxide (II; R = Ph) indicating the formation of free phenyl radicals in at least one reaction path.[1]



$$\mathrm{Bu^tN{=}O} + \mathrm{R\cdot} \longrightarrow \mathrm{Bu^t{-}\overset{\overset{\displaystyle O\cdot}{|}}{N}{-}R}$$

(I) (II)

In this work, similar treatment of *N*-benzoyl-*N'*-methyl- and *N*-benzoyl-*N'*-benzyl-hydrazine gave intense e.s.r. signals of the corresponding methyl t-butyl (II; R = Me) and benzyl t-butyl nitroxide (II; R = $PhCH_2$). Both nitroxides were readily identified from the characteristic hyperfine splitting patterns. However, in both cases, minor e.s.r. signals of other radicals were observed but these appeared to be secondary products (see later) and liberation of methyl or benzyl radicals appeared to be the predominant mode of reaction.

TABLE 1

Hyperfine coupling constants (mT) of the nitroxides $Bu^tN(O\cdot)R$ in benzene

Radical trapped, R·[a]	a_N nitroxide	a_H	a_N Pyridyl	a_H Ring
·Me[b,c]	1·53	1·13		
·CH_2Ph[b]	1·44	0·73		
Ph[d]	1·25			$a_{H\cdot2} = a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}19$, $a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}09$
2-Pyridyl[d]	1·02		0·23	$a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}15$, $a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}08$
3-Pyridyl	1·18		0·10	$a_{H\cdot2} = a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}14$, $a_{H\cdot5} = 0{\cdot}08$
4-Pyridyl	1·01		0·21	$a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}13$, $a_{H\cdot2} = a_{H\cdot6} = 0{\cdot}07$

[a] From reaction of the corresponding benzoylhydrazine with sodium hydride and oxygen and 2-methyl-2-nitrosopropane (except 4-pyridyl, see text). [b] Also prepared by oxidation of the corresponding benzoylhydrazine with mercuric oxide. [c] Also prepared by oxidation of the corresponding hydrazine with silver oxide. [d] Also prepared from the corresponding trifluoroacetylhydrazine.

TABLE 2

Hyperfine coupling constants (mT) of aromatic nitroxide radicals $Bu^tN(O\cdot)R$

Radical trapped, R·[a]	Method of production[b]	Solvent	a_N Nitroxide	a Other
Phenyl	A, B, C	Methanol[d]	1·33	$a_{H\cdot2} = a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}175$, $a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}085$
2,4,6-Trichlorophenyl[c,e]	A, C	Benzene	1·26	$a_H = 0{\cdot}080$, $a_{Cl} = 0{\cdot}024$
2-Pyridyl	A, B, C	Methanol[d]	1·07	$a_{N\cdot1} = 0{\cdot}23$, $a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}15$, $a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}076$
3-Pyridyl	A, B, C	Methanol[d]	1·24	$a_{N\cdot1} = 0{\cdot}11$, $a_{H\cdot2} = a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}16$, $a_{H\cdot5} = 0{\cdot}09$
4-Pyridyl	A, B	Methanol[d]	1·05	$a_{N\cdot1} = 0{\cdot}20$, $a_{H\cdot3} = a_{H\cdot5} = 0{\cdot}125$, $a_{H\cdot2} = a_{H\cdot6} = 0{\cdot}66$
Benzothiazol-2-yl[f]	B	Benzene	0·934	$a_{N\cdot3} = 0{\cdot}26$, $a_{H\cdot4} = a_{H\cdot6} = 0{\cdot}13$, $a_{H\cdot5} = a_{H,7} = 0{\cdot}02$
2-Quinolyl	B	Methanol	1·00	*h*
1-Naphthyl[g]	B	Methanol	1·40	
9-Acridyl	B	Methanol	1·35	*i*
2-Pyrimidyl	A	Benzene	0·80	*h*

[a] Trapped by 2-methyl-2-nitrosopropane. [b] A, $ArNH_2$ + pentyl nitrite in benzene; B, $ArNHNH_2$ + HgO or Ag_2O in benzene or methanol; C, ArNHNHCOPh + HgO in benzene or methanol. [c] See also ref. 1. [d] Similar results were obtained in benzene (Table 1.) [e] J. A. Pederson and K. Torssell, *Acta Chem, Scand*, 1971, **25**, 3151. [f] Also produced by photolysis of the corresponding iodide (see K. Torssell, *Tetrahedron*, 1970, **26**, 2759). [g] Also produced by oxidation of naphthyl-t-butylhydroxylamine with silver(I) oxide (see ref. 17). [h] Much fine structure resolved but coupling constants not extracted. [i] No other structure resolved.

Encouraged by these results, we prepared *N*-benzoyl-*N'*-2-pyridyl- (III) and *N*-benzoyl-*N'*-3-pyridyl-hydrazine (IV) as potentially convenient sources of 2- and 3-pyridyl radicals in synthesis. Treatment of the hydrazines (III) and (IV) in benzene with sodium hydride in the presence of air and the nitroso-compound (I) produced green solutions having strong e.s.r. signals of the nitroxides (II; R = 2-pyridyl) and (II; R = 3-pyridyl). To complete the series, t-butyl 4-pyridyl nitroxide (II; R = 4-pyridyl) was obtained by direct oxidation of 4-pyridylhydrazine with mercuric oxide. The hyperfine coupling constants are shown in Table 1.

BzNHNHR

(III) R = 2-pyridyl

(IV) R = 3-pyridyl

As expected by analogy with phenyl t-butyl nitroxide,[1] the e.s.r. spectra of the three isomeric pyridyl t-butyl nitroxides show coupling of the free electron to all ring hydrogen nuclei as well as to the ring nitrogen. The signals from the 2- and 4-pyridyl nitroxides are similar to each other but quite different from those of the 3-pyridyl nitroxide, a result in keeping with the observed couplings for *ortho*-, *meta*-, and *para*-hydrogen nuclei in the phenyl nitroxide (II; R = Ph). The same pyridyl nitroxides were also produced from other pyridyl radical progenitors (see Table 2 and later discussion).

Our attempts to produce t-butyl pyridyl nitroxides by photolysis of the corresponding iodopyridines in the presence of 2-methyl-2-nitrosopropane were unsatisfactory because of the instability of the nitroso-compound to u.v. radiation. Further, it has recently been shown that pyridyl radicals generated by this photolytic method are susceptible to ring opening.[4] E.s.r. spectra of free pyridyl or phenyl radicals have not been observed in solution but, at low temperature, spectra consisting of a limited number of ill-defined lines have been obtained;[4,5] the spectra of the trapped pyridyl radicals show much more fine structure (Figures 1—3) than the latter.

The reaction between sodium hydride and *N*-aryl-*N'*-benzoylhydrazines in the presence of oxygen produces benzoic acid in high yield. In our previous work,[1] we explained the formation of benzoic acid in terms of a

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[4] P. H. Kasai and D. McLeod, *J. Amer. Chem. Soc.*, 1970, **92**, 6085; 1972, **94**, 720.

[5] J. E. Bennett and B. Mile, *J. Phys. Chem.*, 1971, **75**, 3432.

rapid reaction between oxygen and benzoyl radicals formed by homolysis of the key intermediate azo-compound (V). It has been demonstrated that free benzoyl radicals are readily trapped and identified using 2-methyl-2-nitrosopropane.[6,7] Under reaction conditions similar to those described later in this report,

$$\underset{\text{(V)}}{\text{PhN=NCOPh}} \longrightarrow \text{Ph}\cdot + \text{N}_2 + \text{PhCO}\cdot$$

oxidation of benzaldehyde in benzene with mercuric oxide gave an intense e.s.r. signal of benzoyl t-butyl nitroxide (II; R = Bz), easily recognised from its narrowly spaced (*ca.* 0·8 mT) triplet.[6,7] If the reaction between sodium hydride and *N*-benzoyl-*N'*-phenylhydrazine had gone *via* decomposition of the intermediate azo-compound (V), then there seems no reason why the benzoyl nitroxide (II; R = Bz) should not have been observed as well as the phenyl nitroxide (II; R = Ph). For this reason, we now propose a modified reaction sequence (Scheme) which accommodates this new evidence. Rearrangement of the intermediate (VI) is analogous to work on the oxidation of 9-substituted fluorenyl anions,[8] and may be similar to the conversion of nitroso-amides to diazo-acylates.[9] Breakdown of the intermediate (VI) could produce benzoate anion directly without intervention of benzoyl radicals. As previously stated,[1] benzoate appears to arise directly from one of the reaction intermediates because methyl benzoate is not detectable when the reaction is quenched with methanol. The nitroso-compound, ArNHN=O, and its tautomer ArN=NOH, are the likely intermediates in the

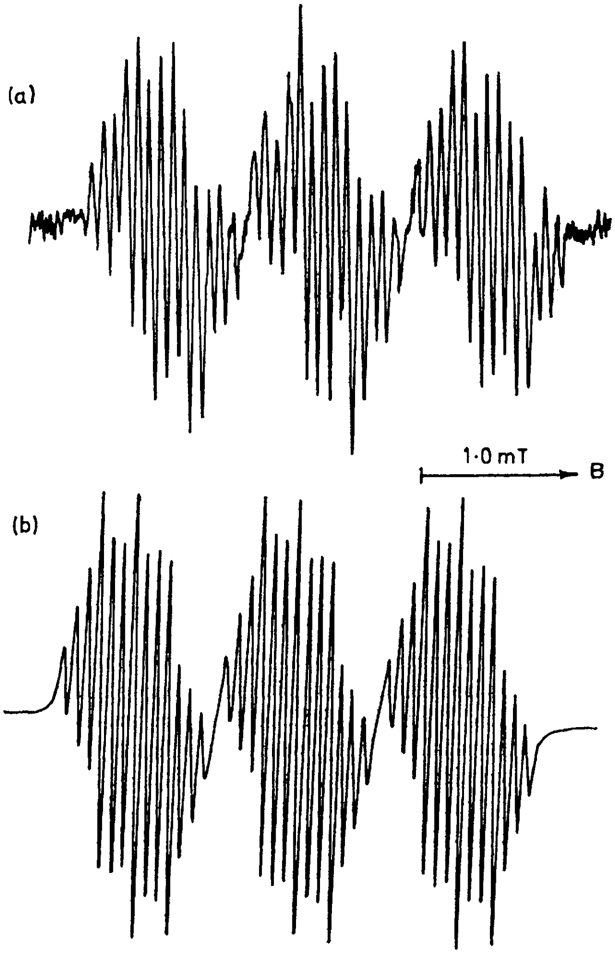

FIGURE 1 (a) E.s.r. spectrum of 2-pyridyl t-butyl nitroxide in methanol and (b) computer simulation of this spectrum

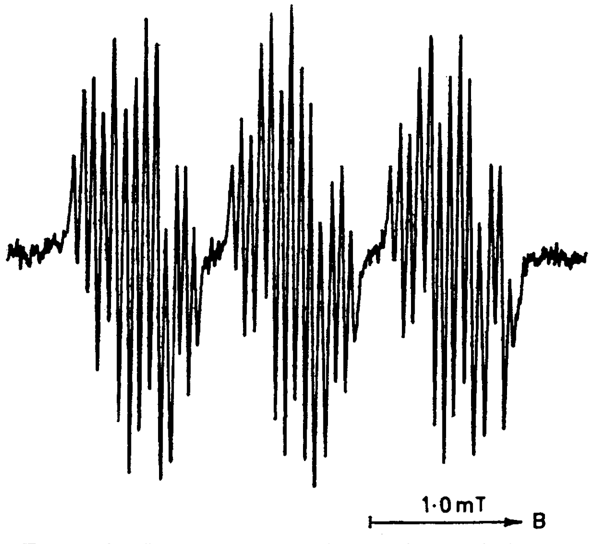

FIGURE 2 E.s.r. spectrum of 4-pyridyl t-butyl nitroxide in methanol

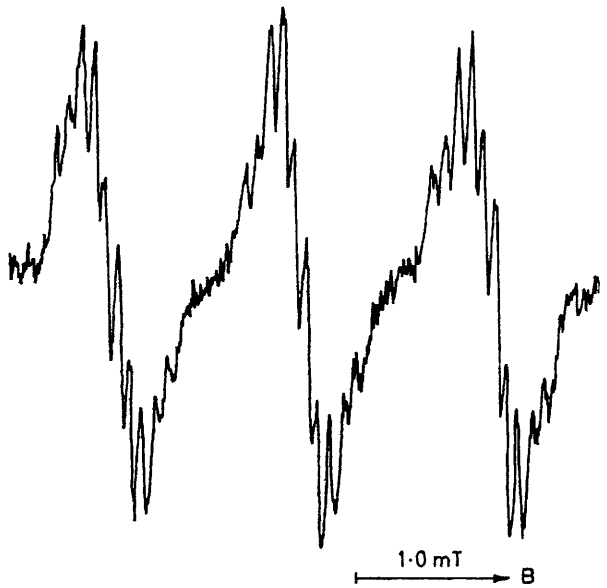

FIGURE 3 E.s.r. spectrum of 3-pyridyl t-butyl nitroxide in methanol

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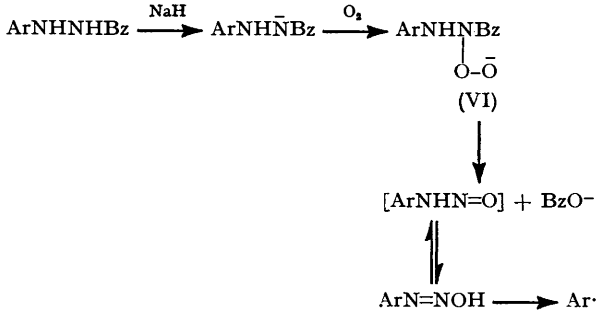
[6] A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 1968, **24**, 1623.

[7] A. Ledwith, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1972, 1925.

[8] D. Bethell, R. J. E. Talbot, and R. G. Wilkinson, *Chem. Comm.*, 1968, 1528; D. Bethell and R. J. E. Talbot, *J. Chem. Soc.* (*B*), 1968, 638.

[9] 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.*, ed. R. O. C. Norman, 1970, No. 24, ch. 2–4.

Gomberg reaction [10] and in the reaction between aromatic amines and pentyl nitrite.[3] The diazotate anion, the corresponding radical, and related species are now well-established intermediates in these arylation reactions.[9]



SCHEME

Oxidation of Aromatic Hydrazines.—Mercuric oxide has long been used for heterogeneous oxidation of hydrazines [11] and is also a convenient reagent for producing radicals from *N*-aryl-*N'*-benzoylhydrazines. Our results using this and other oxidants on substituted hydrazines and their hydrochlorides in benzene or methanol are collated in Tables 1 and 2.

Solutions of arylhydrazines in benzene or methanol were oxidised rapidly at room temperature by mercuric oxide, silver oxide, nickel peroxide, *p*-benzoquinone, or cerium(IV) ammonium nitrate and, in the presence of the radical scavenger (I), intense e.s.r. signals of the corresponding nitroxides (II) were observed. The case of cerium(IV) ammonium nitrate is notable since it indicates that 2-methyl-2-nitrosopropane can be used to study cerium(IV) oxidations, many of which are thought to involve radical intermediates.[12]

The reported yields of biphenyl from the oxidation of phenylhydrazine with mercuric oxide are low [11] and not comparable with the yields obtained from the action of sodium hydride on *N*-aroyl-*N'*-arylhydrazines. Because oxidation of phenylhydrazine with mercuric oxide is complicated by formation of some diphenylmercury, we used silver oxide, manganese dioxide, and copper(II) sulphate to study the oxidation in more detail. The results are summarised in Table 3. The yield of biphenyl is substantially increased as the concentration of phenylhydrazine is reduced and as the temperature is increased. Hardie and Thomson [11] used comparatively concentrated solutions of phenylhydrazine and obtained less than 10% of biphenyl using silver oxide. In agreement with these workers, we found silver oxide gave the highest yields and cleanest reactions and it was used in most of our subsequent experiments. The other major product of the oxidation of phenylhydrazine is benzene but the results in Table 3 do not include yields of benzene because this same substance was used as solvent. Naphthalene is a major product of the oxidation of 2-naphthylhydrazine with silver oxide in benzene.[11] To check the formation of benzene and the yield, we oxidised *N*-deuteriated phenylhydrazine with silver oxide in benzene and calculated that the yield of benzene was *ca.* 69% (see Experimental section), and this suggests that the preferred reaction pathway is abstraction of hydrogen from the hydrazino-group by the phenyl radical rather than direct attachment of the radical to the solvent benzene. This preferential attack is less marked in some substituted phenyl radicals. For example, oxidation of *p*-bromophenylhydrazine gave a 36% yield of 4-bromobiphenyl.[11] Similarly, 2,4-dinitrophenyl-hydrazine and pentafluorophenyl-hydrazine gave respectively 2,4-dinitro- (39%) [11] and 2,3,4,5,6-pentafluoro-biphenyl (*ca.* 70%).[13] It was suggested [13] that the substituted phenyl radicals formed in the above reactions were more electrophilic than phenyl radicals so that attack on the solvent benzene was more favourable. A similar effect was found in the reactions of substituted benzoyl peroxides with toluene where attack at the methyl group of toluene decreased as the electrophilic character of the substituted benzoyl peroxide increased.[14] Oxidation of a 1% solution of thiazol-2-ylhydrazine in benzene afforded 2-phenylthiazole in 12% yield, very similar to the yield of biphenyl given by phenylhydrazine (Table 3). This suggests that the electrophilic characters of the thiazol-2-yl and phenyl radical are similar.

TABLE 3

Oxidation of phenylhydrazine [a]

Run no	Volume of benzene (ml)	Oxidant [c]	Product [b] biphenyl (%)	Comment
1	0·5	S(0·5 g)	4	*d*
2	5·0	S(0·37 g)	9	*d*
3	50	S(0·53 g)	45	*d*
4	50	S(0·51 g)	55	*e*
5	50	S(0·54 g)	58	*e*
6A	50	S(0·5 g)	40	*d*
6B	50	S(0·5 g)	24	*d, f*
7	5·0	M(0·38 g)	9	*d, g*
8	50	M(0·38 g)	34	*d*
9	5·0	C(0·61 g)	5	*d*
10	50	C(0·61 g)	25	*d*

[a] Nominally 0·1 g in benzene at room temperature. [b] Azobenzene (~2%) is also formed; terphenyl was not detected; benzene is a major product (see Discussion section). [c] S = Silver oxide; M = manganese dioxide; C = copper sulphate (blue). [d] Oxidant added last. [e] Oxidant added first, phenylhydrazine in benzene added slowly to refluxing benzene. [f] In the presence of a two-fold excess of benzylidene-t-butylamine *N*-oxide. [g] Formation of biphenyl (26%) and azobenzene (3%) have been independently observed (I. Bhatnagar and M. V. George, *J. Org. Chem.*, 1968, **33**, 2407).

In view of the small concentration of phenylhydrazine in benzene during oxidation, the low yields of biphenyl indicate that attack of phenyl radicals on phenyl-

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[10] M. Gomberg and W. E. Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; M. Gomberg and J. C. Pernert, *ibid.*, 1926, **48**, 1372.

[11] R. L. Hardie and R. H. Thomson, *J. Chem. Soc.*, 1957, 2512; see also H. Ohta and K. Tokumaru, *Bull. Chem. Soc. Japan*, 1971, **44**, 3478.

[12] W. H. Richardson, 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, ch. 4; R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 6688.

[13] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 1962, 4966.

[14] J. K. Hambling, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1962, 487. For further discussion see D. I. Davies, D. H. Hey, and B. Summers, *J. Chem. Soc. (C)*, 1970, 2653.

hydrazine (or possibly a reaction intermediate) must be facile.

Alternatively, the possible intermediate phenyldiazene is known to undergo bimolecular reaction to give benzene and might be involved especially at high concentrations of phenylhydrazine and low temperatures.[15] The increased yields of biphenyl at higher dilutions rule out an intramolecular, hydrogen-transfer reaction for the formation of benzene. Control experiments showed that the increased yields of biphenyl at higher dilutions (Table 3) were due neither to extra solvent extracting product more efficiently from the heterogeneous reaction mixture, nor to the cooling effect of more solvent. Although the temperature of the solutions increased as the silver oxide was added during runs 1 and 2 of Table 3, further control experiments showed that careful addition of silver oxide to cooled solutions of phenylhydrazine actually decreased the yield of biphenyl.

When blue copper(II) sulphate was added to phenylhydrazine in benzene, it turned green, and up to 25% biphenyl was formed but, unlike the other oxidations, very few bubbles of gas were observed. Further, in the presence of the radical scavenger (I) no phenyl radicals were trapped although, in benzene or aqueous acetonitrile solution, a weak unidentified e.s.r. signal (triplet of doublets) was observed. Indirectly, this supports the proposal for the heterolytic removal of the hydrazino-function by copper(II) sulphate.[16]

Oxidation of heterocyclic hydrazines was used to produce some of the heterocyclic nitroxides listed in Table 2.

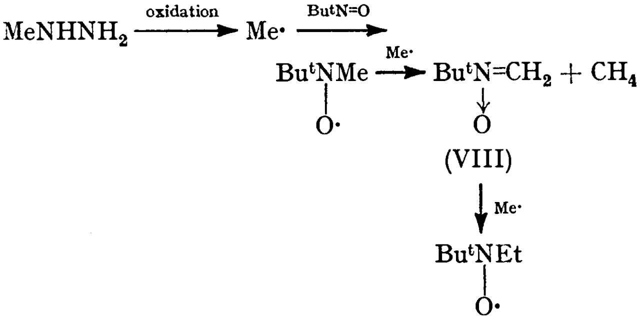
Oxidation of Aromatic Amines.—Following the success of radical scavenging with the nitroso-compound (I) under the various oxidising conditions listed above, we examined the diazotisation of aromatic amines with pentyl nitrite as a potentially more convenient source of aromatic radicals. Addition of pentyl nitrite to solutions of aromatic, particularly heterocyclic amines, afforded intense e.s.r. signals for the expected nitroxides (Table 2), and allowed us to determine the hyperfine coupling constants listed.

E.s.r. Spectra of Nitroxides (II).—The nitroxides were examined either in benzene or in methanol and usually the hyperfine coupling constants are slightly larger and the spectra better resolved in methanol than in the less polar benzene. All nine lines of the e.s.r. spectrum of benzyl t-butyl nitroxide were clearly resolved in methanol but not in benzene.

The hyperfine coupling constants to nitrogen (a_N) for the aryl t-butyl nitroxides vary from 1·40 to 0·80 mT. It is thought that larger a_N values (*e.g.* 1-naphthyl, 1·40 mT) indicates that the free electron is less delocalised than in the phenyl nitroxide (1·33 mT) because the nitroxide function is twisted out of conjugation with the aromatic ring.[17] Conversely, the smaller a_N values indicate greater electron delocalisation than for phenyl. Thus, the 2-pyridyl nitroxide (II; R = 2-pyridyl) has $a_N = 1{\cdot}07$ mT and, with two nitrogen atoms in the ring, as for the 2-pyrimidyl nitroxide (II; R = 2-pyrimidyl), the value of a_N falls to 0·80 mT. The increased delocalisation of electron density in the 2-pyridyl case compared with phenyl or 3-pyridyl seems to be reflected in the reaction products. Oxidation of phenylhydrazine with mercuric oxide in benzene yields little diphenylmercury but a relatively large amount of biphenyl. In contrast, similar oxidation of 2-pyridylhydrazine gives a large amount of di-2-pyridylmercury but very little 2-phenylpyridine. These effects may be due to the reduced electrophilicity of the 2-pyridyl radical compared with the phenyl radical.

The coupling constants given in Tables 1 and 2 are difficult to extract by inspection and were obtained with the aid of computer simulations of the spectra. Actual and simulated spectra for some of the nitroxides are shown in Figures 1—3.

During the trapping of methyl radicals in the oxidation of methylhydrazine with either metallic oxides or cerium(IV) salts, we observed the characteristic 12 line spectrum (triplet of 1 : 3 : 3 : 1 quartets) of methyl t-butyl nitroxide together with other signals which increased in intensity with increasing concentration of reactants. The extra signals comprising a triplet of 1 : 2 : 1 triplets with $a_N = 1{\cdot}54$, $a_H = 1{\cdot}02$ mT corresponded to the minor signals observed in the spin-trapping experiments with *N*-benzoyl-*N'*-methylhydrazine and sodium hydride. Within experimental error, the minor signals are identical with those of t-butyl ethyl nitroxide ($a_N = 1{\cdot}52$, $a_H = 1{\cdot}04$ mT).[18] Based on related observations by Perkins *et al.*[19] we suggest a similar explanation for the formation of the ethyl nitroxide. Methylene-t-butylamine *N*-oxide (VIII) is an efficient scavenger of short-lived radicals.[19,20]



Conclusions.—The variety of oxidants and experimental conditions used in these experiments further

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[15] P. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, 1968, **90**, 2367.

[16] K. Schofield and T. Swain, *J. Chem. Soc.*, 1950, 392; H. E. Baumgarten and H. Chien-Fan Su, *J. Amer. Chem. Soc.*, 1952, **74**, 3828.

[17] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London and New York, 1968, p. 210.

[18] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395.

[19] G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401.

[20] N. H. Anderson and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1971, 993.

establishes the versatility of this radical-trapping technique as a guide to reaction mechanisms. In these studies, the intermediate radicals trapped by the scavenger give intense e.s.r. spectra and, from product studies, appear to be formed along the main reaction path. Hyperfine coupling constants have been obtained for a variety of aromatic nitroxides.

The previously reported[11] low yield of biphenyl from the oxidation of phenylhydrazine in benzene is probably due to the competitive formation of more benzene by bimolecular reaction(s). By minimising the concentration of phenylhydrazine, yields of biphenyl up to 60% can be obtained. In dilute solution, phenylhydrazine appears to be an efficient and reliable source of phenyl radicals.

EXPERIMENTAL

All the substances used in this study were checked by n.m.r. (Varian A60 or HA100) and mass spectrometry[21] (A.E.I. MS 12 and MS 902). M.p.s are uncorrected. E.s.r. spectra (Varian V4500 or E4) were obtained with 100 kHz modulation and X-band frequency microwaves; the field sweep was calibrated with alkaline aqueous solutions of potassium nitrosodisulphonate having $a_N = 1{\cdot}309$ mT and $g = 2{\cdot}0055$. The g factors of the nitroxides studied were all in the range 2·005—2·006. The synthesis and use of 2-methyl-2-nitrosopropane have been described previously.[1,7,22] Simulations of e.s.r. spectra were made with the aid of a KDF 9 computer.[23]

Preparations.—*N*-Benzoyl-*N'*-methylhydrazine prepared from methylhydrazine and methyl benzoate,[24] had m.p. 84·5—86° (lit.,[24] 86—88°). *N*-Benzoyl-*N'*-benzylhydrazine obtained by reduction (5% Pd–C and hydrogen) of benzylidenebenzoylhydrazine had m.p. 113—115° (lit.,[25] 115°). 2-Pyridylhydrazine was obtained from 2-chloropyridine[26] and converted into *N*-benzoyl-*N'*-2-pyridylhydrazine, m.p. 194—197° (lit.,[27] 193°), by treatment with benzoyl chloride in pyridine.[27] N-2-*Pyridyl*-N'-*trifluoroacetylhydrazine* was prepared by addition of trifluoroacetic anhydride (11·2 ml) to 2-pyridylhydrazine (5·56 g) in ether (50 ml) at 0°. The solid which separated was treated with excess of aqueous sodium hydrogen carbonate and extracted with ether to give a yellow solid (9·1 g); the latter, purified by sublimation at 100° and 1 mmHg, had m.p. 144—146° (Found: C, 40·9; H, 2·7; N, 20·4. $C_7H_6N_3F_3O$ requires C, 40·9; H, 2·9; N, 20·5%). 3-Pyridylhydrazine was prepared from 3-aminopyridine.[28] 3-Pyridylhydrazine (1 mol. equiv.) with benzoic anhydride (1 mol. equiv.) in ether at 0° containing a suspension of potassium carbonate after 0·5 h gave N-*benzoyl*-N'-3-*pyridylhydrazine*, m.p. 114—116° (from ethanol–water). After sublimation at 130° and 1 mmHg, a white solid, m.p. 172—176°, was obtained. The i.r. and n.m.r. spectra of the two samples were identical and the higher melting form was obtained also on treatment of 3-pyridylhydrazine with benzoyl chloride in pyridine (Found: C, 67·2; H, 5·2; N, 19·9. $C_{12}H_{11}N_3O$ requires C, 67·6; H, 5·2; N, 19·7%). 4-Pyridylhydrazine hydrochloride was prepared by heating 4-chloropyridine with hydrazine hydrate in n-propanol in a sealed tube at 100° for 12 h.[29] After cooling, the solid was filtered to give the hydrochloride, m.p. 247—251° (lit.,[30] 242—243°).

Product Studies.—The products of oxidation of phenylhydrazine have been identified previously[1,11] and, in this study, their amounts were estimated by g.l.c. of the crude reaction mixture. In the cases of the pyridylhydrazines, the major reaction products in benzene were pyridine, pyridylbenzenes, and bipyridyls.

Chromatography was carried out on a 5 ft × ¼ in column of 3% O.V.1 at 170° using n-hexadecane as an internal standard. Azobenzene had almost the same retention time as n-hexadecane and so was estimated by leaving out the standard and comparing the peak area for azobenzene with that of biphenyl. No peaks corresponding to terphenyls were observed in these oxidations. Pyridine was determined by g.l.c. at 80°.

Phenylhydrazine (0·8 g) was treated for 5 days with $[^2H]$methanol (5 ml) to give a mixture containing mostly $[^2H_3]$- and $[^2H_2]$-phenylhydrazine ($^2H : {^1H} = 2{\cdot}38 : 1$ on hydrazino-group, by mass spectrometry). To the mixture of deuteriated phenylhydrazines (0·091 g) in benzene (0·396 g) was carefully added silver oxide (0·56 g). The solution became warm, nitrogen was evolved and, at the end of the experiment, the total weight of reaction mixture was 0·05 g less than expected; presumably a small quantity of benzene had been lost by evaporation. The benzene remaining at the end of the reaction was examined by mass spectrometry ($C_6H_6 : C_6H_5{^2H} = 24 : 2{\cdot}1$ after allowing for ^{13}C isotopes).

In a typical experiment, 2-pyridylhydrazine was dissolved in benzene and treated with mercuric oxide. The mixture was warmed until reaction appeared to have ceased (no gas evolution) and, on working up the mixture, di-2-pyridylmercury (33%), 2-phenylpyridine (5%), 2,2'-dipyridyl (12%), and pyridine (25%) were obtained; the yields are only representative since they vary considerably with reaction conditions (see earlier discussion on phenylhydrazine oxidation). Similar results were obtained with 3- and 4-pyridylhydrazine. With 3-pyridylhydrazine, a small amount of 3,3'-azopyridine was produced.

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