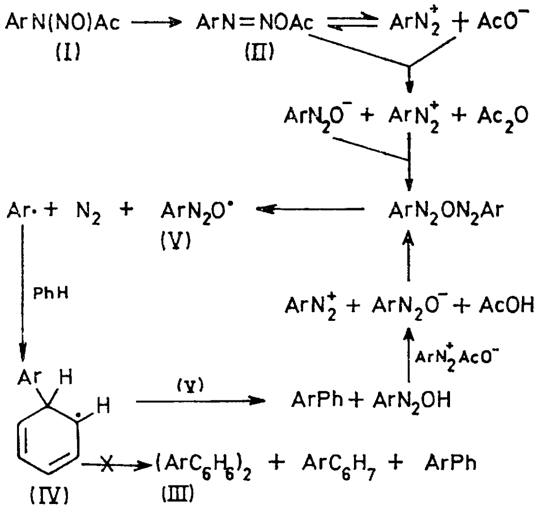
# Acylarylnitrosamines. Part I. Electron Spin Resonance Studies Relevant to the Mechanism of Decomposition of Acylarylnitrosamines in Various Solvents.†

By **J. I. G. Cadogan,***‡ **R. M. Paton,** and **C. Thomson,** Department of Chemistry, The University, St. Andrews, Scotland

An e.s.r. spectroscopic investigation of a wide series of acylarylnitrosamines in several series of solvents has been carried out. In general the signals were either, or both, of two types: those of the PAPN type [ArN(NAr·Acyl)·O·], and in this Chalfont and Perkins' assignment of structure is confirmed, and those of the (phenylazo)oxyl $\sigma$-radical type (PhNNO·). These assignments have been established by study of the effect of variation of substituents on the resulting spectra, by theoretical calculations and by computer simulation in selected cases. The constancy of appearance of the (phenylazo)oxyl radical compared with the absence of PAPN in some cases (*e.g.* mesitylene) but not in others (*e.g.* benzene) suggests that the former is the more significant chain carrying radical in the decomposition of acylarylnitrosamines in such solvents. It is also concluded that electron transfer involving the diazonium cation and the intermediate arylcyclohexadienyl radical cannot be ruled out as a key step in the decomposition. The identification and mechanistic significance of other signals observed in ether and cumene are discussed.

The behaviour of acylarylnitrosamines (I) in solution has been a series of puzzles, for some seventy years.[1] It is now well established that aryl radicals are involved [2] and that these arise *via* the diazoacylate (II) [3] which is in equilibrium with the diazonium acylate ion pair.[4] It is also known that aryl radicals do not arise *via* simple homolysis of the diazoacylate because this would also give an acyloxyl-radical, and hence carbon dioxide, rather than the high yield of carboxylic acid (>90%) which is observed. The reaction products are often very tarry but tetrahydroquaterphenyls (III) or dihydrobiaryls, which might have been expected to have arisen *via* dimerisation of the first-formed cyclohexadienyl radicals (IV) are not formed (Scheme 1).[5] Various explanations in terms of 'cage' reactions of phenyl radicals have been shown to be untenable; the results point to the participation of free phenyl radicals.[5]



Scheme 1

In 1964, Rüchardt and Freudenberg produced [6] an elegant and apparently complete explanation of the reaction (Scheme 1) the key step of which involved a stable (phenylazo)oxyl $\pi$-radical, ArN=N–O· (V), capable of abstracting a hydrogen atom and thus cleanly oxidising arylcyclohexadienyl to biaryl. Another satisfactory feature of the mechanism involved the formation of the carboxylic acid by a chain process from acylate ions, known to be present,[4] and not from the unstable acyloxyl-radical. The mechanism required that trace amounts, only, of acetic anhydride should be formed.

The mechanism was supported by the observation of a long-lived e.s.r. spectral signal (Figure 1),[7] believed to correspond to the (phenylazo)oxyl $\pi$-radical (V). Further, it was claimed that this assignment was supported by McLachlan MO calculations.[7,8] A more detailed investigation by use of $^{15}N$ labelled materials [9] disclosed a discrepancy however; contrary to predictions (McLachlan) the results assigned the major splitting ($a_N = 11{\cdot}61$ gauss) to the nitrogen (2) and not to nitrogen (3) in $PhN^3{=}N^2{-}O^\bullet$. The rationalisation of the discrepancy assumed large contributions from the spin density on neighbouring atoms.

This apparently satisfactory explanation for the e.s.r. signal and, subsequently, the Rüchardt and Freudenberg mechanism, was brought into question by the suggestion by Hey, Perkins, and colleagues [10] that the observed e.s.r. signal was that of *N*-phenylacetamido

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† Preliminary communications: J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Comm.*, 1969, 614; 1970, 229.

‡ *Present address:* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ.

[1] J. I. G. Cadogan, in 'Essays on Free Radical Chemistry,' ed. R. O. C. Norman, *Chem. Soc. Special Publ.*, 1970, **24**, 71.

[2] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon Press, London, 1960.

[3] R. Huisgen and H. Nakaten, *Annalen*, 1951, **573**, 181; D. H. Hey, J. Stuart-Webb, and G. H. Williams, *J. Chem. Soc.*, 1952, 4657.

[4] P. Miles and H. Suschitzky, *Tetrahedron*, 1962, **18**, 1369; H. Suschitzky, *Angew. Chem. Internat. Edn.*, 1967, **6**, 596.

[5] E. L. Eliel and J. G. Saha, *J. Amer. Chem. Soc.*, 1964, **86**, 3581.

[6] C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 1964, 3623.

[7] G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, 1966, **88**, 173.

[8] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

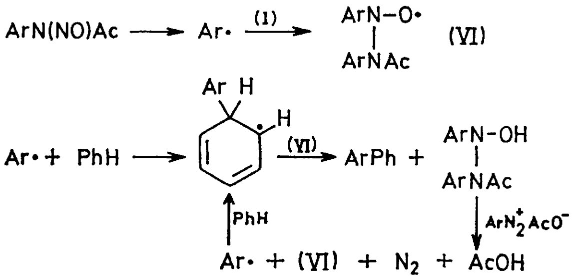
[9] G. Binsch, E. Merz, and C. Rüchardt, *Chem. Ber.*, 1967, **100**, 247.

[10] G. Chalfont, M. J. Perkins, D. H. Hey, and K. S. Y. Liang, *Chem. Comm.*, 1967, 367.

phenyl nitroxide (PAPN) (VI; Ar = Ph) produced by scavenging of a phenyl radical.

$$\text{Ph}\cdot + \text{PhN(NO)Ac} \longrightarrow \text{(PhNAc)PhNO}\cdot$$

This was supported by the production of identical signals from synthetic PAPN and from *N*-nitrosoacetanilide in benzene,[11,12] and led to the suggestion of a new mechanism for the decomposition of *N*-nitrosoacetanilide * (Scheme 2), very similar to that in Scheme 1



SCHEME 2

but differing in that the nitroxide PAPN (VI; Ar = Ph) was the key chain-carrying radical rather than the (phenylazo)oxyl (V; Ar = Ph). A weakness in Scheme 2, however, involved the fact that it required initiation by a phenyl radical, produced by direct homolysis of the diazoacylate.

In view of the confliction between Schemes 1 and 2 we have reinvestigated the decomposition of a series of acylarylnitrosamines in a wide range of solvents with particular emphasis on the e.s.r. signals so produced.

## EXPERIMENTAL

*Preparation of Acylarylnitrosamines*.—These were prepared by nitrosation of the corresponding acylarylamines which, with exceptions recorded below, were common materials and had the correct literature constants. The method of France, Heilbron, and Hey [13] (A) was used in the case of soluble acylarylamines and that of Miles and Suschitzky [4] (B) for sparingly soluble cases. The results are summarised in Table 1.

N-*Nitroso*[1-$^2$H]*formanilide*. [1-$^2$H]Formanilide (m.p. 47—49°) was prepared from aniline and [$^2H_2$]formic acid (99% min. $^2$H) and showed no $^1$H n.m.r. absorption at $\tau$ 1·64 and had i.r. spectral absorptions at 2200 and 2160 cm$^{-1}$, due to C–$^2$H stretching modes. The mass spectrum showed 97·5% deuteriation (*m*/*e* 122 : 121). The product was nitrosated in the absence of acid as follows: a solution of [1-$^2$H]formanilide (0·05 g, 0·0041 mol) in a mixture of anhydrous ether (9 ml) and anhydrous pyridine (0·37 g, 0·0041 mol) was stirred at 0°. Nitrosyl chloride (0·30 g, 0·0046 mol) as a 25% solution in ether was added over 10 min, and stirring was continued for a further hour. The white precipitate of pyridine hydrochloride was removed by filtration through cold apparatus and the filtrate was distilled at room temperature and 20 mmHg pressure to remove ether. Unchanged pyridine was evaporated off at 0·05 mmHg to leave *N*-nitroso[1-$^2$H]formanilide (62%), as an unstable yellow-brown solid, m.p. 44—47° (decomp.).

The i.r. spectrum indicated incomplete nitrosation of the amide and partial conversion of the nitrosamide to a diazonium salt: 3280—3160 (complex, w, NH), 2290 (m, $-\overset{+}{\mathrm{N}}{\equiv}\mathrm{N}$), 2200 (br, m, C–$^2$H formyl), 1735 (s, C=O of nitrosamide), 1670 cm$^{-1}$ (m, C=O of un-nitrosated amide). The nitrosamide decomposed rapidly at room temperature and was stored over solid carbon dioxide, in the dark. Under the latter conditions, generally, the acylarylnitrosamines were stable for up to six weeks, the i.r. and e.s.r. spectra being indistinguishable from freshly prepared compounds. Decomposition was detected by the appearance of the diazonium $ArN_2^+$ absorption at 2300 cm$^{-1}$.

TABLE 1

Preparation of *p*-$R^1\cdot C_6H_4\cdot N(NO)\cdot COR^2$

| $R^1$ | $R^2$ | Method | Yield (%) | M.p. (decomp.) |
|---|---|---|---|---|
| H | H | A | 46 | 45—46° (lit.,[a] 45—46) |
| Bu$^t$ | H | B | 78 | 30—32 |
| Me | Me | A | 86 | 73 (lit.,[b] 73) |
| Bu$^t$ | Me | A | 92 | 57—57·5 (lit.,[c] 57) |
| $NO_2$ | Me | B | 72 | 70 (lit.,[a] 68—70) |
| $CO_2Et$ | Me | A | 90 | 53 |
| H | Et | A | 83 | 49—50 (lit.,[a] 53) |
| H | Pr$^i$ | B | 58 | 32—33 (lit,.[a] 35) |
| Me | H | B | 90 | 71—72 (lit.,[d] 83—84) |
| Cl | H | B | 88 | 71 (lit.,[b] 71) |

[a] Ref. 3. [b] Ref. 4. [c] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 3352. [d] J. W. Haworth, and D. H. Hey, *J. Chem. Soc.*, 1940, 361.

*Purification of Solvents*.—Benzene was distilled and dried over sodium. Toluene, ethylbenzene, cumene, mesitylene, *p*-xylene, and t-butylbenzene were distilled, dried over sodium, and passed down an alumina column immediately before use. Alcohols were boiled under reflux over calcium hydride, fractionally distilled, and stored over molecular sieve. Pyridine was distilled and dried (KOH). Ethers were distilled and dried over sodium. Furan was distilled and passed down an alumina column immediately before use. 2,6-Dimethylfuran was treated similarly and stored at −10°. Carbon tetrachloride was dried over calcium chloride and fractionally distilled.

*E.s.r. Spectroscopy*.—*Instrumentation*. Spectra were obtained by use of a Decca X3 spectrometer, with a Newport Instruments 11-inch magnet system. Simple detection with 100 kHz magnetic field modulation was used throughout. The manufacturer's specifications state a klystron frequency of 9270·4 MHz (microwave *X*-band) and magnetic field homogeneity of 20 mG. Spectra were recorded at room temperature, unless otherwise stated, and then the temperature was controlled by means of a Decca variable-temperature cavity insert.

Simulations of e.s.r. spectra were carried out on an IBM 360/44 computer by use of the IBM 1327 plotter. The programme used was a modified version of Programme QCPE83, obtained from Quantum Chemistry Programme Exchange, Indiana University.

*Procedure*.—Solutions of known concentration ($\leqslant$250

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* *N*-nitrosoacetanilide in this paper is referred to as NNA.

[11] G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 1967, **89**, 3054.

[12] A. R. Forrester, *Chem. and Ind.*, 1968, 1483; S. Terake and R. Konaka, *J. Amer. Chem. Soc.*, 1969, **91**, 5655.

[13] H. France, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 1940, 369.

mg/ml) of the acylarylnitrosamine were examined in a quartz tube. Wherever possible, 5 mm (i.d.) tubes were used, but with polar solvents it was necessary to use 3 mm tubes. Evolution of nitrogen during the decomposition and the formation of tarry products prevented recording of the spectra over long periods of time in some cases, but for most compounds the spectra were monitored for more than 30 min. A number of decompositions were carried out in degassed solvents with results indistinguishable from non-degassed solvents, which were used in the studies reported here.

TABLE 2

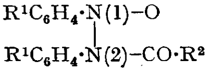
Splitting constants, linewidths, and *g*-value of the PAPN radical from *N*-nitrosoacetanilide in various solvents

| Solvent | $a_N$ | $a_N$ | $a_{o-H}$ | $a_{m-H}$ | $a_{o,p-H}$ | $\Delta H_{\frac{1}{2}}$/G | $g$ |
|---|---|---|---|---|---|---|---|
| PhH | 11·62 | 1·67 | 2·73 | 0·89 | 2·60 | 0·30 | 2·0053 |
| PhBu$^t$ | 11·51 | 1·67 | 2·73 | 0·89 | 2·60 | 0·30 | 2·0053 |
| MeOH | 11·90 | 1·67 | 2·73 | 0·89 | 2·60 | 0·25 | 2·0052 |
| EtOH | 11·84 | 1·67 | 2·73 | 0·89 | 2·60 | 0·25 | 2·0053 |
| PrOH | 11·75 | 1·67 | 2·73 | 0·89 | 2·60 | 0·30 | 2·0053 |
| EtBr | 11·72 | 1·69 | 2·74 | 0·89 | 2·62 | 0·25 | 2·0053 |
| Me$_2$CO | 11·87 | 1·69 | 2·75 | 0·89 | 2·62 | 0·30 | 2·0053 |
| Furan * | 11·80 | 1·69 | 2·75 | 0·89 | 2·62 | 0·30 | 2·0053 |
| Pyridine | 11·77 | 1·68 | 2·74 | 0·89 | 2·61 | 0·30 | 2·0053 |

* No signal of any type was detected in 2,5-dimethylfuran at 400 mg/ml.

TABLE 3

Hyperfine splitting constants of substituted PAPN radicals in different solvents



$$\begin{array}{l}R^1C_6H_4{\cdot}N(1){-}O\\ \quad\quad\quad\;\;|\\ R^1C_6H_4{\cdot}N(2){-}CO{\cdot}R^2\end{array}$$

| R$^1$ | R$^2$ | Solvent | $a_{N(1)}$ | $a_{N(2)}$ | $a_{o-H}$ | $a_{o'-H}$ | $a_{m-H}$ | $a_R$ | $\Delta H_{\frac{1}{2}}$ | $g$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Bu$^t$ | Me | PhH | 11·73 | | | | | | 0·32 | 2·0052 |
| | | MeOH | 12·02 | | | | | | | |
| | | EtOH | 11·91 | | | | | | | |
| | | PrOH | 11·88 | | | | | | | |
| | | BuOH | 11·86 | | | | | | | |
| | | C$_5$H$_{11}$OH | 11·86 | | | | | | | |
| | | Bu$^t$OH | 11·82 | | | | | | | |
| | | C$_5$H$_5$N | 11·88 | 1·71 | 2·73 | 2·59 | 0·90 | | 0·30 | 2·0052 |
| MeO | Me | PhH | 12·30 | 1·60 | 2·75 | 2·75 | 0·78 | 0·39 | 0·20 | 2·0052 |
| NO$_2$ | Me | C$_5$H$_5$N | 12·44 | | | | | | | 2·0051 |
| | | C$_5$H$_5$N | 10·59 | 1·57 | 2·59 | 2·59 | 0·90 | 0·65 | 0·25 | 2·0056 |
| Me | Me | PhH | 11·94 | | | | | | | 2·0052 |
| | | C$_5$H$_5$N | 11·95 | 1·65 | 3·0 | 3·0 | 0·95 | 2·90 | 0·40 | 2·0052 |
| CO$_2$Et | Me | PhH | 10·70 | | | | | | | |
| | | C$_5$H$_5$N | 11·04 | 1·66 | 2·58 | 2·58 | 0·92 | | 0·34 | 2·0054 |
| H | H | PhH | 11·65 | | | | 0·89 | | | 2·0053 |
| | | C$_5$H$_5$N | 11·76 | 1·25 | (2·6) | (2·6) | 0·89 | 3·12 | 0·40 | |
| Bu$^t$ | H | C$_5$H$_5$N | 11·85 | | | | 0·89 | | 0·37 | 2·0053 |
| H | D | PhH | 11·65 | | | | 0·89 | 0·48 | | 2·0053 |
| H | Et | PhH | 11·64 | 1·67 | 2·74 | 2·61 | 0·89 | 2·61 | | 2·0053 |
| | | C$_5$H$_5$N | 11·80 | 1·68 | 2·75 | 2·62 | 0·90 | 2·62 | | 2·0053 |
| H | Pr$^i$ | PhH | 11·70 | | | | | | | 2·0053 |
| H | Ph | C$_5$H$_5$N | 12·08 | 1·40 | 2·79 | 2·79 | 0·94 | 2·79 | 0·38 | 2·0052 |

*Determination of Splitting Constants, g-Values, and Linewidths.*—Measurements were made by comparison with a saturated sodium carbonate solution of Fremy's salt (potassium nitrosodisulphonate) for which $a_N = 13{\cdot}091 \pm 0{\cdot}004$ gauss, and $g = 2{\cdot}00550 \pm 0{\cdot}00005$. A sealed capillary tube containing this solution was either placed inside, or attached to the outside, of the sample tube. The estimated accuracy in the quoted *g*-values is ±0·0001. Linewidth measurements were measured peak to peak on the non-overlapped lines on the outside of the spectra. The results are summarised in Table 2—4.

*Description of E.s.r. Spectra of Acylarylnitrosamines in Various Solvents.*—Depending on the nature of the reactants either, or both, of two types of signal were obtained in most cases. For reasons discussed below these were assigned structures related to *N*-phenylacetamido phenyl nitroxide (VI; Ar = Ph) (PAPN) or (phenylazo)oxyl($\sigma$) (PhN⁚NO•) (V; Ar = Ph).

(i) *Decomposition of* N-*Nitrosoacetanilide in Aromatic Hydrocarbons.*—(a) *Benzene.* By use of a concentration of 130 mg/ml and 100 kHz modulation amplitude (mod.) varying between 0·23 and 0·023 gauss, the intense signal reported by Rüchardt,[7,9] and assigned by Chalfont and Perkins[11] to the *N*-phenylacetamido phenyl nitroxide (PAPN) radical, was observed. The signal, which was still detectable after two days, is shown is Figure **1**.

When a more concentrated solution (250 mg/ml) in a mod. of 1·27 gauss were used a second weak signal, superimposed on the first and not reported by previous workers was observed. This signal, consisting of a triplet of triplets, which decayed rapidly until it was undetectable after 30 min, can be seen in Figure 2 straddling the intense

TABLE 4

Hyperfine splitting constants of (arylazo)oxyl radicals ($p$-RC$_6$H$_4$–N(2)–N(1)–O)

| R | Solvent | $a_{N(1)}$ | $a_{N(2)}$ | $g$ |
|---|---|---|---|---|
| H | PhH | 30·7 | 2·30 | 2·0017 |
| | CCl$_4$ | 30·6 | 2·31 | |
| Bu$^t$ | PhEt | 30·5 | 2·35 | |
| | CCl$_4$ | 30·5 | 2·39 | 2·0016 |
| | BrCCl$_3$ | 30·6 | 2·39 | 2·0015 |
| MeO | PhPr$^i$ | 30·6 | 2·36 | |
| NO$_2$ | PhPr$^i$ | 31·0 | 2·41 | 2·0014 |
| Me | PhPr$^i$ | 30·7 | 2·30 | |
| CO$_2$Et | PhPr$^i$ | 30·9 | 2·33 | 2·0014 |

*N*-phenylacetamido phenyl nitroxide (PAPN) signal. It was assigned to the (phenylazo)oxyl radical.

(b) *Mesitylene, toluene, ethylbenzene,* p-*xylene, cumene, and t-butylbenzene.* In the case of mesitylene, by use of a concentration of 250 mg/ml and 1·27 gauss modulation the PAPN signal was very weak, while that of the (phenylazo)-oxyl radical was weak, but now entirely discernable (Figure 3). For 0·23 gauss modulation no signal was detected.

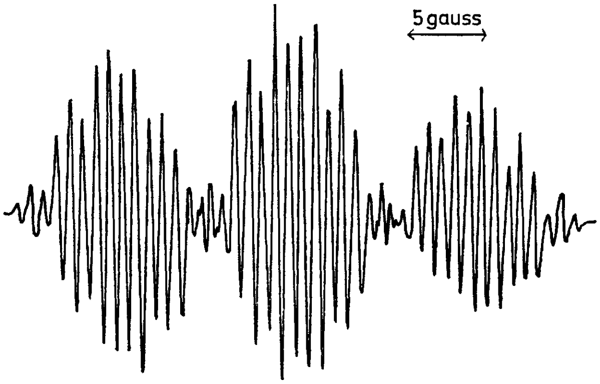


FIGURE 1 Signal from NNA in benzene, apparently due to PhNAc·NPh·O· (modulation amplitude 0·04 gauss)

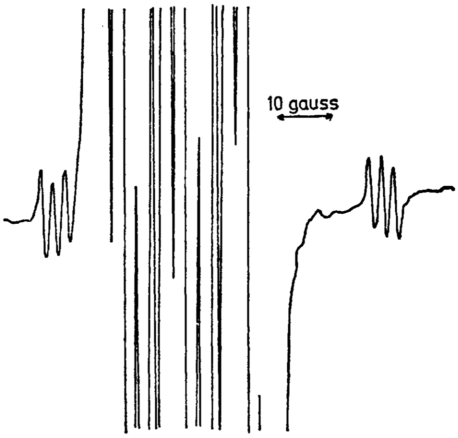


FIGURE 2 Remodulated signal recorded in Figure 1, showing the presence of PhNNO· (modulation amplitude 1·3 gauss)

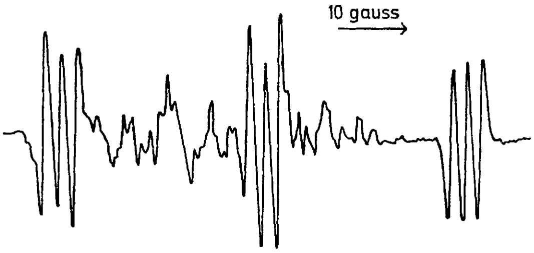


FIGURE 3 Signal due to PhNNO· from NNA in mesitylene (modulation amplitude 1·3 gauss)

During the course of the decomposition a gelatinous precipitate was formed; after 20 min this had occurred sufficiently to trap bubbles of the nitrogen gas evolved in the reaction. The resultant detuning of the spectrometer prevented further study.

In cumene (250 mg/ml; mod. 1·27 gauss) (Figure 4) the signal consisted of a weak (phenylazo)oxyl signal and a further weak triplet (1 : 1 : 1 intensity). At 0·23 gauss modulation only the latter was detected.

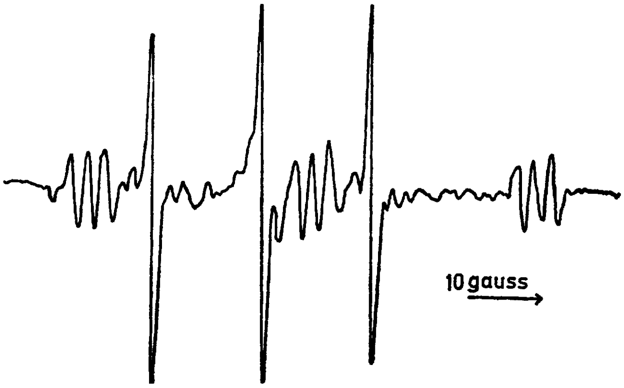


FIGURE 4 NNA in cumene

In t-butylbenzene the signal was essentially identical with that produced in benzene. These and the results obtained in the remainder of the aromatic hydrocarbons studied are summarised in Tables 2, 3, and 4.

(c) *Other solvents.* In methanol, ethanol, and propanol (130 mg/ml), only the PAPN signal was detected.

In diethyl ether the dominant signal at 250 mg/ml was PAPN with a second, superimposed, signal, which became dominant at 130 mg/ml. A similar signal was obtained by use of *N*-nitroso-*p*-t-butylacetanilide (Figure 5). In carbon tetrachloride, using a concentration of 130 mg/ml and 0·23 gauss modulation, no signal was detected. At 200—400 mg/ml and 1·27 gauss modulation a 1 : 1 : 1 triplet of 1 : 1 : 1 triplets (PhNNO) indistinguishable from that found for the aromatic hydrocarbon solvents, was observed. The signal was weak and lasted about 30 min. At the outset the PAPN signal could not be detected but after about 15 min a very weak 1 : 1 : 1 broad triplet appeared superimposed on the triplet of triplets: the separation of the broad lines was about 12 gauss, but the signal could not be resolved further.

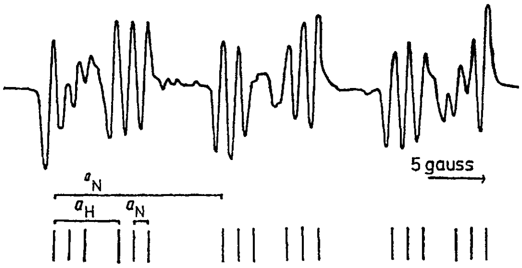


FIGURE 5 *p*-Bu$^t$NNA in diethyl ether with reconstructed spectrum

The precipitation of solids during the course of the decomposition prevented spectra being recorded after *ca.* 30 min. In bromotrichloromethane and 1,1,2,2-tetrabromomethane a weak PhNNO signal only was detected (30 min duration) and in methylene chloride and ethyl bromide a weak PhNNO (15 min) and a strong PAPN signal (several h) were detected. In hexafluorobenzene both PAPN and PhNNO signals were detected. After 30 min both were replaced by an intense single line of width 15 gauss, which could not be resolved. In pyridine the PhNNO radical was not detected and in 2,5-dimethylfuran no signals were detected at 400 mg/ml.

(ii) *Decompositions of substituted* N-*nitrosoacetanilides*. The results are summarised in Tables 2, 3, and 4. In most cases signals corresponding to those from *N*-nitrosoacetanilide were produced.

## DISCUSSION

The conflicting views, represented by Schemes 1 and 2, on the mechanism of the decomposition of *N*-nitrosoacetanilide in solution differ mainly in the assignment of structure to the radical giving rise to the observed e.s.r. signal in benzene. In a comprehensive attempt to resolve these views we have investigated the decomposition of a series of acylarylnitrosamines in a series of solvents. In all cases, except 2,5-dimethylfuran, which will be the subject of a separate communication, e.s.r. signals were observed. In general these were either, or both, of two types: the PAPN type [ArN(NAr·Acyl)·O·] (VI), or the (arylazo)oxyl type (ArNNO) (V). In certain cases additional or alternative signals attributable to other radicals were detected. The results are qualitatively summarised in Table 5 and the evidence on which the assignments are based is discussed below.

TABLE 5

Summary of signals detected on decomposition of acylarylnitrosamines (ANNA) in various solvents

| ANNA ‡ | Solvent | PAPN * type | PhNNO * type | Other * signals |
|---|---|---|---|---|
| 1, 2, 6, 10, 11 | PhH | + | + | — |
| 1 | PhMe | + | + | — |
| 1, 2 | PhEt | + | + | — |
| 1—6, 10, 11 | $PhPr^i$ | — | + | + |
| 1 | $PhBu^t$ | + | + | — |
| 1 | *s*-$Me_3C_6H_3$ | + | + | — |
| 1 | *p*-$Me_2C_6H_4$ | + | + | — |
| 1 | Furan | + | + | — |
| 1—8, 10—14 | $C_5H_5N$ | + | — | — |
| 1 | $C_6F_6$ | + | + | + |
| 1, 2 | MeOH | + | — | — |
| 1, 2 | EtOH | + | — | — |
| 1, 2 | PrOH | + | — | — |
| 2 | BuOH | + | — | — |
| 2 | $Bu^tOH$ | + | — | — |
| 2 | *n*-$C_5H_{11}OH$ | + | — | — |
| 1, 2 | $Et_2O$ | + | — | + |
| 1 | $C_4H_8O$ | + | — | + |
| 1 | $(MeOCH_2)_2$ | + | — | + |
| 1 | $Me_2CO$ | + | + | — |
| 1 | EtBr | + | + | — |
| 1 | $CCl_4$ | + | + | — |
| 1 | $BrCCl_3$ | — | + | — |
| 1 | $CH_2Cl_2$ | + | + | — |
| 1 | $(Br_2CH)_2$ | — | + | — |
| 1 | 2,5-$Me_2$-furan | — | — | — |
| 2 | $CCl_4$ | — | + | — |
| 2 | $BrCCl_3$ | — | + | — |
| 3, 4, 5, 7, 9 | PhH | + | — | — † |
| 7, 8 | $PhPr^i$ | — | — | + |

* + = present; — = absent; see text and Table 9 for details of relative intensities. ‡ 1. PhN(NO)Ac; 2. *p*-$Bu^t$-$C_6H_4N(NO)Ac$; 3. *p*-$MeOC_6H_4N(NO)Ac$; 4. *p*-$MeC_6H_4N$-(NO)Ac; 5. *p*-$NO_2C_6H_4N(NO)Ac$; 6. *p*-$EtO_2CC_6H_4N(NO)Ac$; 7. PhN(NO)CHO; 8. *p*-$Bu^tC_6H_4N(NO)CHO$; 9. PhN(NO)CDO; 10. PhN(NO)COEt; 11. PhN(NO)COPr; 12. PhN(NO)COPh; 13. PhN(NO)CO·$C_6H_4Cl$(*p*); 14. *p*-$Bu^tC_6H_4N(NO)COPh$.
† Conditions unsuitable, due to insolubility, for detection of signal, even if present.

*E.s.r. Signals Attributed to* N-*Arylacylamido Aryl Nitroxide* π-*Radicals* (PAPN).—Chalfont and Perkins[11] assigned the PAPN structure (VI) to the radical giving rise to the e.s.r. signal observed previously[6,7,9,11] on decomposition of *N*-nitrosoacetanilide in benzene. As a result of our substituent studies, and for the reasons below, we confirm this assignment. Typical spectra are reproduced in Figures 1, 9, and 10.

*Hyperfine coupling constants of various* PAPN *radicals*. The magnitude of the coupling of the unpaired electron with the various magnetic nuclei in the radical gives a clear indication of its delocalisation throughout the π-system. That PAPN is a typical nitroxide can be seen from Table 6; the $a_N$ and $a_H$ values of the phenyl ring compare well with those of other well-established radicals of this class.

TABLE 6

$a_N$ and $a_H$ values (in gauss) for nitroxides $R^1R^2NO$

| $R^1$ | $R^2$ | $a_N$ | $a_{o,p-H}$ | $a_{m-H}$ | Ref. |
|---|---|---|---|---|---|
| Ph | NPhAc | 11·6 | 2·7 | 0·9 | *a* |
| Ph | H | 9·1 | 3·0 | 1·0 | *b* |
| Ph | Ph | 10·9 | 2·0 | 0·8 | *c* |
| Ph | $Bu^t$ | 13·4 | 1·9 | 0·8 | *d* |
| $Bu^t$ | $Bu^t$ | 15·4 | | | *e* |
| Ph | $\overline{O\cdot[CH_2]_3\cdot CH}\cdot O$ | 15·1 | 3·1 | 1·1 | *f* |
| $Bu^t$ | $OBu^t$ | 28·0 | | | *g* |

[a] This work. [b] T. A. J. W. Wajer, A. Mackor, T. J. de Boer, and J. D. W. Van Voorst, *Tetrahedron Letters*, 1967, 1941. [c] Ref. 34. [d] Ref. 18. [e] Ref. 33. [f] D. J. Cowley and L. H. Sutcliffe, *Chem. Comm.*, 1968, 201. [g] Ref. 22.

The relative sizes of the values of $a_N$ and ring $a_H$ for nitroxides depend on the extent to which the spin density is delocalised from the NO group throughout the radical. Thus, the near planar phenyl nitroxide (Ph–NH–O·) has small $a_N$ and large ring $a_H$, while the more sterically hindered t-butyl phenyl nitroxide has higher $a_N$ and lower $a_H$ values.

*Variation with solvent of* $a_N$, *g-value and linewidth*. The observed variations of these parameters with solvent are in accord with the postulated structure of PAPN.

TABLE 7

$a_N$ and $\delta g$ for nitroxides in alcohols *

| Solvent | DPNO † | PAPN | *p*-$Bu^t$-PAPN |
|---|---|---|---|
| MeOH | 10·45 (4) | 11·90 (27) | 12·02 (32) |
| EtOH | 10·21 (0) | 11·84 (24) | 11·91 (29) |
| PrOH | 10·21 | 11·81 | 11·88 (29) |
| BuOH | 10·22 | | 11·86 (29) |
| PentOH | 10·18 | | 11·86 (29) |
| $Bu^tOH$ | | | 11·82 (28) |

* $a_N$ values: ref. 16. *g* values: ref. 14. $\delta g = g$ [Fremy's salt (2·00550)] — *g* (sample). † Diphenyl nitroxide.

The influence of solvent on the larger nitrogen hyperfine splitting constant exhibited by PAPN and *p*-$Bu^t$-PAPN in alcohols is summarised in Table 7. The observed dependence [*e.g.* $\Delta a_N$ (MeOH, $C_5H_{11}OH$) = 0·16 gauss] is similar to, but smaller than, that observed with diphenyl nitroxide ($\Delta a_N = 0{\cdot}27$ gauss). This difference can be understood in terms of the redistribution of the $\pi$-electron spin-density in the N–O bond, as a result of hydrogen bonding or local complexes between solvent and radical; thus the $a_N$ value will increase with the relative contribution of the dipolar form in $R_2N{-}O\cdot \longleftrightarrow R_2\overset{+}{N}{-}O^-$. The effect is therefore much greater in alcohols, as observed.

Solvent effects on the $g$-value of nitroxides have been studied by Kawamura *et al.*[14] They found that for diphenyl nitroxide and di-t-butyl nitroxide the $g$-value decreased with increasing solvent polarity. The $g$-value is dependent, according to Stone's theory,[15] on the unpaired electron on the oxygen and the lone pair on the nitrogen of the nitroxide. The more polar the solvent is, the less likely are structures containing this nitrogen lone pair and unpaired spin on the oxygen, and thus the lower becomes the $g$-value.

The $g$-values for the *p*-t-butyl-PAPN radical were measured as $\delta g$ with reference to the standard Fremy's salt signal for which $g = 2{\cdot}00550$, and are listed in Table 7. Comparison of Kawamura's $\delta g$ values [14] for diphenyl nitroxide in methanol and ethanol with the corresponding values for *p*-Bu$^t$-PAPN signals show that the changes in $g$ with variation of solvent are very similar although the $g$-values themselves are of course different.

The solvation of nitroxides by alcohols [16] also has a noticeable effect on the resolution of the hyperfine lines of their e.s.r. spectra. The resultant reduction in solute motion causes changes in the relaxation times, and the lines of the higher magnetic field group become strongly broadened compared with those at lower field. This observation leads to the determination of the sign of the $a_N$ value, by use of the following expression relating linewidth to magnetic quantum number:

$$T_2^{-1}(m) = A + Bm + Cm^2 + \ldots$$

The line-width theory developed by Kivelson [17] shows that $B < 0$, with the assumption that the positive value for $\rho_N$ which theoretical calculations indicate. Thus only when $a_N > 0$ and $m = 1$ and $-1$ for the low- and high-field groups should the observed line-width effects take place. This was observed and Figure 6 shows that this phenomenon is greater in t-butyl alcohol than in methanol, the higher viscosity of the former reducing radical-tumbling and thus increasing the anisotropic contributions to the line width.

*Variation of the* para-*substituent in* PAPN. Since the hyperfine splitting constant is related to the unpaired-electron density the variation of $a_N$ with the *para*-substituent in aryl nitroxides can be related to the Hammett $\sigma$ constant.[18,19] A plot of the data summarised in Table 8 for various PAPN-type radicals gives a good straight line thus emphasising the typical nitroxide behaviour of these radicals. A least-squares fit gives $a_N = 11{\cdot}801 - 1{\cdot}621\sigma$ (standard deviation 0·159 gauss) which compares well with $a_N = 9{\cdot}655 - 1{\cdot}602\sigma$ obtained for *para*-substituted diphenyl nitroxides.[19]

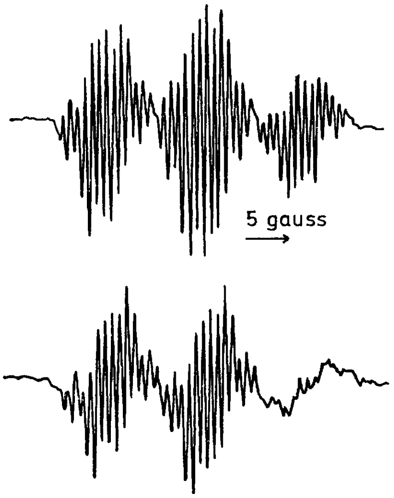


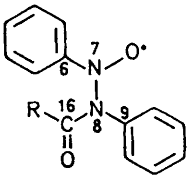
FIGURE 6 *p*-Bu$^t$NNA in methanol (top) and t-butyl alcohol (bottom)

*Variation of the acyl group.* The effect on the signal of variation of the acyl group was much greater than variation of the *para*-substituent. The accidental coincidence of hyperfine lines which occurs for PAPN itself is destroyed on changing the acyl group, and more complex spectra result. The variations in the two nitrogen splitting constants can be related to the twist around the N(7)–N(8), N(8)–C(9), and N(8)–C(16) bonds and is caused by the different steric requirements of the acyl groups.

TABLE 8

Variation of $a_N$ with *p*-substituents in PAPN radicals [$RC_6H_4N(NAc{\cdot}C_6H_4{\cdot}R){\cdot}O\cdot$] in pyridine

| R | MeO | Me | Bu$^t$ | H | CO$_2$Et | NO$_2$ |
|---|---|---|---|---|---|---|
| $\sigma$ | −0·268 | −0·170 | −0·151 | 0 | 0·45 | 0·778 |
| $a_N$(gauss) | 12·44 | 11·95 | 11·88 | 11·77 | 11·04 | 10·59 |



(VII)

In the case of *N*-nitrosoacetanilide (VII; R = Me) no splitting is observed for the methyl group protons.

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[14] T. Kawamura, S. Matsunami, Y. Yonezawi, and K. Fukui, *Bull. Chem. Soc. Japan*, 1965, **38**, 1935; T. Kawamura, S. Matsunami, and Y. Yonezawi, *ibid.*, 1967, **40**, 1111.

[15] A. J. Stone, *Mol. Phys.*, 1963, **6**, 509.

[16] K. Umemoto, Y. Deguchi, and H. Takaki, *Bull. Chem. Soc. Japan*, 1963, **36**, 560.

[17] D. Kivelson, *J. Chem. Phys.*, 1960, **33**, 1094.

[18] H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. France*, 1965, 372.

[19] P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforsch. (B)*, 1966, **21**, 1036.

Since methyl proton splittings are related by the McConnell type equation to the spin densities on the contiguous carbon atom by $a^{\text{Me}}_{\text{H}} = Q^{\text{H}}_{\text{CMe}}\,\rho_{\text{C}}$,[20] where $\rho_{\text{C}}$ is the $\pi$-electron spin density at the carbon to which the methyl group is attached, and the value of $Q^{\text{H}}_{\text{Me}}$ lies in the range +18 to + 38 gauss, the absence of methyl splittings indicates that $\rho_{16}$ must be very low. The most obvious explanation of this would be for the acyl group to be forced out of the plane by rotation about the N(8)–C(16) bond. In accord with this McLachlan calculations indicate that the angle of twist is as high at 70°.

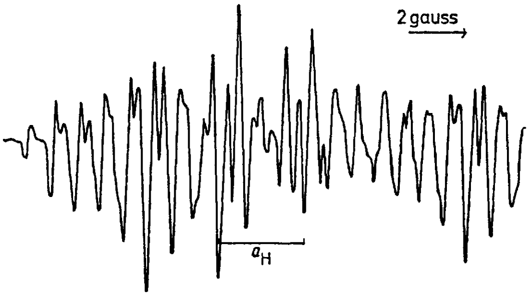

FIGURE 7 *N*-Nitrosoformanilide in pyridine

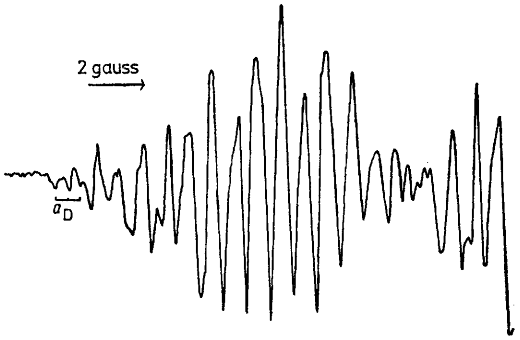

FIGURE 8 *N*-Nitroso[$^2$H]formanilide in benzene

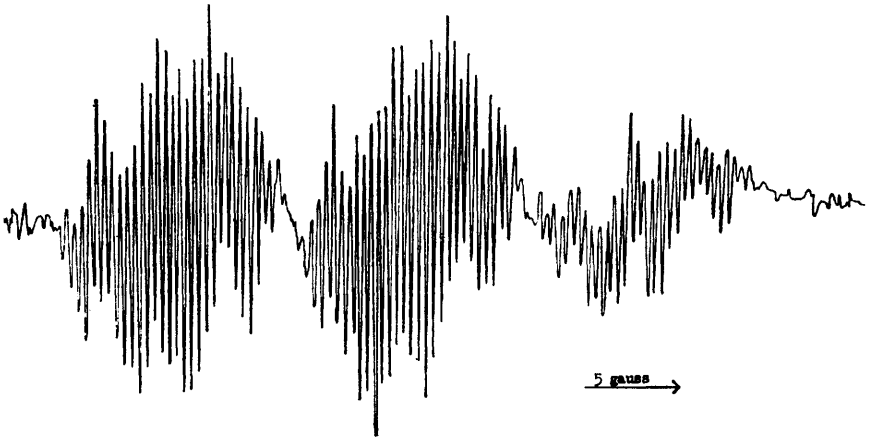

FIGURE 9 *p*-MeO·NNA in benzene

For the radicals from *N*-nitrosopropionanilide and *N*-nitrosoisobutyranilide (VII; R = Et and Pr$^{\text{i}}$), the spectra are very little changed with the exception of the intensities. The larger groups probably increase the angle of twist, and so slightly change the two nitrogen coupling constants.

In the case of *N*-nitrosobenzanilide (VII; R = Ph) however, the radical has a markedly different hyperfine spectrum, since the second nitrogen splitting constant is reduced from 1·7 to 1·4 gauss, whilst $a_{\text{N(7)}}$ increases to 12·08 gauss. This increase can be rationalised in terms of twisting of the N(7)–N(8) bond which reduces $\rho_{\text{N(8)}}$ but increases $\rho_{\text{N(7)}}$. The additional splitting in this spectrum of 0·3 gauss which was also present for (VII; R = $p$-$\mathrm{ClC_6H_4}$) is most probably due to the proton attached to C(12).

The hyperfine structure of the spectrum detected during the decomposition of *N*-nitrosoformanilide (Figure 7) was more complex than that found for *N*-nitrosoacetanilide (Figure 1), there being an extra doublet splitting of 3·12 gauss. In order to test whether this was due to coupling of unpaired electron with the proton of the formyl group, *N*-nitroso[$^2$H]formanilide was synthesised and the e.s.r. spectra, observed during its decomposition, was studied. Comparison of Figure 7 with Figure 8 shows that the doublet ($a_{\text{H}} = 3{\cdot}12$ gauss) has been replaced by a 1 : 1 : 1 triplet ($a_{\text{D}} = 0{\cdot}48$ gauss). This is in accordance with the change of nuclear spin from $\frac{1}{2}$ to 1 and the ratio of 6·5 for the nuclear *g*-factors for the proton and the deuteron. Therefore the presence of the acyl group in the radical is firmly established. Molecular models show that instead of the acyl group being almost completely out of the radical plane, as in the case of (VII; R = Me) the system can be almost coplanar, and this is reflected in the observation of a large splitting involving the formyl proton. By use of the McConnell equation [20] and with the assumption of a value of $Q_{\text{CH}}{}^{\text{H}} = 23{\cdot}7$ gauss, $\rho_{\text{C(16)}}$ is found to be 0·131. Thus the coplanarity in the radical produces a large spin density on the acyl group [C(16)] compared with those on the aryl ring positions.

[20] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 764; 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968.

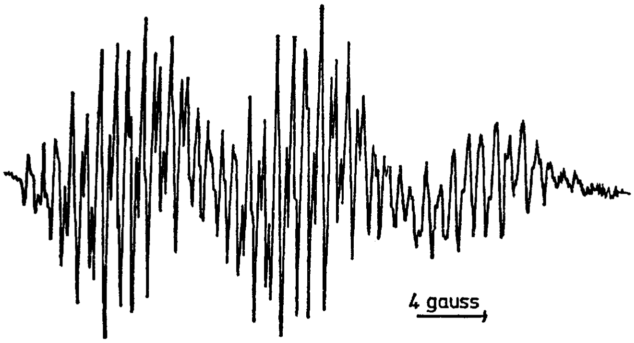

FIGURE 10 *p*-$NO_2$·NNA in pyridine

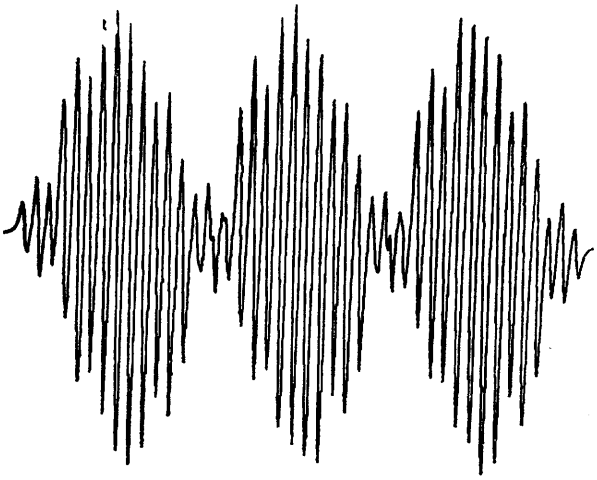

FIGURE 11 Simulation of PAPN in benzene (Figure 1)

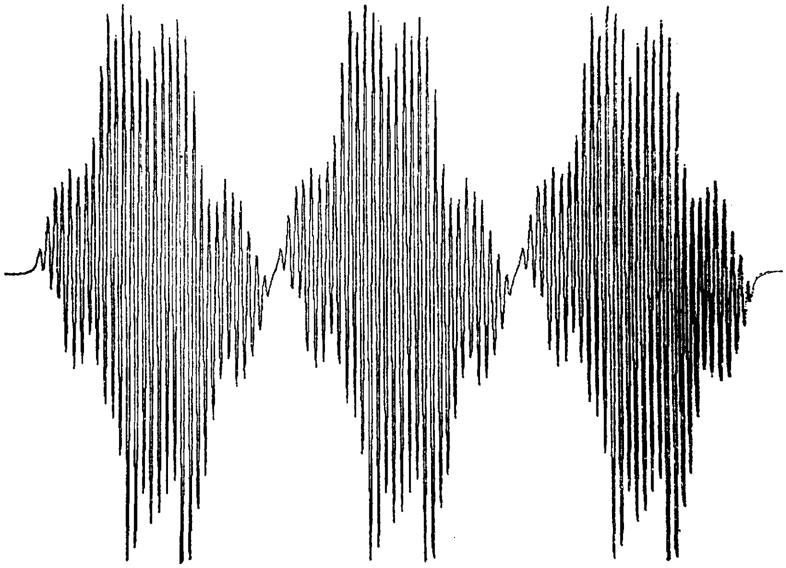

FIGURE 12 Simulation of signal from *p*-MeO·NNA in benzene (Figure 9)

*McLachlan spin density calculations and computer simulations of the spectrum.* The results of the McLachlan calculations, described elsewhere,[21] provide further confirmation of Chalfont and Perkins' assignment of the e.s.r. signal to the PAPN $\pi$-radical. By use of parameters that had been found satisfactory for the well established $\pi$-nitroxides, diphenyl nitroxide, and phenyl nitroxide, the agreement between the calculated and experimental spin densities was very good. The geometry of the radicals was also estimated from the calculations since twisting can be taken into account by a variation of the resonance integral parameter for the bonds involved. Thus the twists involving N(8)–C(9) and N(8)–C(16) were estimated at 60 and 70° respectively; this accounts for the absence of splitting involving the second aryl ring, or the acyl group in the PAPN signal.

Spectra were simulated and resulting coupling constants were determined with excellent agreement with experiment for PAPN in a wide variety of solvents, and for *p*-methoxy- and *p*-nitro-PAPN in pyridine (*e.g.* Figures 11—13).

*E.s.r. Signals Attributed to (Arylazo)oxyl $\sigma$-Radicals* (PhNNO).—The spectrum obtained (*e.g.* Figure 3) in the case of *N*-nitrosoacetanilide was a 1 : 1 : 1 triplet of 1 : 1 : 1 triplets ($a_N = 30{\cdot}7$, $a_N = 2{\cdot}3$ gauss; $g = 2{\cdot}0015$) and shows two unusual features: the major nitrogen coupling constant of 30·7 gauss is abnormally high for $\pi$-radicals in solution, while the *g*-factor of 2·0015 is less than the free-spin value of 2·0023. This suggests that the radical is not a typical $\pi$-nitroxide like diphenyl nitroxide, phenyl nitroxide, and PAPN, for which $a_N = 9$—12 gauss and $g = 2{\cdot}0050$—$2{\cdot}0055$. The same conclusion can be drawn from the insensitivity of the signal to changes in the acyl and aryl groups of the nitrosamide. Identical spectra resulted from the decomposition of *N*-nitrosoacetanilide, and *N*-nitrosoisobutyranilide, while on changing the *para*-substituent of the aryl group from methoxy to nitro the major $a_N$ value

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[21] R. M. Paton and C. Thomson, *Theor. Chim. Acta*, in the press; C. Thomson, unpublished observations.

varied only from 30·6 to 31·0 gauss, an *increase* of 1·3%. This compares with a *decrease* from 12·44 to 10·59 gauss (15%) for the same substituents in PAPN.

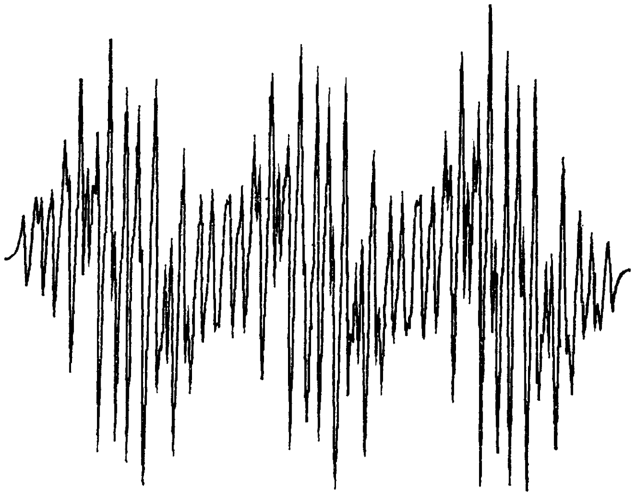
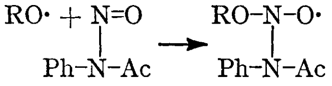


FIGURE 13 Simulation of signal from $p$-$NO_2$·NNA in pyridine (*cf.* Figure 10)

In view of the magnitude of the $a_N$ value, two types of radical are considered. The first is the nitroxide formed by the addition of an alkoxy-radical, possibly formed from oxidation of the solvent, across the nitroso-group of the nitrosamide. Alkoxy alkyl nitroxides have been reported [22] to have nitrogen splitting-constants in the region of 25—30 gauss, and in this case a nine-line spectrum might be expected through unequal coupling of the unpaired electron with the two nitrogen nuclei. However, this assignment can be rejected on the grounds that the *g*-factor of 2·0015 is inconsistent with the values of *ca.* 2·0055 found for nitroxides of all types.



$$RO\cdot + \underset{Ph-N-Ac}{N{=}O} \longrightarrow \underset{Ph-N-Ac}{RO-N-O\cdot}$$

The second type of radical with $a_N$ values of the correct magnitude is the iminoxyl-radical derived from the oxidation of oximes. Thus from *syn*- and *anti*-benzaldehyde oxime, and benzophenone oxime, signals with $a_N = 29{\cdot}2$, 31·6, and 31·4 gauss, respectively, were observed [23] and the large coupling constants attributed to the location of the unpaired electron in a σ-orbital with a high $s:p$ ratio.[24]

Our present assignment of the triplet of triplets signal to the PhNNO σ-radical explains several features of the spectrum by analogy with the results obtained for *syn*-PhCHNO.[23,25] Thus, (*i*) the large $a_N$ value of 30·7 gauss is consistent with the unpaired electron occupying a molecular orbital in the plane of the phenyl ring, with a high $s:p$ ratio and comprised of the $sp^2$ hybrid orbitals of the two nitrogen atoms and a $2p$ atomic orbital of the oxygen. (*ii*) The coupling of the unpaired electron with the protons of the phenyl ring is small and remains unresolved, the minimum linewidth for the spectrum being 0·5 gauss. The hyperfine structure thus consists of nine lines arranged as a triplet of triplets. (*iii*) For the PhNNO σ-radical, variation of the *para*-substituent of the aryl ring has little effect on the $a_N$ values, unlike the PAPN π-nitroxide case when Hammett behaviour is exhibited. In addition the absence of the acyl group in the postulated radical explains why identical signals result from the decompositions of *N*-nitrosoacetanilide, *N*-nitrosopropionalide, and *N*-nitrosoisobutyranilide.

The *g*-factor of 2·0015 differs from that of 2·0055 found for iminoxyl-radicals, but is typical of other well established σ-radicals such as formyl (2·0009),[26] vinyl (2·0022),[27] carbamoyl (2·0017),[28] and the nitrosobenzene cation (2·0007).[29] This inconsistency in the values for PhNNO and PhCHNO probably arises from the additional lone pair of electrons on the second nitrogen atom, the importance of which is stressed in the *g*-value theory developed by Stone.[15]

Theoretical calculation (CNDO/2),[30] described by some of us elsewhere,[21] have been used to test whether the (phenylazo)oxyl radical would in fact be expected to have σ- rather than π-symmetry. The method was found to be valid for a number of known σ- and π-radicals [σ: PhCHNO· (*syn* and *anti*) $CH_2{=}N\cdot$, $\cdot CH{=}O$, $CH_2{=}CH\cdot$, $NH_2CO\cdot$, Ph·, and $PhNO^{+}\cdot$; π: $H_2NO\cdot$ and $PhNO^{-}$]. Extension to PhNNO supports the assignment of the triplet of triplets signal to the *trans*- rather than the *cis*-phenylazoxyl radical. Not only is the unpaired electron assigned to a molecular orbital of σ-symmetry, but the calculated hyperfine coupling constants are of the correct magnitude and the predicted splitting for the phenyl-ring protons is less than the observed line widths. The more sophisticated INDO calculations,[31] which allow for σ–π exchange interactions also clearly point [21] to the same conclusion for both the HNNO and PhNNO *trans*-σ-radicals. Thus for the latter (VIII) the minimum energy appears when α ~125° and the calculated values of $a_N^{12} = 8$, $a_N^{13} = 23$ gauss are encouragingly close to the experimental value.

An alternative to (VIII) is $PhN_2\cdot$. This is discounted on the basis of similar INDO calculations [21] which lead to calculated coupling constants of $a_{N(1)} = 4{\cdot}4$ and $a_{N(2)} = 5{\cdot}1$ gauss, which are greatly at variance with the experimental values.

### *E.s.r. Signals Attributed to Other Nitroxide Radicals*

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[22] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. Van Voorst, *Tetrahedron Letters*, 1967, 385.

[23] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446.

[24] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 283; *J. Chem. Soc.*, 1963, 1189.

[25] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1966, 722.

[26] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1661.

[27] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[28] T. Yonezawa, I. Noda, and T. Kawamura, *Bull. Chem. Soc. Japan*, 1968, **41**, 766.

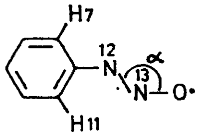
[29] C. Cauquis, M. Genies, H. Lemaire, A. Rassat, and J. P. Ravet, *J. Chem. Phys.*, 1967, **47**, 4642.

[30] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1964, **44**, 3289.

[31] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

*Detected in Ethers and in Cumene.—Cumene.* During the decomposition of all the nitrosamides in cumene a 1 : 1 : 1 triplet e.s.r. spectrum (Figure 14) was observed, for

(VIII)



which $a_N = 15{\cdot}00$ gauss and $g = 2{\cdot}0059$. This signal was assigned to dicumyl nitroxide [$(PhCMe_2)_2NO\cdot$]. The e.s.r. spectrum of dicumyl nitroxide has been observed by de Boer,[22] who found $a_N = 15{\cdot}1$ gauss in cumene, and by Hoffmann,[32] who found $a_N = 14{\cdot}9$ gauss in n-heptane. We also detected $^{13}C$ satellite lines [33] (Figure 15).

In the case of *N*-nitrosoformanilide two additional signals were observed. The first was a triplet of triplets ($a_N = 18{\cdot}10$ gauss, $a_N = 1{\cdot}36$ gauss, $g = 2{\cdot}0059$) very similar to that reported for *N*-phenylacetamido t-butyl nitroxide,[11] and was thus assigned to the *N*-phenylformamido cumyl nitroxide which would result from the addition of a cumyl radical across the nitroso-group of *N*-nitrosoformanilide. The second new signal appearing later in the reaction and lasting several days, showed hyperfine structure due to the five protons of a phenyl ring and one nitrogen. The coupling constants of this signal are identical to those observed for the stable radical formed during the azobisisobutyronitrile-catalysed oxidation of aniline,[34] the reaction of t-butylhydroperoxide with phenylhydroxylamine or triphenylhydrazine,[35] the reaction of nitrosobenzene with sodium methoxide in methanol,[36] and the reaction of sodium dithionite with nitrosobenzene.[37] Several authors [35,36] assigned this signal to the radical PhNOH, or to a time average of PhNOH and PhNHO. However, Russell [37] considered that the stability of this ubiquitous species and the absence of a hydroxyl proton splitting, although such a coupling ($a_H = 0{\cdot}38$ gauss) can be detected [38] for $PhNO_2H$, made this assignment improbable and a more likely structure was $PhN(O\cdot)OX$ where X = PhNH. The $a_N$ value of 14·9 gauss reported by de Boer [22] for $PhN(O\cdot)OBu^t$ is much larger than the value of 11·69 gauss observed for the *N*-nitrosoformanilide system and makes the structure $Ph{-}N(O\cdot)OCMe_2Ph$ improbable. While the alkyl aryl nitroxide $PhN(O\cdot)CMe_2Ph$ is a possibility, the structure assigned by Russell seems the most probable.

*Ethers.* In diethyl ether, signals showing hyperfine structure due to coupling with two nitrogen nuclei and one proton $a_N = 15{\cdot}4$, $a_H = 5{\cdot}8$, and $a_N = 1{\cdot}4$ gauss were detected (Figure 5) and is assigned to the nitroxide produced by addition of the 1-ethoxyethyl radical to the nitroso-compound [$Me(EtO)CH\cdot N(NAcPh)\cdot O\cdot$]. Smaller couplings with the protons of the rest of the solvent residue and of the phenyl ring probably account for the observed large linewidth of 0·6 gauss.

FIGURE 14 Signal from $p$-$NO_2\cdot NNA$ in cumene [$(PhCMe_2)_2NO\cdot$]

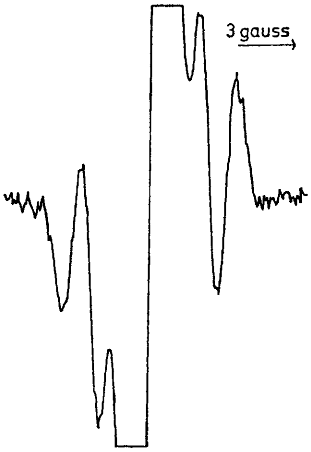


FIGURE 15 $(PhCMe_2)_2NO\cdot$ showing $^{13}C$ satellites

A similar nitroxide spectrum was detected by Chachaty and Forchioni [39] during the photolysis of nitroalkanes in tetrahydrofuran; the coupling constants being $a_N = 14{\cdot}7$ gauss and $a_H(THF) = 6{\cdot}9$ gauss.

In dimethoxyethane and tetrahydrofuran complex unresolved signals were observed.

*The Relevance of the* PAPN, PhNNO, *and Other Signals to the Mechanism of the Decomposition of Acylarylnitrosamines in Various Solvents.—Solvents which give* PhNNO-*type signals.* This type of signal was detected in aromatic hydrocarbons, furan, hexafluorobenzene, and halogenated alkanes. In some cases the PAPN signal (Table 5) was also observed. A striking feature of the results (Table 9) is the variation of the relative intensities of the two signals with the solvent. If we first take the series of aromatic compounds, it can be seen that the PAPN signal is not present in all solvents and that its intensity is high only in benzene, t-butylbenzene, and

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[38] R. L. Ward, *J. Chem. Phys.*, 1963, **38**, 2588.

[39] C. Chachaty and A. Forchioni, *Tetrahedron Letters*, 1968, 1079.

furan, and is weak or not detectable in solvents having an easily abstractable hydrogen atom which leads to the formation of a stabilised benzyl-type radical. Thus, in mesitylene the PhNNO signal is dominant (Figure 3) while in cumene the PAPN signal is absent (Figure 4). Further the PhNNO signal is present at constant intensity in all of these solvents, including benzene. In the latter case the PAPN signal is intense and almost obliterates that from PhNNO. The latter becomes clear only at higher modulation amplitude (Figures 1 and 2) and for this reason, presumably, it was overlooked by previous workers.

TABLE 9

Relative intensities of PAPN and PhNNO signals

| Solvent | PAPN | PhNNO |
|---|---|---|
| PhH | Intense | weak |
| PhMe | weak | weak |
| PhEt | v. weak | weak |
| $PhPr^i$ | absent | weak |
| $PhBu^t$ | intense | weak |
| $p$-$Me_2C_6H_4$ | v. weak | weak |
| $s$-$Me_3C_6H_4$ | v. v. weak | weak |
| $C_5H_4O$ | intense | v. weak |
| $C_6F_6$ | medium | weak |
| $CCl_4$ | absent | weak |
| $BrCCl_3$ | absent | weak |
| $(Br_2CH)_2$ | absent | weak |
| $CH_2Cl_2$ | weak | weak |
| EtBr | medium | weak |

A similar situation is evident in the series of halogenated solvents. Those which can react by abstraction to give relatively stable polyhalogenoalkyl radicals (*e.g.* $\cdot CCl_3$) exhibit only the PhNNO signal.

The constancy of the PhNNO signal in all of these solvents indicates that this radical is involved in the major product forming sequence in each case. This cannot be said for the PAPN radical. This evidence therefore points strongly to the operation of Scheme 1 proposed by Freudenberg and Rüchardt, but rejected by Chalfont and Perkins, with the important modification that the chain carrying radical is $\sigma$-PhNNO as now found and not $\pi$-PhNNO as previously postulated. The question now arises as to whether the PAPN radical also takes part in the chain, *via* Scheme 2. Clearly in those solvents where it is absent, there is no strong case for it to be invoked. It could be argued, however, that in these cases, all of which can give rise to resonance stabilised benzyl type radicals, that PAPN is removed by radical coupling *e.g.* $R_2NO\cdot + PhCH_2\cdot \longrightarrow PhCH_2$-$ONR_2$, of the type demonstrated by Calder, Forrester, and Thomson.[40] This is indeed likely, but since this is a chain termination step, which reduces the stationary concentration of PAPN to an undetectable limit, it is a further argument against the participation of Scheme 2 in the cases where the PAPN signal is absent. Two possibilities therefore present themselves. (*i*) That Scheme 1 which involves the chain-carrier PhNNO operates in all cases and that Scheme 2 which involves PAPN also operates in some solvents such as benzene and t-butylbenzene but not in others such as mesitylene. (*ii*) That Scheme 1 involving PhNNO operates in all relevant cases and that PAPN is not the required chain carrier, but that it is a relatively unimportant side product, possibly irrelevant to the formation of phenyl radicals. This side product could be suppressed in solvents which give stabilised radicals by abstraction by phenyl radicals, whether through scavenging of the PAPN radical in a chain-termination step as described above and/or because the removal of phenyl radicals by the combined reactions of abstraction and nuclear addition (say) becomes more important than removal by their reaction with unchanged *N*-nitrosoacetanilide. These possibilities differ only in the significance of PAPN as a chain carrying radical. It is possible that diphenyl nitroxide is capable of acting as the chain carrier[41,42] radical in decompositions of diazonium salts but this evidence when extrapolated to the present case does not favour PAPN any more or less than PhNNO. It is also possibly significant that, in benzene, the PAPN signal persists sometimes for days, long after the decomposition of *N*-nitrosoacetanilide, the mechanism of which is the subject of the investigation, has been completed.

It appears, therefore, that the case in favour of decomposition of *N*-nitrosoacetanilide *via* Scheme 1 and PhNNO is strong but that the case for additional participation of PAPN *via* Scheme 2, while it cannot be discounted, has still to be made.

Decomposition of *N*-nitrosoacetanilide in cumene gave an addition signal attributed to dicumyl nitroxide (Figure 4) the probable mode of formation being as in Scheme 3. Hence the possibility of decomposition *via* dicumyl nitroxide as a chain carrier cannot be ruled out. In the related case of *N*-nitrosoformanilide, both PAPN and PhNNO were absent. In addition to dicumyl nitroxide, *N*-phenylformanido cumyl nitroxide (IX) formed by scavenging of a cumyl radical by the nitroso-

$$PhCMe_2\cdot + PhN(NO)CHO \longrightarrow PhCMe_2(PhNCHO)\cdot NO\cdot \qquad (IX)$$

compound was detected, as was a third radical of uncertain structure (see above). In this case therefore participation of these radicals, also in the decomposition must be considered to be possible.

$$Ph\cdot + PhCHMe_2 \longrightarrow PhH + PhCMe_2\cdot$$

$$PhN(NO)Ac \longrightarrow NO$$

$$PhCMe_2\cdot + NO \longrightarrow PhCMe_2NO\cdot \xrightarrow{Ph\dot{C}Me_2} (PhCMe_2)_2NO\cdot$$

SCHEME 3

*Solvents giving signals other than the* PhNNO-*type*. It is known[43] that *N*-nitrosoacetanilide decomposes in diethyl ether in an unusual fashion to give benzene

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[40] A. Calder, A. R. Forrester, and R. H. Thomson, *J. Chem. Soc.* (*C*), 1969, 512.

[41] C. Rüchardt, personal communication.

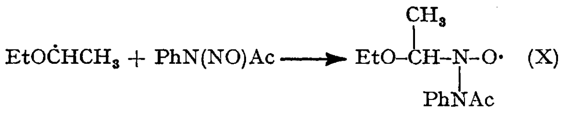
[42] R. M. Cooper and M. J. Perkins, *Tetrahedron Letters*, 1969, 2477.

[43] D. B. Denney, N. E. Gershman, and A. Appelbaum, *J. Amer. Chem. Soc.*, 1964, **86**, 3180.

(52%), 1-ethoxyethyl acetate (22%), and acetaldehyde (50%), but no satisfactory mechanism has been suggested. The present e.s.r. spectroscopic observation enable such a mechanism to be put forward. In diethyl ether, tetrahydrofuran, and 1,2-dimethoxyethane. PhNNO was absent and PAPN was present, as were radicals of the type (X), formed by addition of the 1-ethoxyethyl radical (XI) say, to the nitroso-group. The absence of PhNNO and the evidence for the intermediacy of the 1-ethoxyethyl radical suggest the mechanism, outlined in Scheme 4 which involves the phenyl radical as a chain carrier in this case. A similar redox transfer step involving the diazonium ion has been suggested by Rüchardt and Werner in the Meerwein reaction of diazonium salts in 1,3-dioxolan.[44]

$$\text{Initiation } \textit{via} \text{ Scheme 1} \longrightarrow \text{Ph}\cdot \longrightarrow \text{PAPN}$$

$$\text{Ph}\cdot + \text{Et}_2\text{O} \longrightarrow \text{PhH} + \text{EtO}\dot{\text{C}}\text{HCH}_3 \quad \text{(XI)}$$



$$\text{EtO}\dot{\text{C}}\text{HCH}_3 + \text{PhN(NO)Ac} \longrightarrow \text{EtO–}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{–}\underset{\text{PhNAc}}{\underset{|}{\text{N}}}\text{–O}\cdot \quad \text{(X)}$$

$$\text{EtOCHCH}_3 + \text{PhN}_2{}^+ \longrightarrow \text{EtO–}\overset{+}{\text{C}}\text{HCH}_4 + \text{Ph}\cdot + \text{N}_2$$

$$\text{Ph}\cdot + \text{Et}_2\text{O} \longrightarrow \text{PhH } \textit{et seq.}$$

$$\text{EtO}\overset{+}{\text{C}}\text{HCH}_3 + \text{AcO}^- \longrightarrow \text{EtOCH(OAc)CH}_3$$

SCHEME 4

The detection of the PAPN e.s.r. signal during the decomposition of *N*-nitrosoacetanilide in alcohols indicates that a free phenyl radical is also involved in this system. The failure to detect the (phenylazo)oxyl triplet of triplets signal and formation of the product benzene only by the abstraction of α-hydrogen atoms, as indicated by the formation of $<1\%$ $C_6H_5D$ from the reaction in EtOD,[45] supports the recently proposed[46] mechanism depicted in Scheme 5, which is similar to that proposed above for decomposition in ether.

$$\text{Ph}\cdot + \text{R}_2\text{CHOH} \longrightarrow \text{PhH} + \text{R}_2\dot{\text{C}}\text{OH}$$

$$\text{R}_2\dot{\text{C}}\text{OH} + \text{PhN}_2{}^+ \longrightarrow \text{PhN}_2\cdot + \text{R}_2\overset{+}{\text{C}}\text{OH}$$

$$\text{PhN}_2\cdot \longrightarrow \text{Ph}\cdot + \text{N}_2$$

$$\text{R}_2\overset{+}{\text{C}}\text{OH} + \text{AcO}^- \longrightarrow \text{R}_2\text{C:O} + \text{AcOH}$$

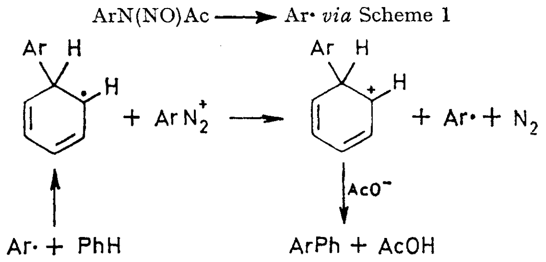
SCHEME 5

This scheme received added support from Huisgen's study of the decomposition of *o*-methyl-*N*-nitrosoacetanilide.[47] In chloroform, indazole was formed in almost quantitative yield, but in ethanol a high yield of acetaldehyde was given, with negligible formation of indazole; thus oxidation must have been achieved at the expense of cyclisation by some species containing nitrogen. The electron-transfer process outlined in Scheme 5 would account for the results.

The variation in the intensity of the *p*-Bu$^t$-PAPN signal in a series of alcohols [Bu$^t$OH (intense) > MeOH (medium) > EtOH > Pr$^n$OH > Bu$^t$OH > *n*-$C_5H_{11}$OH (all weak) > Pr$^i$OH (v. weak)] can be rationalised in a similar fashion to the aromatic hydrocarbons and polyhalogenoalkanes. The intensity decreases with the increasing stability of the solvent residue radical suggesting removal of the nitroxide by the coupling reaction and/or competition by hydrogen abstraction by the phenyl radical compared with addition in the nitroso-group.

The fact that satisfactory mechanisms can be proposed for the reaction in both ethers and alcohols, which do not involve PAPN as the chain carrier, and yet its e.s.r. signal is detected in each case, supports the proposal that its formation may only be a non-product-forming side reaction.

The suggestion of a redox reaction between the diazonium cation and radicals such as $R_2\dot{C}OH$ and $EtO\cdot\dot{C}HCH_3$ can be extended to the case of *N*-nitrosoacetanilide decomposition in benzene. *Thus, the possibility that part of the decomposition proceeds as in Scheme* 6 *cannot be excluded.*



SCHEME 6

This scheme is perhaps the most attractive for the decomposition of NNA in aromatic solvents, since it accommodates the data concerning the appearance and nonappearance of PhNNO and PAPN and requires Scheme 1, or a lesser extent Scheme 2, to act merely as a trigger for the reaction in providing an aryl radical. The redox reaction could then play an important part, undetected by e.s.r., and give rise to acetic acid, biaryl, and nitrogen *via* a chain reaction involving the aryl radical as a chain carrier. Further, under preparative conditions, *i.e.* high dilution, when e.s.r. signals are either absent or very weak it could be argued that the redox reaction (Scheme 6) might be dominant. Thus, in aromatic solvents, we conclude that (*i*) initiation of the decomposition is most likely *via* σ-ArNNO as in Scheme 1 and that propagation by this route must also occur, otherwise a stationary concentration of ArNNO would not have been obtained and observed, (*ii*) propagation *via* PAPN or other nitroxides cannot be ruled out, but is unlikely to be very important, and (*iii*) propagation *via* redox reaction as in Scheme 6 is also a very likely possibility. The relative importance of these factors is likely to vary with the solvent and concentration.

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[44] C. Rüchardt and R. Werner, *Tetrahedron Letters*, 1969, 2407.

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[47] R. Huisgen and H. Nakaten, *Annalen*, 1954, **586**, 84.

Only pyridine and the polyhalogenomethanes remain to be considered. The PAPN signal only was observed in pyridine. This and other considerations such as anomalous isomer ratios for phenylation by use of *N*-nitrosoacetanilide [48] and other anomalous behaviour to be referred to in a succeeding paper [49] suggest that a quite different mechanism is operable in this solvent, as in 2,5-dimethylfuran, which exhibits no e.s.r. signals at all and gives anomalous products. The mechanism of the reaction in polyhalogenomethanes is also more complex, despite the detections of PhNNO, as evidenced by the precipitation of diazonium chloride for example, in the case of carbon tetrachloride,[50] and will be referred to in a later paper.

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[0/773 *Received, May* 11*th*, 1970]

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