# New Evidence on the Mechanism of the Decomposition of Acetylarylnitrosamines in Diethyl Ether

By J. I. G. CADOGAN,*† R. M. PATON, and C. THOMSON

(*Department of Chemistry, University of St. Andrews, The Purdie Building, St. Andrews, Fife*)

*Summary* An e.s.r. signal attributable to the radical Me(EtO)CH·N(NAc·Ar)·O· has been observed during the decomposition of acetylarylnitrosamines in diethyl ether.

DECOMPOSITION of *N*-nitrosoacetanilide (NNA) in diethyl ether is known to give benzene (52%), 1-ethoxyethyl acetate (22%), and acetaldehyde (50%),[1] but a fully satisfactory mechanism for the reaction has yet to be suggested. We now report the results of an e.s.r. spectroscopic investigation of the reaction which enables a satisfactory mechanism to be put forward.

Decomposition of *N*-nitrosoacetanilide in diethyl ether (concentration: 250 mg/ml) in the cavity of the e.s.r. spectrometer at room temperature led to two e.s.r. signals, (i) a weak signal identical with that of the (*N*-phenylacetamido)phenyl nitroxide radical (PAPN: I)[2,3] formed by scavenging of phenyl radicals by NNA, dominated by a second signal for which three coupling constants could be determined: $a_N = 15\cdot4$ gauss, $a_H = 5\cdot8$ gauss, $a_N = 1\cdot4$ gauss. A similar signal was obtained in the case of the corresponding decomposition of the more soluble *p*-t-butyl-*N*-nitrosoacetanilide. The Figure depicts the spectrum obtained after 15 min. using modulation amplitude of 0·13 gauss, with a reconstruction of the spectrum using the following coupling constants: $a_N = 15\cdot30$, $a_H = 5\cdot77$, $a_N = 1\cdot35$ gauss. These signals thus show hyperfine structure due to coupling with two nitrogen nucleii and one proton, and are assigned to nitroxide radicals (II) formed by the addition of the 1-ethoxyethyl radical, resulting from the abstraction of a hydrogen atom from diethyl ether, across the NO group of the nitrosamide.

A similar spectrum was detected by Chachaty and Forchioni[4] during the photolysis of nitroalkanes in tetrahydrofuran, the coupling constants being $a_N = 14\cdot7$ gauss and $a_{H(THF)} = 6\cdot9$ gauss. By analogy the signal due to (II) exhibits coupling with the nitrogen of the nitroxide group ($a_N = 15\cdot3$—$15\cdot4$ gauss), with the nitrogen of the acetamido-group ($a_N = 1\cdot4$ gauss) and the α-ethoxyethyl proton ($a_H = 5\cdot8$ gauss). Smaller couplings of the remainder of the alkyl protons and of the aryl ring probably account for the large line width of 0·6 gauss.

We have previously presented evidence (a) that the radical (I) is unlikely to be a significant chain carrier in decompositions of NNA in aromatic solvents and (b) that the chain carrier is a σ-radical formulated as PhNNO· (III).[5] In the present investigation no signal corresponding to PhNNO· was detected, suggesting that an alternative route to phenyl radicals is predominant. This, coupled with the observation of a signal corresponding to radical (II) and hence the precursory α-ethoxyethyl radical points to the mechanism outlined in the Scheme, where the key step involves electron transfer between the diazonium cation and the α-ethoxyethyl radical to give a phenyl radical, *which then becomes the chain carrier in this case*, and the α-ethoxyethyl carbonium ion, which is scavenged by acetate ion to give the observed product. A similar electron transfer step in the Meerwein reaction of diazonium salts in 1,3-dioxolan has recently been postulated by Werner and Rüchardt,[6] whom we thank for keeping us informed of their work prior to its publication.

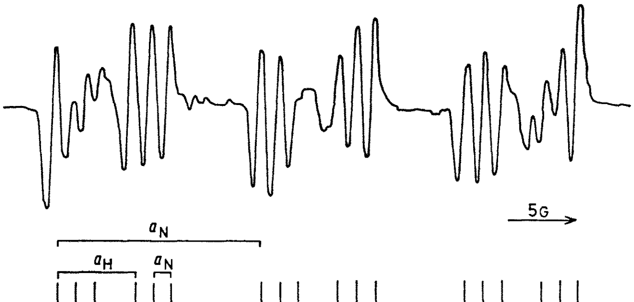
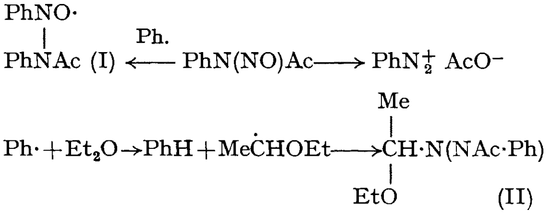


FIGURE. p-*t-Butyl*-N-*nitrosoacetanilide in* $Et_2O$ *with reconstructed spectrum.*



$$\begin{array}{l} \text{PhNO}\cdot \\ \quad | \\ \text{PhNAc (I)} \xleftarrow{\text{Ph.}} \text{PhN(NO)Ac} \longrightarrow \text{PhN}_2^+\ \text{AcO}^- \end{array}$$

$$\text{Ph}\cdot + \text{Et}_2\text{O} \rightarrow \text{PhH} + \text{Me}\dot{\text{C}}\text{HOEt} \longrightarrow \underset{\text{EtO}}{\overset{\text{Me}}{\text{CH}}}\cdot\text{N(NAc}\cdot\text{Ph)O}\cdot \quad \text{(II)}$$

$$\text{Me}\dot{\text{C}}\text{HOEt} + \text{ArN}_2^+ \longrightarrow \text{Ph}\cdot + \text{N}_2 + \text{Me}\overset{+}{\text{C}}\text{HOEt}$$

$$\text{Me}\overset{+}{\text{C}}\text{HOEt} + \text{AcO}^- \longrightarrow \text{MeCH(OEt)OAc}$$

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

$$\text{Me}\dot{\text{C}}\text{HOEt} \longrightarrow \text{MeCHO} + \text{Et}\cdot$$

(*Received, December* 31*st*, 1969; *Com.* 1973.)

---

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

[1] D. B. Denney, N. E. Gershman, and A. Appelbaum, *J. Amer. Chem. Soc.*, 1964, **86**, 3180.
[2] G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 1967, **89**, 3054.
[3] A. R. Forrester, *Chem. and Ind.*, 1968, 1483.
[4] C. Chachaty and A. Forchioni, *Tetrahedron Letters*, 1968, 1079.
[5] J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Comm.*, 1969, 614.
[6] C. Ruchardt and R. Werner, *Tetrahedron Letters*, 1969, 2407.