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AN EPR INVESTIGATION OF HYDRAZYL RADICALS FORMED IN AZO COMPOUND PHOTOLYSES

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Recently[1], the photolysis of symmetric alkyl azodicarboxylates, **1**, in solution has been postulated to occur by a one-bond scission mechanism

$$\underset{\mathbf{1}}{RO_2C{-}N{=}N{-}CO_2R} \xrightarrow{h\nu} \underset{\mathbf{2}}{RO_2C{-}N{=}N\cdot} + \cdot CO_2R$$

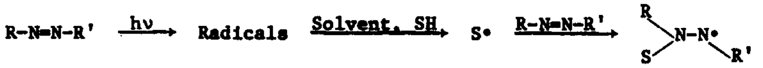
This conclusion was based largely on the observation of EPR signals attributed to carboalkoxy diazenyl radicals, **2**. We present here the results of an analogous EPR study of the photodecomposition of the unsymmetric azo compounds

$$\underset{\mathbf{3}}{Ph{-}C(CH_3)_2{-}N{=}N{-}Ph} \qquad \underset{\mathbf{4}}{Ph{-}N{=}N{-}CO_2C_2H_5} \qquad \underset{\mathbf{5}}{Ph{-}N{=}N{-}C(CH_3)_2\ CH{=}CH_2}$$

These results cast doubts on the conclusions drawn by the earlier workers[1].

Photolysis of **1** ($R{=}C_2H_5$) in 20:80 isopentane:methylcyclohexane was repeated and the spectrum obtained (Fig 1a) was essentially as previously published[1], though less well resolved (<u>i.e.</u> peak-to-peak line width 0.8 G instead of 0.3 G). When **3** and **4**[2] were irradiated in the same solvent the spectra shown in Fig 1b [(1:1:1)-triplet of (1:1:1)-triplets] and Fig 1c [(1:1:1)-triplet of unassigned[3] multiplets] were observed, respectively.[4]

Photolysis of **3** and **4** in both benzene and toluene gave no signals, but irradiation of **3** in cyclohexane produced a complex spectrum clearly different from that shown in Fig 1b. Also, no signals were seen on photolysis of **5** in solvents where Ph-N=N• has been shown to be produced.[5] These observations force us to attribute each EPR signal observed to the attack of a solvent-derived radical on the starting azo compound to yield a relatively stable hydrazyl radical.



$$R{-}N{=}N{-}R' \xrightarrow{h\nu} \text{Radicals} \xrightarrow{\text{Solvent, SH}} S\cdot \xrightarrow{R-N=N-R'} \overset{R}{\underset{S}{>}}N{-}N\cdot{\searrow}R'$$

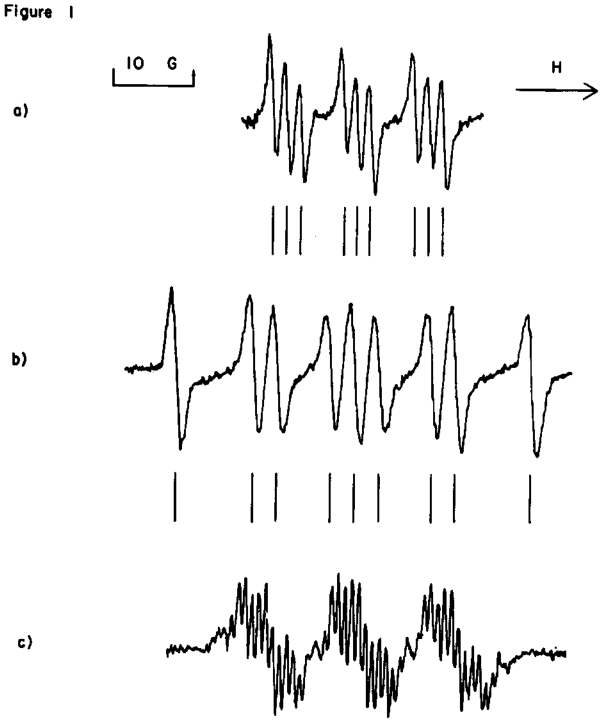
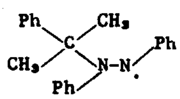


Figure 1. EPR spectra at ca. 30°C for the photolysis of azo compounds in 20:80 isopentane:methylcyclohexane; (a) 1 ($R{=}C_2H_5$); (b) 3; (c) 4.

If diazenyl radicals were responsible for the signals observed, the spectrum obtained on photolysis of 4 (Fig 1c) should resemble that in Fig 1a or 1b. Instead this spectrum is very similar to that of an authentic hydrazyl radical, 6, generated during the photoreduction of azobenzene, 7, in cumene[6] and structurally analogous to those likely to be formed in our work. The likely structures of the hydrazyls formed from 1, 3, 4, and 7 (see Table I) are



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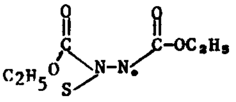

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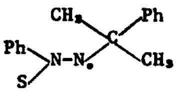

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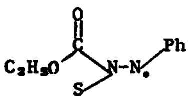

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Table I: Properties of radicals observed on photolysis of azo compounds.

Compound Photolyzed	Proposed Radical	a_N,G	g-Value	Halflife,[a] min	Ref
1	**8**[b]	8.50, 1.85	2.0063	1	1
3	**9**[b]	12.34, 9.41	2.0040	4	-[b,c]
4	**10**[b]	10.50, ---[d]	2.0054	1.2 x 10^2	-[b,c]
5	-	no signals were observed			-[b]
7	**6**	11.80, 0.88	2.0032	---[e]	6

[a] 25°C. [b] Present work. [c] The a- and g-values have maximum uncertainties of *ca*. 0.05G and 0.0001, respectively, and were taken at *ca*. 30°C. [d] See ref 3. [e] Several hours.

The formation of hydrazines by radical addition to alkyl azodicarboxylates is well known[7] and preparatively useful. It has been shown[8] that thermally or photochemically dimethyl azodicarboxylate decomposes in dodecane with only 7% nitrogen formation, the rest of the azo compound being consumed in a polymerization involving radical addition to the N=N bond. The observation of hydrazyl radicals on decomposition of these azodicarboxylates is, therefore, not surprising.[9]

CIDNP studies[10] have led us to predict that Ph-N=N• is a sigma-type radical, and should have a low g-value - below free spin - and a large $a_{\alpha\text{-}N}$ value (>50 G). These predictions stand in direct contrast to the values observed herein for these hydrazyl radicals which are probably pi-type.[11]

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References

1. P. Stilbs, G. Ahlgren, and B. Åkermark, *Tetrahedron Lett.*, 2387 (1972).

2. G. Heller, *Justus Liebigs Ann. Chem.*, **263**, 269 (1891).

3. Only the (1:1:1)-triplet splitting could be unambiguously assigned. The subsidiary multiplet structure appears consistent with weak couplings from one nitrogen nucleus and non-equivalent phenyl-group protons.

4. The equipment and procedures were essentially as described previously [P. Smith and R. D. Stevens, *J. Phys. Chem.*, **76**, 3141 (1972)] except that (a) the Corning filters were usually omitted (identical spectra were obtained with the use of such filters); and (b) the solutions were irradiated as static samples in 3 mm i.d. Suprasil tubes, which had been sealed off after repeated freeze-pump-thaw degassing with the use of a high-vacuum line; 0.1 M solutions were employed and all solvents were carefully purified [N. A. Porter and L. J. Marnett, *J. Amer. Chem. Soc.*, submitted for publication].

5. a) N. A. Porter and P. M. Iloff, *Chem. Comm.*, 1575 (1971); b) N. A. Porter, M. E. Landis, and L. J. Marnett, *J. Amer. Chem. Soc.*, **93**, 795 (1971).

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7. *E.g.*, L. Horner and W. Naumann, *Justus Liebigs Ann. Chem.*, **587**, 81 (1954).

8. A. Jones, E. R. Morris, and J.C.J. Thynne, *J. Phys. Chem.*, **72**, 2677 (1968).

9. The observation[1] that these radicals are not scavenged by oxygen but their spectra merely undergo reversible broadening is another example of documented hydrazyl chemistry, *e.g.*, A. R. Forrester, J. M. Hay, and R. H. Thomson, "The Organic Chemistry of Stable Free Radicals," Academic Press, New York, 1968, p 152.

10. N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, *J. Amer. Chem. Soc.*, **94**, 3664 (1972).

11. Very recently [D. E. Wood, C. A. Wood, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 9278 (1972)] the isotropic EPR spectra of three alkylhydrazyl radicals in an admantane matrix have been reported. Not surprisingly, their spectroscopic properties are most similar to those of **9**, *e.g.*, for $(CH_3)_2N$-NH, a_N equals 11.4 and 9.6 G and the g-value is 2.0036.