Aryloxyl Radicals by Photorearrangement of Nitro-compounds

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Oxyl radicals have been found to be formed from various types of hindered nitro-compounds by photolysis under degassed conditions. This observation is strong evidence which supports the formation of nitrites by photochemical rearrangements of nitro-groups. This report discusses the usefulness of the reaction for the identification of oxyl radicals.

CHAPMAN *et al.* reported a photochemical rearrangement of β-methyl-β-nitrostyrene (VII) to 1-hydroxyimino-1-phenylpropan-2-one (VIII).[1] They assumed that the reaction was initiated by a rearrangement of the hindered nitro-group to a nitrite as shown in step (c) of the Scheme.[2] Thereafter, similar photochemical rearrangements of nitro-groups have been reported.[2-5] However, no intermediates which support the assumed rearrangement to nitrites have been isolated or detected. We report here the detection of several types of oxyl radicals which strongly suggest the formation of nitrites in the photochemically induced rearrangement of nitro-groups; an interesting application of the detection of the oxyl radicals is presented.

EXPERIMENTAL

Samples were illuminated with a medium-pressure arc lamp (300 W) at a distance of 10 cm for 5—20 min. Shorter wavelengths were cut off with a Pyrex filter. A conventional *X*-band e.s.r. spectrometer with 100 KHz field modulation was used for the measurements of the samples after illumination. Sample solutions used were degassed by several freeze–pump–thaw cycles.

Benzene solutions (5×10^{-3}M) of 6-nitrobenzo[*a*]pyrene (I), which was prepared by treating benzo[*a*]pyrene with fuming nitric acid,[6] and *N*-methyl-*NN'*-dinitroguanidine (IV), which was prepared by the McKay's method,[7] were illuminated and the e.s.r. spectra were recorded at room temperature. The spectra were also observed in toluene, methanol, and dioxan. 9-Nitroanthracene (IX) was recrystallized from ethanol. 2,6-Dimethyl-1-nitrobenzene (X) was used after distillation. β-Methyl-β-nitrostyrene (VII) was a generous gift of Professor T. Kinugasa. Benzene solutions (1×10^{-1}M) of the three compounds did not show e.s.r. spectra either during or after illumination at room temperature. Illuminations and e.s.r. measurements for these compounds were also carried out in rigid solution at 77 K. Solvents were dehydrated with sodium wire before use. Silica-gel coated t.l.c. was used for the isolation and characterization of reaction products.

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[1] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Leng, and J. Reasoner, *Pure Appl. Chem.*, 1964, **9**, 585.

[2] O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Comm.*, 1966, 101; O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Amer. Chem. Soc.*, 1966, **88**, 5550.

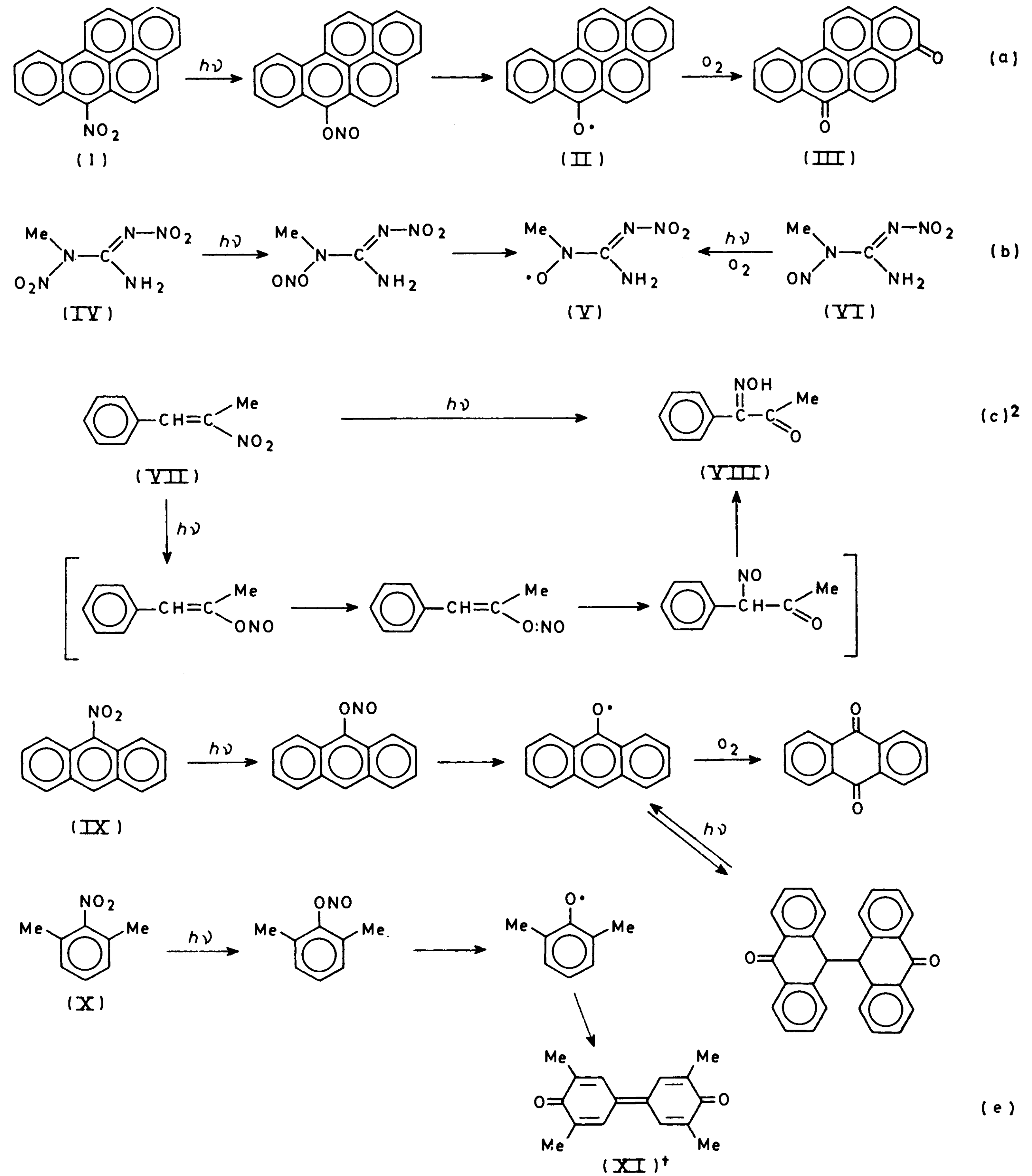
[3] J. T. Pinhey and E. Rizzardo (*a*) *Chem. Comm.*, 1965, 362; (*b*) *Tetrahedron Letters*, 1973, 4057.

[4] R. Hunt and S. T. Reid, *J.C.S. Perkin I*, 1972, 2527.

[5] Y. Kitaura and T. Matsuura, *Tetrahedron*, 1971, **27**, 1583; I. Saito, M. Takami, and T. Matsuura, *Tetrahedron Letters*, 1975, 3155.

[6] M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford, *J. Chem. Soc.*, 1956, 3572.

[7] A. F. McKay, *J. Amer. Chem. Soc.*, 1949, **71**, 1968.

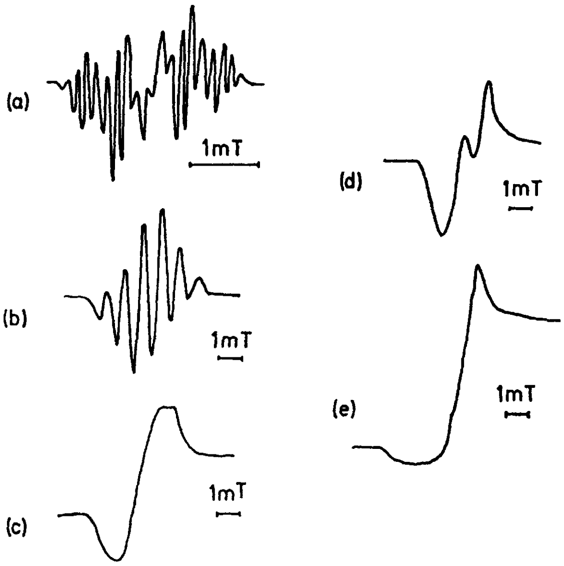


SCHEME † *E.g.* R. G. R. Bacon and A. R. Izzat, *J. Chem. Soc.* (*C*), 1966, 791

RESULTS AND DISCUSSION

The reason why the assumed nitrite intermediates in photochemical transformation of nitro-groups have never been detected may be due to their subsequent photochemical conversion to other products during u.v. illumination. Therefore we attempted to confirm the formation of nitrites by detecting oxyl radicals. Various types of nitro-compounds including β-methyl-β-nitrostyrene (VII) and 9-nitroanthracene (IX) [1,2] were examined. We have obtained e.s.r. spectra, two of them showing well resolved hyperfine structures.

6-Nitrobenzo[*a*]pyrene (I) showed an e.s.r. signal upon illumination with u.v. light in degassed solution at room temperature. It was composed of *ca.* 180 lines whose splittings show the hyperfine couplings of unpaired electron with ring protons. Spectrum (a) in this Figure was obtained at larger modulation width and is composed of 18 lines centred at *g* 2.004. The spectrum is identical with that of benzo[*a*]pyren-6-oxyl radical (II) produced by abstracting a hydrogen atom from benzo[*a*]pyren-6-ol in benzene solution.[8] This shows that formation of the oxyl radical is a consequence of the photorearrangement of the nitro-group by illumination of (I). The yield of the radical was low, when the solution of (I) was illuminated under air, probably due to the conversion into other products [(III), *etc.*] by reactions with molecular oxygen.



First derivative *X*-band e.s.r. spectra obtained by illumination of benzene solutions of: (a) 6-nitrobenzo[*a*]pyrene; (b) *N*-methyl-*NN'*-dinitroguanidine; (c) β-methyl-β-nitrostyrene; (d) 9-nitroanthracene; and (e) 2,6-dimethyl-1-nitrobenzene

By illumination of *N*-methyl-*NN'*-dinitroguanidine (IV) in degassed solutions, we obtained an e.s.r. spectrum composed of six lines centred at *g* 2.007. The hyperfine-structure of the spectrum is identical with that of the nitroxide radical (V) formed from *N*-methyl-*N'*-nitro-*N*-nitrosoguanidine (VI) under air.[9] Splitting into six lines was produced by hyperfine coupling of electron spin with the nuclear spins of the H_3CN group. This is clear evidence for the formation of (V) by photorearrangement of the hindered nitro-group in (IV).

On the other hand, the three nitro-compounds, β-methyl-β-nitrostyrene (VII), 9-nitroanthracene (IX), and 2,6-dimethyl-1-nitrobenzene (X), did not give e.s.r. signals upon u.v. illumination at room temperature. However, they gave e.s.r. signals in rigid solution at 77 K. This shows that these free radicals have been trapped in solvent matrices, though they are unstable at room temperature. They show asymmetric spectra without hyperfine splitting because of [10] anisotropy and broadening in the rigid phase. These free radicals change into other products at higher temperature (Scheme).

Photochemical rearrangements of nitrites are well known (*e.g.* the Barton reaction).[11] Therefore it is reasonable to consider that nitrites have not been detected in photolysis of nitro-compounds because of their instability under experimental conditions. In the present report, we have detected oxyl radicals by e.s.r. measurement and have found that oxyl radicals are formed by photolysis of nitro-compounds, which supports the initial photochemically induced nitro–nitrite rearrangement. Oxyl radicals are usually unstable and the observation of the hyperfine structure is not easy. The present success in observing hyperfine structures of the oxyl radicals derived from the nitro-derivatives seems due to the choice of highly conjugated aromatic compounds which stabilize the free radicals by delocalizing the unpaired electron. Our method may be applied to detect unstable oxyl radicals produced by photolysis of nitro-compounds in the absence of a proton donor.[12]

The formation of oxyl radicals (RO·) from hindered nitro-derivatives by illumination under degassed conditions is of special interest in relation to distinguishing them in reactions involving free radicals. The *g* values of peroxyl radicals ($RO_2\cdot$) fall in the range 2.014—2.019,[13] and are rather large compared with that of a free electron, possibly due to spin–orbit coupling on oxygen. Furthermore, alkyl radicals (R·), whose *g* values are close to that of a free electron, usually react with molecular oxygen reversibly,[14] ($R\cdot + O_2 \rightleftharpoons RO_2\cdot$). Thus, $RO_2\cdot$ and R· can be distinguished by examining the effect of molecular oxygen. However, no characteristic difference exists in the e.s.r. spectra R· and RO·.[15] It is useful to be able to assign preferentially RO· in a reaction mixture. The present photochemical reaction offers a convenient method for identifying oxyl radicals by using nitro-derivatives whose preparations are usually easy.

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[8] C. Nagata, M. Inomata, M. Kodama, and Y. Tagashira, *Gann*, 1968, **59**, 289; C. Nagata, Y. Tagashira, and M. Kodama in 'Chemical Carcinogenesis,' eds. P. O. P. Ts'o and J. A. DiPaolo, Marcel Dekker, New York, 1974, p. 87.

[9] Y. Ioki, A. Imamura, C. Nagata, and M. Nakadate, *Photochem. and Photobiol.*, 1975, **21**, 387.

[10] *E.g.* G. E. Pake, in 'Paramagnetic Resonance,' Benjamin, New York, 1962.

[11] D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, 1960, **82**, 2640; P. Kabasakalian and E. R. Townley, *J. Amer. Chem. Soc.*, 1962, **84**, 2711, 2716; M. Akhtar, *Adv. Photochem.*, 1964, **2**, 263.

[12] Different reactions might proceed after protonation of the nitro-group in aprotic solvents: *cf.* ref. 3*a*; R. G. Green, L. H. Sutcliffe, and P. N. Preston, *J.C.S. Perkin II*, 1975, 1380.

[13] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147; M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 959; K. U. Ingold and J. R. Morton, *ibid.*, p. 3400.

[14] E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Amer. Chem. Soc.*, 1967, **89**, 1176.

[15] *E.g.* R. Hoskins, *J. Chem. Phys.*, 1956, **25**, 788; Y. Deguchi, *Bull. Chem. Soc. Japan*, 1962, **35**, 260; T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.