A Convenient and Mild Method for Photogeneration of Nitroaromatic Radical Anions in Aqueous Solution

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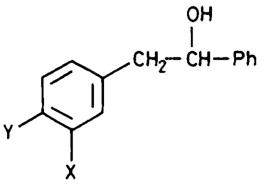
Photolysis of appropriately substituted nitroaromatic compounds in aqueous solution *via* a retro-aldol type process provides a convenient and mild method for generating nitroaromatic radical anions of the reacting substrate, and also of added nitroaromatic compounds (*via* electron transfer) for study at various pH values.

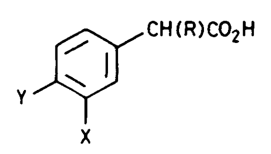
Nitroaromatic radical anions have been studied extensively owing to their relative stability in basic medium,[1,2] and also their relevance in radiotherapy.[3] The literature reveals a host of methods for producing nitroaromatic radical anions for e.s.r. studies: electrochemical reduction [in MeCN and dimethylformamide (DMF)];[4,5] reduction by alkali metals;[2,6] radiolysis;[7] photoreduction in basic medium;[8] reduction by reaction with carbanions in basic solution;[9—12] and *via* reaction with α-hydroxyalkyl radicals.[13] Although the methods listed here are not exhaustive, they comprise methods† for which authenticated e.s.r. spectra of the nitroaromatic radical anions have been reported. By far the most widely used and probably the most general method involves electrochemical reduction,[1,2] which is carried out in non-aqueous solvents. We report here a convenient photochemical method for the generation of a variety of nitroaromatic radical anions in essentially wholly aqueous solution, *via* initial photoretro-aldol type reaction of several nitroaromatic derivatives, which provides the electron source. This method makes possible the study of nitroaromatic radical anions with respect to their reactivity and stability, as well as electron charge densities, at different pH values *via* a relatively simple experimental procedure.

The photoretro-aldol type reaction[14] of 2-(*p*-nitrophenyl)-1-phenylethanol (**1**) in basic medium gave high yields (>50%) of *p,p*′-dinitrobibenzyl (**6**), in addition to the expected benzaldehyde and *p*-nitrotoluene products. The same observation has also been made in the photodecarboxylation of *p*-nitrophenylacetic acid (**3**) at high pH.[15] The corresponding *meta*-isomers (**2**) and (**4**), respectively, gave only trace yields of *m,m*′-dinitrobibenzyl, the major product being *m*-nitrotoluene [in addition to benzaldehyde for (**2**) and CO_2 for (**4**)]. To account for these observations, it was proposed[14] that photogenerated *p*-nitrobenzyl carbanions are readily oxidized in solution, *via* electron transfer to a molecule of substrate (Scheme 1), whereas *m*-nitrobenzyl carbanions are protonated by solvent very rapidly. Support of this mechanism comes from the work of Russell and Janzen[9] who have observed that the thermally generated *p*-nitrobenzyl carbanion disproportionates to give good yields of (**6**). E.s.r. studies have shown that the *p*-nitrotoluene radical anion is generated in the medium.[9]

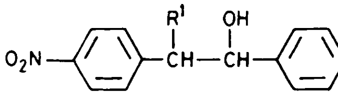
Photolysis of 0.01M argon-saturated solutions of (**1**) and (**3**) (Oriel 200 W Xe–Hg lamp; pH 12; 10—30% MeCN; 23 °C) in a quartz flat cell placed inside the cavity of a Bruker E200TT e.s.r. spectrometer gave strong e.s.r. spectra assignable to the radical anions of (**1**) and (**3**) [Figure 1(a)]. The lifetimes of these radical anions can be readily measured by following the decay of the e.s.r. signal intensity after turning off the lamp. Thus, the lifetime of ($\mathbf{3}^{\bullet-}$) was about 1 min at pH 12, decreasing to less than 15 s at pH 7; ($\mathbf{1}^{\bullet-}$) had a lifetime of about 5 min at pH 12; no e.s.r. signal was observed at pH 7 since (**1**) reacts inefficiently in neutral pH.[14] Additionally, only very weak e.s.r. signals were observed for the *meta*-isomers (**2**) and (**4**), consistent with the lack of electron transfer reaction in these substrates. A variety of other *para*-nitro-substituted radical anions can also be generated *via* this method. Thus we have observed the radical anions of (**7**)—(**11**), all of which react *via* a photoretro-aldol reaction in basic medium. The utility of the approach becomes apparent when an equimolar mixture of (**1**) and *p*-nitrobenzoic acid is used, which gave only the e.s.r. signal of the radical anion of *p*-nitrobenzoic acid [Figure 1(b)]. Photolysis of *p*-nitrobenzoic



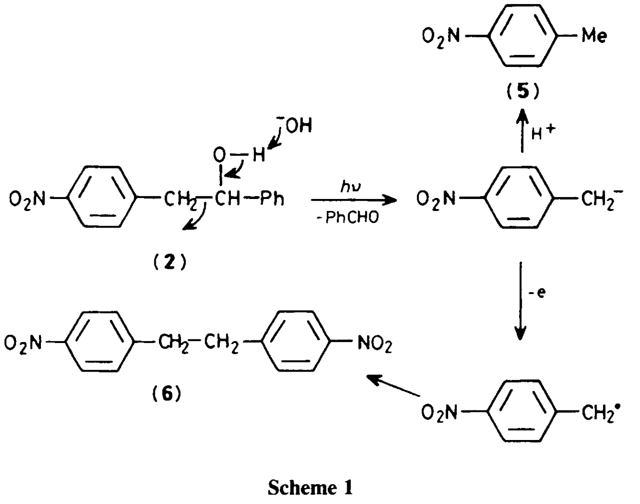
(**1**) X = H; Y = NO_2
(**2**) X = NO_2; Y = H



(**3**) X = H; Y = NO_2; R = H
(**4**) X = NO_2; Y = H; R = H
(**11**) X = H; Y = NO_2; R = Me



(**7**) R^1 = H; R^2 = Me
(**8**) R^1 = H; R^2 = OMe
(**9**) R^1 = Me; R^2 = H
(**10**) R^1 = OH; R^2 = H



Scheme 1

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† Reactions in which nitroaromatic radical anions have been proposed as intermediates, but for which no e.s.r. spectra have been reported, are not included.

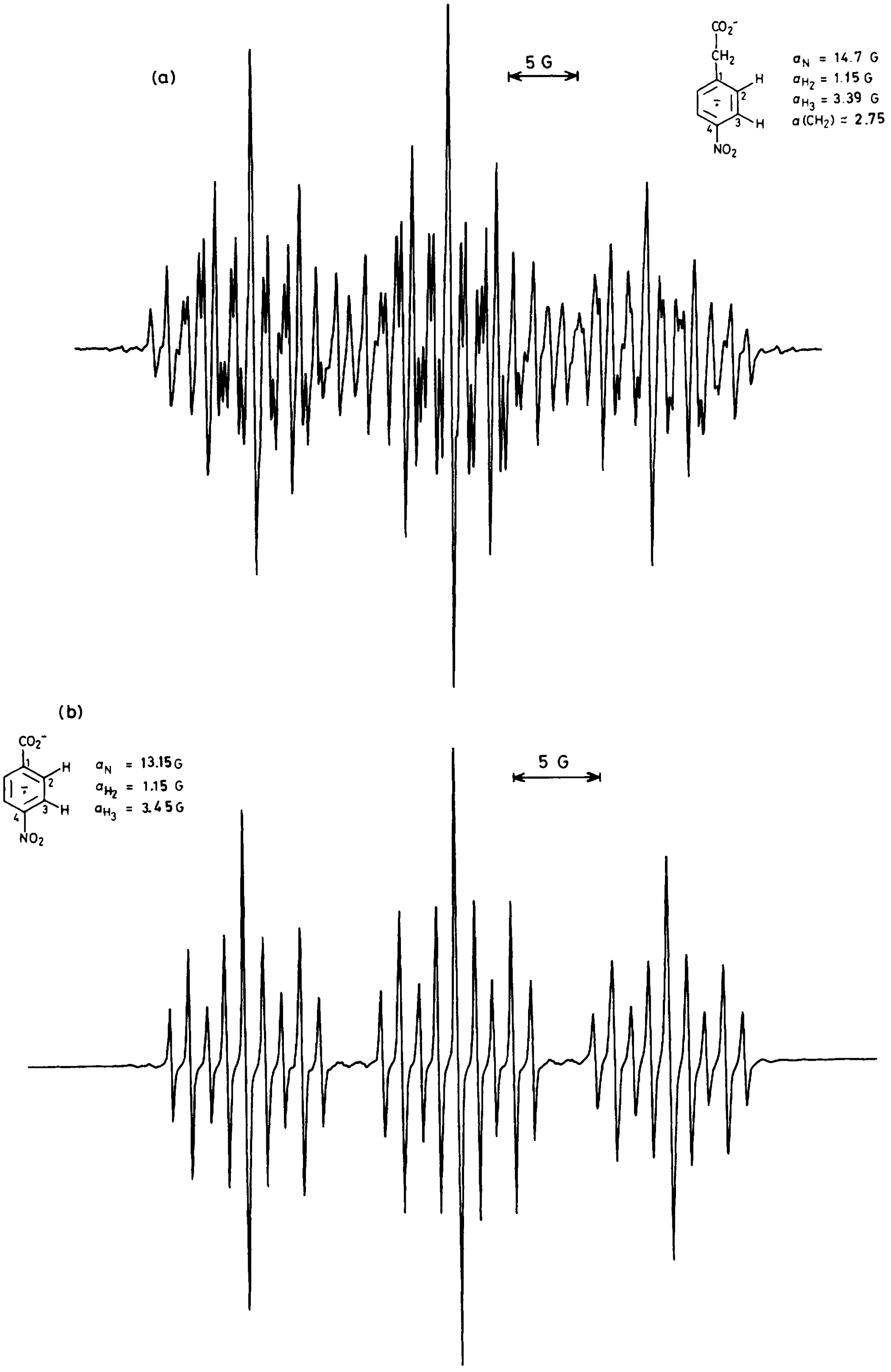
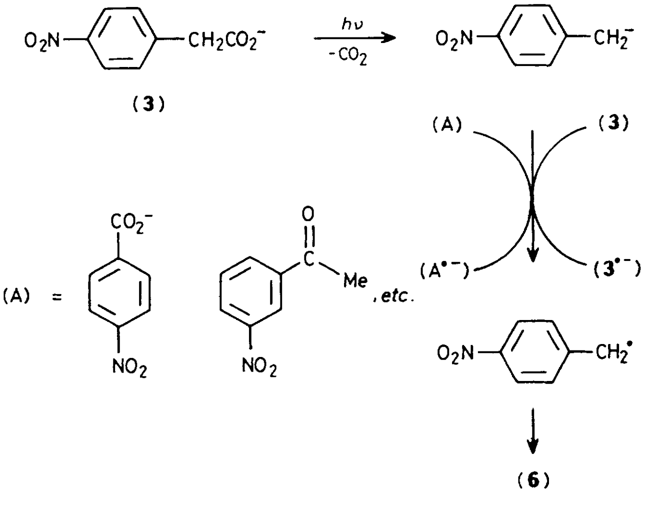


Figure 1. (a) E.s.r. spectrum of the *p*-nitrophenylacetate radical anion formed *via* photolysis of (**3**) in pH 12 (10—30% MeCN). (b) E.s.r. spectrum of the *p*-nitrobenzoate radical anion formed *via* electron transfer from the photogenerated *p*-nitrobenzyl carbanion to *p*-nitrobenzoate in the photoretro-aldol reaction of (**1**) in pH 12. [Hyperfine coupling constants, *a* in G (1G = 10^{-4} T), were obtained by computer simulation of spectra and agree well with known literature values, where available.[1,2]]



Scheme 2

acid alone does not result in any observable e.s.r. signal. The use of other 'acceptors' such as *m*- and *p*-nitroacetophenone, *m*- and *p*-nitrobenzaldehyde, and *m*- and *p*-dinitrobenzene in the presence of a reactive substrate [*e.g.*, (**1**), (**3**), or (**11**)] results in the observation of only the e.s.r. signal of the acceptor (Scheme 2). The photoretro-aldol type reaction is therefore a convenient source of reducing electrons which are transferred quickly to the best electron acceptor in solution. The e.s.r. spectra of nitroaromatic radical anions generated in aqueous solution *via* the above method show considerable simplification in hyperfine structure, compared with those previously reported in the literature. This is due predominantly to the larger a_N coupling constant observed in aqueous solution (typically >12 G, 1 G = 10^{-4} T), and also simplification of the proton hyperfine coupling in many cases. These observations indicate that the study of e.s.r. spectra of nitroaromatic radical anions will give spectra that are more readily interpretable, even *via* first order analysis in some cases.

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References

1 P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen and Company, London, 1967; K. W. Bowers, in 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968.
2 B. H. J. Bielski and J. M. Gebicki, 'Atlas of Electron Spin Resonance Spectra,' Academic Press, New York, 1967.
3 C. L. Greenstock, in 'Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives,' ed. S. Patai, Wiley, New York, 1982.
4 M. Branca, A. Gamba, M. Barzaghi, and M. Simonetta, *J. Am. Chem. Soc.*, 1982, **104**, 6506.
5 M. Barzaghi, A. Gamba, G. Morosi, and M. Simonetta, *J. Phys. Chem.*, 1974, **78**, 49.
6 A. Alberti, G. F. Pedulli, and F. Ciminale, *Tetrahedron*, 1982, **38**, 3605.
7 M. C. R. Symons and W. R. Bowman, *J. Chem. Soc., Chem. Commun.*, 1984, 1445.
8 G. A. Russell and E. J. Geels, *Tetrahedron Lett.*, 1963, 1333.
9 G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, 1967, **89**, 300.
10 G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, 1968, **90**, 347.
11 G. A. Russell, and J. M. Pecoraro, *J. Am. Chem. Soc.*, 1979, **101**, 3331.
12 N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 734.
13 V. Jagannandham and S. Steenken, *J. Am. Chem. Soc.*, 1984, **106**, 6542.
14 P. Wan and S. Muralidharan, *Can. J. Chem.*, 1986, **64**, 1949.
15 J. D. Margerum and C. T. Petrusis, *J. Am. Chem. Soc.*, 1969, **91**, 2467.