Evidence for the Trapping of a Non-Kekulé Intermediate in the Photoretro-aldol Type Reaction of *m*-Nitrobenzyl Derivatives

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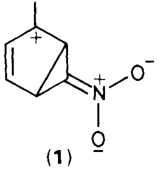
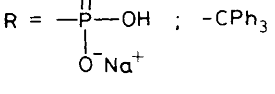
The acid-catalysed photoretro-aldol type reaction of *m*-nitro-substituted derivatives was found to give 3-(*N*-3′-nitrobenzyl-*N*-hydroxyamino)benzyl alcohol (**4**) as the only product derived from the nitrobenzyl fragment; the structure of (**4**) has been determined by *X*-ray crystallography and the mechanism for its formation requires the intermediacy of a non-Kekulé intermediate in which direct transmission of charge between the 1,3-positions of the benzene ring occurs.

The notion of '*meta*-activation' by the nitro substituent in photosubstitution reactions of nitroaromatic compounds has been introduced to rationalize the enhanced reactivity of many *m*-nitro-substituted isomers, as compared to the corresponding *p*-nitro-substituted isomers.[1,2] Zimmerman and Somasekhara[3] have suggested the importance of non-Kekulé† structures of the type (**1**) in the excited state in order to explain the higher quantum yield of photosolvolysis of *m*-nitrophenyl phosphate and trityl ether (as compared to the corresponding *para*-isomers). Structure (**1**) and related non-Kekulé species involve direct conjugation between the 1,3-positions of the


(**1**)


$$R = -\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-Na^+}{|}}{P}}-OH\ ;\ -CPh_3$$

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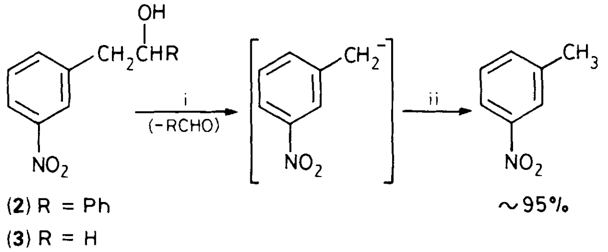
† For the definition of non-Kekulé hydrocarbons, see: M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, p. 232. The definition can be readily extended to heteroatom-substituted aromatic compounds. For examples, see: M. Rule, A. Matlin, D. Seeger, E. Hilinski, D. Dougherty, and J. A. Berson, *Tetrahedron*, 1982, **38**, 787; A. R. Matlin, T. A. Inglin, and J. A. Berson, *J. Am. Chem. Soc.*, 1982, **104**, 4954.

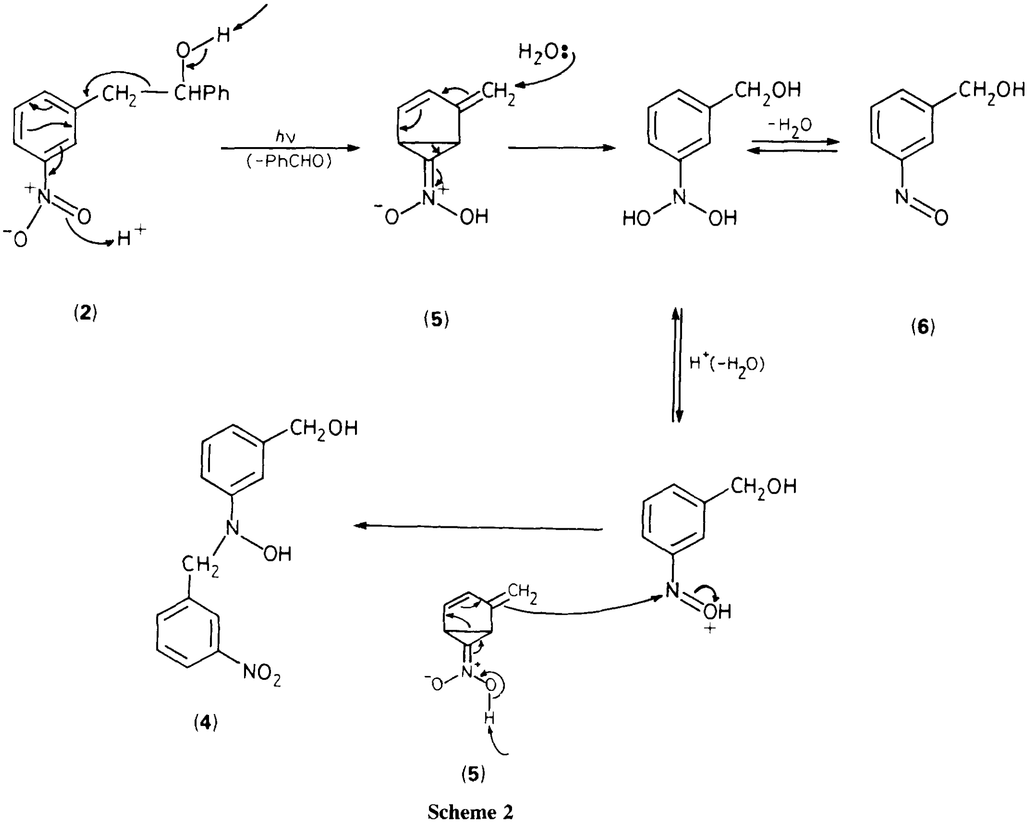
benzene ring, with the nitro group acting as the electron acceptor in the polarized non-Kekulé structure. More recent studies[4–10] have also shown that the *m*-nitro group can initiate several related photochemical reactions, all of which can best be rationalized as due to the enhanced electron withdrawing effect of the *m*-nitro group in the excited triplet state, presumably owing to the importance of contributing non-Kekulé resonance structures similar to (**1**). However, in these [4–10] and previous[1–3] studies, direct evidence for 1,3-transmission of charge in the excited state of these nitrobenzene derivatives, as required in structures of the type (**1**), has been lacking since the overall chemistry does not formally require movement of a pair of electrons between the 1,3-positions. Thus, structures of the type (**1**) have been considered as only crude representations of the excited state and their use in mechanisms has often raised discussion with regard to their validity. We report here evidence to indicate that *direct* transmission of electronic charge through the 1,3-positions does occur in the excited triplet state of certain nitrobenzene derivatives, resulting in an intramolecular redox reaction, in which the nitro group is reduced to nitroso and the alkyl fragment at the corresponding *meta*-position is oxidized.



Scheme 1. *Reagents and conditions:* i, *h*ν, 30% $MeCN–H_2O$, pH 1—14; ii, H^+.

The photoretro-aldol type reactions of several *m*- and *p*-nitrobenzyl derivatives *via* the triplet excited state have recently been reported[6] (Scheme 1). In the alcohol series, base catalysis of reaction is observed consistent with a mechanism involving primary C–C bond heterolysis in the primary photochemical step. For the *m*-nitro isomers, protonation by solvent water is the major reaction pathway (≈95%) for photogenerated *m*-nitrobenzyl carbanion (MNBC). However, when (**2**) was photolysed in aqueous acid solution (H_2SO_4; $H_0 < 0$; in quartz cuvettes at 10^{-6}–10^{-4} M or semipreparative scale reaction at 10^{-3} M; Rayonet RPR 100 photochemical reactor; 254 or 300 nm lamps; argon purged solutions) acid catalysis of photoretro-aldol was observed, as indicated by the clean formation of benzaldehyde, with its yield increasing with increasing acidity (*e.g.*, $\Phi = 0.09$ at H_0 −0.45 and 0.14 at H_0 −1.65 for benzaldehyde formation, as determined by u.v. spectrophotometry with potassium ferrioxalate actinometry[6]). The formation of benzaldehyde indicates that the retro-aldol process was occurring in acid on photolysis. No reaction was observed in the dark. However, the reaction gave no trace of the expected *m*-nitrotoluene from the nitrobenzyl fragment (*via* simple protonation of the incipient MNBC).

The yield of the product derived from the nitrobenzyl fragment in the acid-catalysed process also increased with increasing acidity and was homogeneous by t.l.c. (yield ≈80% at H_0 −1.65). However, its structure proved difficult to



Scheme 2

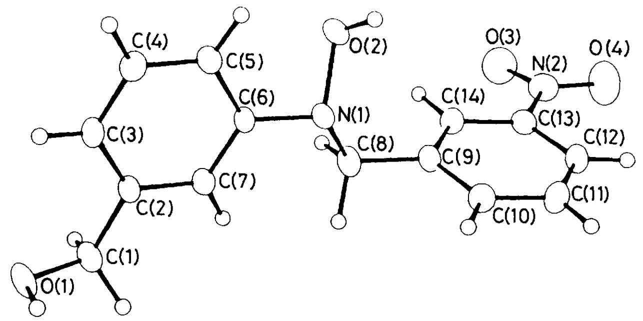


Figure 1. *X*-Ray crystal structure of photoproduct (**4**).

characterize *via* the standard spectroscopic techniques.‡ Mass spectrometry indicated a molecular weight of 274, suggesting coupling of two nitrobenzyl moieties. Photolysis of (**3**) also gave the same product, but in lower yield. The i.r. spectrum showed the presence of at least one nitro group, as well as the presence of a hydroxy group. The structure of the product (**4**) was eventually solved by *X*-ray crystallography§ (Figure 1) from crystals obtained from crystallization from acetone/hexanes.

The product (**4**) is clearly derived from the formal condensation of a *m*-nitrobenzyl carbanion (or equivalent) fragment with *m*-nitrosobenzyl alcohol (**6**) (Scheme 2). It cannot be obtained by simple dimerization of (**6**). Since the quantum yield for benzaldehyde formation (Φ) is independent of substrate concentration (down to $\approx 10^{-6}$ M) and product (**4**) was observed down to 10^{-4} M (limit of concentration used for preparative experiments), we conclude that the primary photochemical step is a unimolecular C–C heterolysis step *assisted* by protons. How the protons assist can be inferred from structure (**4**) and by the absence of any *m*-nitrotoluene product in the acid-catalysed process. In the proposed mechanism (Scheme 2), the proton assists the cleavage by protonating at the nitro group¶ concerted with benzylic C–C bond heterolysis, to generate a non-Kekulé intermediate (**5**). Trapping by water at the benzylic position gives the hydrated form of (**6**), which subsequently condenses with another molecule of (**5**) to give the observed (**4**). Direct evidence (*e.g.*, detection *via* flash photolysis) for the intermediacy of non-Kekulé species (**5**) would have been desirable. However, the lack of any substantial u.v.-visible chromophore in (**5**) would make such detection almost impossible. Although the full details of the reaction mechanism are not completely understood, the results reported here form the basis of a general indirect method for studying these elusive non-Kekulé intermediates in nitroaromatic photochemistry.

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‡ M.p. 127–128 °C; ^{1}H n.m.r. data (250 MHz) for (**4**): ($CDCl_3$), δ 4.15 (1H, t, *J* 5.8 Hz, exchanges with D_2O), 4.59 (2H, d, *J* 6.3 Hz, collapses into a singlet with addition of D_2O), 4.61 (2H, s), 6.91–7.29 (4H, m), 7.61 (1H, t, *J* 7.8 Hz), 7.64–7.88 (1H, m), 8.15 (1H, m), 8.18 (1H, s, exchangeable with D_2O), 8.34 (1H, m); ^{13}C n.m.r. data (62.9 MHz) for (**4**): ([$^2H_6$]acetone, proton decoupled) δ 62.8, 64.3, 64.4, 114.8, 115.1, 120.2, 122.7, 124.1, 129.1, 130.1, 136.2, 141.7, 143.8, 148.7, 154.1 (the peaks at δ 64.3 and 64.4 collapse into a single peak on addition of D_2O). Satisfactory elemental analysis for (**4**) have been obtained.

§ *Crystal data* for (**4**): $C_{14}H_{14}N_2O_4$, $M = 274.3$, triclinic, space group $P\bar{1}$, $a = 9.203(4)$, $b = 9.591(3)$, $c = 7.927(4)$ Å, $\alpha = 103.90(4)$, $\beta = 79.56(3)$, $\gamma = 105.46(4)°$, $U = 649.5$ Å^3, $Z = 2$, $D_c = 1.402$ g cm^{-1}. Data were collected on a Picker diffractometer. Structure solution and refinements were carried out using SHELX-76. The structure was solved by direct methods. Convergence to final values of $R = 0.0466$ and $R_w = 0.0487$ was obtained by using 2286 reflections $[F^2 > 3\sigma(F^2)]$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ There is now a growing collection of data to suggest that protonation of the nitro group in photoexcited nitroaromatic compounds can occur in acid media, resulting in acid-catalysed photochemistry. See refs. 5, 11 and 12.