way (4×) to a constant mp of 215 °C. Conversion to the free base and crystallization from hexane provided a resolved sample of amino alcohol **26**: $[\alpha]^{23}_{365}$ −43.7°, $[\alpha]^{23}_{435}$ −11.4°, $[\alpha]^{23}_{546}$ −0.37°, $[\alpha]^{23}_{578}$ +0.64°, $[\alpha]^{23}{}_D$ +0.86° (toluene, *c* 2.7). The Mosher ester[24] of this material showed no trace of a diastereomer by ^{1}H NMR analysis at 250 MHz.

Preparation of Optically Active Pyrrolidine Ketone 25 from Resolved 26. A mixture of MnO_2 (200 mg, 2.3 mmol), resolved **26** (20 mg, 0.071 mmol), and dry toluene (4 mL) was rapidly stirred for 5 h at room temperature and then filtered through a pad of Celite. The Celite was washed with benzene (200 mL), the filtrate was concentrated, and the residue was purified by rapid flash chromatography on silica gel (0.5 g; 1:4:0.2 EtOAc–hexane–Et_3N) to give 2.5 mg (13%) of ketone **25** and 12 mg (61%) of recovered alcohol **26**. Pyrrolidine ketone **25** prepared in this way showed the following optical rotations: $[\alpha]^{23}_{435}$ +424°, $[\alpha]^{23}_{546}$ +216°, $[\alpha]^{23}_{578}$ +185°, $[\alpha]^{23}{}_D$ +177° (toluene, *c* 0.66).

Rearrangement of 24 to Partial Completion. A solution of oxazolidine **24** (28.1 mg, 0.101 mmol), camphorsulfonic acid (23 mg, 0.10 mmol), and toluene (3 mL) was heated at 60 °C for 20 min (70% completion by ^{1}H NMR analysis). This crude mixture was reduced with $LiAlH_4$, and the resulting crude product was partially reoxidized with MnO_2. Separation on silica gel gave 2 mg of recovered oxazolidine **24** as an oil: $[\alpha]^{23}_{365}$ −573°, $[\alpha]^{23}{}_D$ −159° (100% optical purity), 6 mg of crystalline alcohol **26** after recrystallization from hexane, $[\alpha]^{23}_{365}$ −1.0° (2.3% optical purity), and 2.5 mg of ketone **25** as an oil, $[\alpha]^{23}{}_D$ +4.4° (2.5% optical purity).

In a similar fashion, **24** (36.1 mg, 0.129 mmol), camphorsulfonic acid (37.6 mg, 0.162 mmol), and toluene (4 mL) were heated for 15 min at 60 °C (83% completion). Pyrrolidine alcohol **26** (11.5 mg, 32%) was then isolated after reduction with $LiAlH_4$, chromatographic purification, and crystallization from hexane: $[\alpha]^{23}_{365}$ −2.1° (4.9% optical purity).

Stability of Pyrrolidine Ketone 25 to Racemization. Camphorsulfonic acid (3.3 mg, 0.014 mmol, 0.5 equiv) was added in 1 portion to a 0.032 M solution of resolved ketone **25** (7.5 mg, 0.027 mmol, $[\alpha]^{23}_{365}$ +343°) in toluene (0.85 mL). The resulting solution was stirred at 60 °C for 1 h and then quenched by adding a cold 2 N NaOH solution (2 mL). Product isolation as described in the preparation of **25** from **24** provided 6.0 mg (80%) of chromatographically pure ketone **25** as a colorless oil. Capillary GC analysis[36] showed the purity of this ketone to be greater than 98%: $[\alpha]^{23}_{365}$ +303°. This experiment was repeated four times, and identical control experiments were performed with 1.0 and 1.2 equiv of camphorsulfonic acid. Results are summarized in Table II.

Acknowledgment. We thank Professor R. J. Doedens for assistance with the X-ray crystallography and M. Fisher for DNOE studies. This research was supported by a Javits Neuroscience Investigator Award from the National Institute of Neurological and Communicative Disorders and Stroke. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF Shared Instrumentation Grants.

Supplementary Material Available: Experimental details and characterization data for **11a**, **11b**, **11d**, and **12a**, X-ray data for **12c**, tables of atomic and positional parameters, hydrogen atom coordinates, bond angles, and bond distances, and an X-ray model of Figure 2 with full atom labeling (10 pages). Ordering information is given on any current masthead page.

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[36] A 30-ft SE-30 quartz capillary column was employed for this analysis.

Structure and Mechanism in the Photo-Retro-Aldol Type Reactions of Nitrobenzyl Derivatives. Photochemical Heterolytic Cleavage of C–C Bonds[1]

Peter Wan*[,2] and S. Muralidharan

Contribution from the Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2. Received September 21, 1987

Abstract: The photo-retro-aldol type reactions of several nitroaromatic compounds have been studied in aqueous solution over the pH 1–14 range. These reactions are observed only in aqueous or in predominantly aqueous solution. Catalysis of reaction due to hydroxide ion is observed for several derivatives. Quantum yields of reaction and product ratios (of nitrotoluene vs dinitrobibenzyl) are reported as a function of pH. The proposed mechanism of reaction involves heterolytic cleavage of the benzylic C–C bond from the triplet excited state in the primary photochemical step to generate a nitrobenzyl carbanion and a carbocation-equivalent fragment, except for the nitrophenylacetates **24–26**, which eliminate CO_2 in place of such a fragment. Photogenerated nitrobenzyl carbanions are efficiently trapped by molecular oxygen to give isolable hydroperoxides at pH <12. The pH dependence of quantum yield of reaction along with α-deuterium isotope effects indicates that different transition states for benzylic C–C bond heterolysis are operative, depending on the substrate as well as the pH of the solution. Hydroxide ion catalyzed rate constants for the primary photochemical step are estimated for alcohols **8** and **9** to be $\sim 1 \times 10^9$ M^{-1} s^{-1}. The results show that photochemical C–C bond heterolysis requires favorable stabilization of both the carbanion and carbocation-derived fragments. Hydroxide ion catalysis may also facilitate the process. The use of the nitrobenzyl moiety as the carbanion-stabilizing group appears to be generally applicable, as demonstrated by the systems studied.

Studies of C–C bond forming and cleavage reactions play a central role in organic chemistry. Rupture of a C–C bond may proceed via either homolytic or heterolytic pathways. The homolytic pathway has been studied in some detail, and C–C bond dissociation energies have been extensively tabulated.[3] The less common heterolytic process—in which a carbocation and a carbanion are formed—has not been as extensively studied. Recently, however, there has been interest in developing molecular systems for study of kinetics and thermodynamics and structural requirements of C–C bond heterolysis, as well as in carbocation–anion recombination reactions.[4] Heterolytic C–C bond cleavage processes are also not common in photochemical reactions, al-

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[1] This work has appeared in preliminary form: Wan, P.; Muralidharan, S. *Can. J. Chem.* **1986**, *64*, 1949.

[2] NSERC Canada University Research Fellow, 1984–1989.

[3] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[4] (a) Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172. (b) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *Ibid.* **1984**, *106*, 6726. (c) Arnett, E. M.; Chawla, B.; Molter, K. E.; Amarnath, K.; Healy, M. *Ibid.* **1985**, *107*, 5288. (d) Mitsuhashi, T. *Ibid.* **1986**, *64*, 2239. (e) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.* **1983**, 3299. (f) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173. (g) Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239.

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Table I. Relative Yields (%) of Nitrotoluene vs Dinitrobibenzyl Products in the Photo-Retro-Aldol Type Reactions of **2**, **7–9**, **24**, and **25**[a]

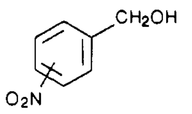
	2		**8**		**24**		**7**		**9**		**25**	
pH[b]	**3**	**4**	**3**	**4**	**3**	**4**	**11**	**12**	**11**	**12**	**11**	**12**
14	2	98	2	98	2	98	95	5	95	5	90	10
13	5	95	5	95	2	98	95	5	93	3	95	5
12	20	80	10	90	10	90					95	5
11	*c*	*c*	20	80	20	80	95	5				
10			50	50					95	5	98	2
7			60	40	70	30	95	5	96	4	98	
4			70	30	80	20			~100	0	~100	0
3			90	10	*c*	*c*			~100	0	*c*	*c*
2			≈100	0								

[a] Relative ratios of **3** vs **4** (or **11** vs **12**) were calculated by ^{1}H NMR integration of the appropriate product signals and normalized to 100%. The error in these results is about 10% of the quoted value. Conversions were taken to 30–100%. [b] Quoted pH is the pH of the water portion of the solvent mixture (30% CH_3CN), except for acids **24** and **25** where direct pH measurements were taken after addition of substrate and additional pH adjustments made with aqueous NaOH or HCl as required. [c] No reaction at this and lower pHs.

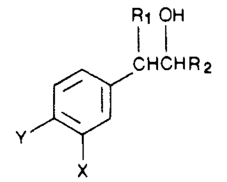
though their importance should not be less significant compared with the corresponding ground-state process. To our knowledge, there are only several examples in the literature in which the proposed mechanism of a photochemical reaction involves heterolytic C–C bond cleavage in the primary step: photodecarboxylation of arylacetate ions,[5] photodeformylation of 9-fluorene and 9-xanthenemethanols,[6] and the photosolvolysis of malachite green leucocyanide.[7] On the other hand, there are a large number of photochemical reactions that proceed via initial C–C bond homolysis.[8] The need to understand the basic structural requirements for photochemical C–C bond heterolysis is therefore evident. In this paper, we report the use of appropriately substituted nitroaromatic derivatives which on photolysis results in formal C–C bond heterolysis, via a reasonably general retro-aldol type process. The results give new insights into the structural and catalytic requirements necessary for achieving C–C bond heterolysis in photochemical reactions.

Results

Product Studies. Previous studies[9] have shown that *m*- and *p*-nitrobenzyl alcohols (**1**) and related compounds react in aqueous solution to give both oxidized and reduced products, via pathways that are topics of current study.[9] A natural extension is to study

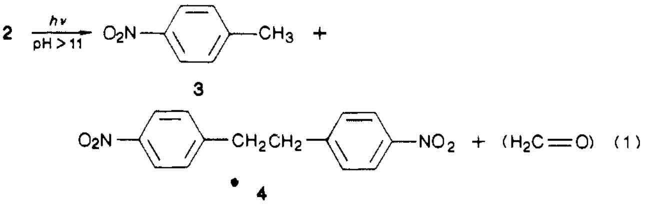


1

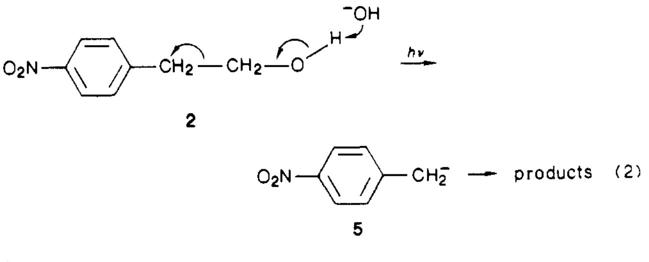


2: R_1 = H, R_2 = H, X = H, Y = NO_2
6: R_1 = H, R_2 = H, X = H, Y = H
7: R_1 = H, R_2 = H, X = NO_2, Y = H
8: R_1 = H, R_2 = Ph, X = H, Y = NO_2
9: R_1 = H, R_2 = Ph, X = NO_2, Y = H
10: R_1 = CH_3, R_2 = Ph, X = H, Y = NO_2

the photochemistry of *p*-nitrophenethyl alcohol (**2**), which differs from **1** only by the addition of an extra methylene unit to the hydroxymethylene side chain. Compound **2** does not react via the pathway reported for *p*-nitrobenzyl alcohol[9a,b] but reacts nevertheless in aqueous base (pH >11; 30% CH_3CN cosolvent; Rayonet RPR 100 photochemical reactor; 254-, 300-, or 350-nm lamps; typical photolysis time 1–2 h) to give *p*-nitrotoluene (**3**) and 4,4′-dinitrobibenzyl **4**; eq 1. The relative yields of the two



products varies with pH (Table I), ranging from >95% of **4** at pH 14 to a ratio of 20:80 of **3** to **4** at pH 12. Conversions of close to 100% may be achieved at sufficiently high pH on extended photolysis, with overall yields of **3** and **4** of up to 90%. The ratios of **3** to **4** do not change at different conversions. The expected formaldehyde product was not isolated. No reaction was observed when **2** was left in the dark for an extended period of time at any pH. Product **4** (eq 1) is not a secondary reaction product of **3**, as confirmed by independent photolysis of **3**, which gave no reaction. Additionally, **4** is photochemically nonlabile under the above conditions. The reaction of **2** is not observed on photolysis in typical organic solvents (e.g., CH_3CN, MeOH, EtOH, diethyl ether, benzene) or in aqueous solution of pH <11. It is also not observed on photolysis in 0.1 M NaOMe/MeOH. The requirement of aqueous base along with the isolation of *p*-nitrotoluene (**3**) suggests initial heterolytic C–C bond cleavage in the photochemical reaction (eq 2), via a retro-aldol type process, to give



initially *p*-nitrobenzyl carbanion (**5**), analogous to the photodecarboxylation of nitrophenylacetate ions reported by Margerum and Petrusis.[5a] The generality of this type of reaction had not been anticipated; thus, we initiated the present study, initially to study the photochemistry of **2** and **7–10** in aqueous solution.

Photolysis of non-nitro-substituted derivative **6** under the above conditions failed to give any reaction, and this finding indicates that the nitro group and aqueous base are necessary for the photoretro-aldol process. As was observed for **2**, *m*-nitrophenethyl alcohol (**7**) also reacts cleanly in aqueous base but differs in chemistry from **2** in that the major product at all pHs (7–14) is *m*-nitrotoluene (**11**); only a trace yield (<5%) of 3,3′-dinitrobibenzyl (**12**) was observed (Table I). The reactivity of **2** and **7** in aqueous base suggests that a general retro-aldol type process is available for appropriately substituted nitroaromatic compounds, using the *p*-nitrobenzyl (or *m*-nitrobenzyl) carbanion moiety as

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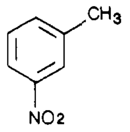
(5) (a) Margerum, J. D.; Petrusis, C. T. *J. Am. Chem. Soc.* **1969**, *91*, 2467. (b) Stermitz, F. R.; Huang, W. H. *Ibid.* **1971**, *93*, 3427. (c) Epling, G. A.; Lopes, A. *Ibid.* **1977**, *99*, 2700. (d) McAuley, I.; Krogh, E.; Wan, P. *Ibid.* **1988**, *110*, 600.

(6) Krogh, E.; Wan, P. *Tetrahedron Lett.* **1986**, 823.

(7) (a) Calvert, J. G.; Rechen, H. J. L. *J. Am. Chem. Soc.* **1952**, *74*, 2101. (b) Fischer, G. J.; LeBlanc, J. C.; Johns, H. E. *Photochem. Photobiol.* **1967**, *6*, 757.

(8) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

(9) (a) Wan, P.; Yates, K. *Can. J. Chem.* **1986**, *64*, 2076. (b) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 136. (c) Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1986**, *51*, 2777.



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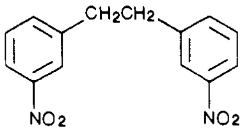

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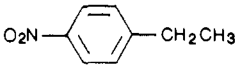

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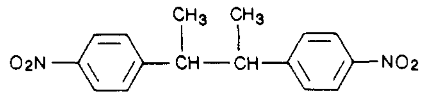
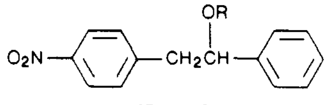


14

the photolabile leaving group. Thus, 1-phenyl-substituted alcohols **8–10** all react via the photo-retro-aldol process cleanly (typical conversions 30–60%) in the pH 1–14 region (in contrast to **2** and **7**, which have appreciable reactivity only in high pH). The products are benzaldehyde (for all of **8–10**) in addition to products **3** and **4** for **8**, products **11** and **12** for **9**, and products *p*-ethylnitrobenzene (**13**) and 2,3-bis(*p*-nitrophenyl)butane (**14**) [as a mixture of meso and (*R*,*R*) and (*S*,*S*) stereoisomers, see the Experimental Section] for **10**. The ratios of the two products derived from the nitrobenzyl fragment (i.e., not benzaldehyde) of para isomer **8** are strongly pH-dependent, in contrast to the meta isomers **7** and **9** (Tables I, II). As was observed for **2**, **8** gave greater proportions of the "bibenzyl" product **4** at high pH, whereas at low pH the predominant product (from the nitrobenzyl fragment) is **3**, derived via simple protonation of the nitrobenzyl carbanion fragment. Compound **10** is anomalous in this regard since it was the only para isomer that did not exhibit this behavior. However, preliminary studies indicate that, in acidic medium (pH <4), the expected products derived from the nitrobenzyl fragment are not observed, even though the photo-retro-aldol process is clearly taking place since benzaldehyde is formed. Instead, as yet uncharacterized products are isolated from the nitrobenzyl fragment, which suggests a change in mechanism at this pH. Investigation of the reaction mechanism at this and lower pH ranges is beyond the scope of the present study. Similar behavior has been observed for **8** and **9**, but in more acidic medium (vide infra).

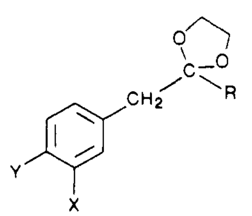
The photo-retro-aldol reactions of **8–10** can be followed conveniently by UV spectrophotometry (Figure 1) and thus provides a means for monitoring the extent of conversion under dilute conditions. In these studies (typical substrate concentration $\sim 10^{-4}$ M), the photogenerated benzaldehyde (λ_{max} 252 nm) is stable for several days even at pH 14 in deaerated solution, whereas preparative studies usually result in depressed yields of benzaldehyde, presumably due to facile air oxidation during product isolation.

p-Nitro-substituted derivatives **15** and **16** were studied to test for reaction when the hydroxyl group of **8** is replaced by methoxy and acetoxy, respectively. Both **15** and **16** failed to react over the range pH 1–12, as indicated by UV spectrophotometry; **15** also failed to react even up to pH 14 (**16** was not studied above pH 12 due to its residual thermal hydrolysis, to give alcohol **8**).

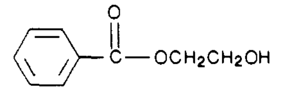


15: R=CH$_3$
16: R=COCH$_3$

The requirement of an abstractable hydroxyl proton at the β-position (to nitrophenyl) is not, however, a necessary requirement for reaction in these systems. This was demonstrated by studying ketals **17–19**, all of which reacted cleanly via an analogous photo-retro-aldol process in aqueous solution (pH ≥7). Thus, **17** and **8** gave hydroxy ester **20**, and **19** gave hydroxy ester **21**. In addition, the corresponding nitrotoluenes and dinitrobibenzyls were also observed, the relative yields of which depended on pH in a manner similar to that reported for alcohols **8** and **9** in Table I. The isolation of **20** and **21** implicates the formation of dioxocarbocation intermediates in the reaction, which are trapped by solvent water to give a hemiorthoester, which ultimately leads to the ester products (eq 3).



17: R=Ph, X=H, Y=NO$_2$
18: R=Ph, X=NO$_2$, Y=H
19: R=CH$_3$, X=H, Y=NO$_2$



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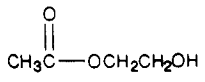
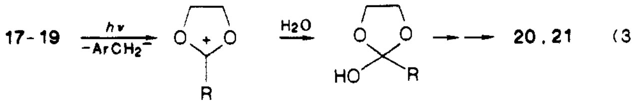


$$\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OCH_2CH_2OH}$$

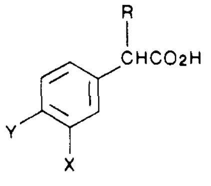
21



(3)

22: R=CH$_3$
23: R=Ph

To complete the study of the photo-retro-aldol process, the photodecarboxylations of nitrophenylacetic acids **24–26** were examined. Relative yields of the two products derived from the nitrophenyl fragment are tabulated in Tables I and II as a function of pH. As was observed for the para isomers of the alcohols and ketals, the "protonation" product (*p*-nitrotoluene or *p*-ethylnitrobenzene) dominates in lower pH and the dinitrobibenzyls dominate at higher pH. The similarity in product distributions (Tables I, II) derived from the nitrobenzyl fragment in all of the reactions studied (with the probable exception of **10**) suggests that a common mechanism is operative for the alcohols (**2**, **7–10**), ketals (**17–19**), and acetates (**24–26**).



24: R=H, X=H, Y=NO$_2$
25: R=H, X=NO$_2$, Y=H
26: R=CH$_3$, X=H, Y=NO$_2$

Photolysis in Oxygenated Solution. Carbanions generated in the ground state are known to react efficiently with molecular oxygen to give hydroperoxides, which in many cases dehydrate to the corresponding carbonyl compounds.[10] Russell and coworkers[11] have shown that *p*-nitrobenzyl carbanion reacts with molecular oxygen in basic solution (potassium *tert*-butoxide/*tert*-butyl alcohol) to give *p*-nitrobenzoic acid as the final oxidation product. That nitrobenzyl carbanion intermediates are implicated in these photo-retro-aldol type reactions suggests that a similar reaction may be feasible with the present nitroaromatic compounds on photolysis in aqueous solution, but under much less basic conditions. The more reactive substrates **8**, **9**, and **24–26** were photolyzed in oxygenated aqueous base. The relative reactivities of these compounds in oxygenated vs deoxygenated solution were measured by comparing the quantum yield for loss of substrate for **24–26**, and by measuring the quantum yield for formation of benzaldehyde for **8** and **9**, in the two media. No significant difference in reaction efficiency was observed, and typically $\Phi_{Ar}/\Phi_{O_2} = 1.0 \pm 0.05$, where Φ_{Ar} and Φ_{O_2} represent the quantum yields for loss of substrate (or benzaldehyde formation) in argon- and oxygen-saturated solutions, respectively.

In the pH 1–12 region, photolysis of **8** and **9** gave the corresponding nitrobenzyl hydroperoxides and benzaldehyde (eq 4) in

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[10] (a) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979. (b) Jones, J. R. *The Ionisation of Carbon Acids*; Academic: London, 1973.

[11] Russell, G. A.; Moye, A. J.; Janzen, E. G.; Mak, S.; Talaty, E. R. *J. Org. Chem.* **1967**, *32*, 137.

Table II. Relative Yields (%) of *p*-Ethylnitrobenzene (**13**) vs 2,3-Bis(*p*-nitrophenyl)butane (**14**) in the Photo-Retro-Aldol Reactions of **10** and **26**[a]

	10		26	
pH[b]	**13**	**14**	**13**	**14**
14	*c*	*c*	0	~100
13	0	~100	0	~100
10	0	~100	0	~100
8	0	~100	0	~100
6	<5	~95	20	80
4	*d*	*d*	20	80
3	*d*	*d*	*e*	*e*

[a] Relative ratios of **13** vs **14** were calculated by ^1H NMR integration and normalized to 100%. [b] See footnote *b*, Table I. [c] Thermal retro-aldol reaction observed at this pH. [d] Expected products from nitrobenzyl fragment are not observed, and this is believed to be due to change in reaction mechanism (see the text). [e] No reaction at this or lower pH.

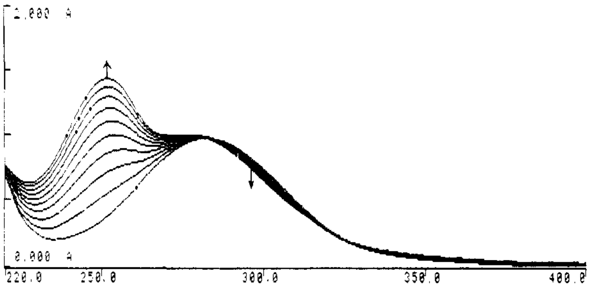
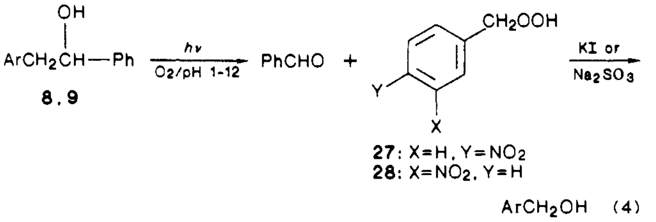


Figure 1. Photochemical UV traces for photo-retro-aldol reaction of 2-(*p*-nitrophenyl)-1-phenylethanol (**8**) in pH 12 (20% CH_3CN cosolvent). Each trace represents ~30-s photolysis at 300 nm.

>60% yield, with only low yields (<15%) of the corresponding nitrotoluenes and dinitrobibenzyls; the remainder of the product mixture is recovered starting material. The hydroperoxides were



(4)

characterized by standard spectroscopic techniques and also via reduction to the corresponding nitrobenzyl alcohols (eq 4), which are known compounds. Traces of *p*-(or *m*-)nitrobenzaldehyde were observed in the product mixture, which are believed to arise via secondary photochemistry of **27** (or **28**) since independent photolysis of these hydroperoxides in aqueous solution (or in pure CH_3CN) gave the corresponding nitrobenzaldehydes, in addition to some as yet unidentified decomposition products.

Photolysis of **8** and **9** in oxygenated aqueous solution at pH >12 gave *p*- and *m*-nitrobenzoic acids, respectively, in addition to **27** and **28**. The proportion of nitrobenzoic acid increased with increasing pH. In high pH, the initially formed hydroperoxides **27** and **28** are presumably unstable and photooxygenated further. Alternatively, **27** and **28** may suffer base-promoted dehydration to give the corresponding nitrobenzaldehydes, which are known to undergo photooxygenation in base to give the corresponding nitrobenzoic acids, as shown by control experiments.

Similar chemistry was observed for nitrophenylacetic acids **24**–**26** on photolysis in oxygenated solution, with the only difference being that **26** gave *p*-nitroacetophenone as an additional oxidation product at pHs >12. That all of these photooxygenation reactions proceed via an initial photo-retro-aldol process is supported by the observation that these reactions are not observed in solvents where the photo-retro-aldol pathway does not take place, viz., in organic solvents. Additional support is provided by the observation that the photooxygenation reactions of **8** and **9** are base catalyzed in the same manner as the usual photo-retro-aldol process. That is, the yields of hydroperoxides **27** and **28** and nitrobenzoic acids increase with increasing pH above pH 11 in a manner similar to that shown in Figure 2. These results indicate that it is possible to add oxygen to photogenerated *m*- and *p*-nitrobenzyl carbanions in aqueous solution, whereas only the *p*-nitrobenzyl carbanion has been oxygenated under thermal reaction conditions.[11]

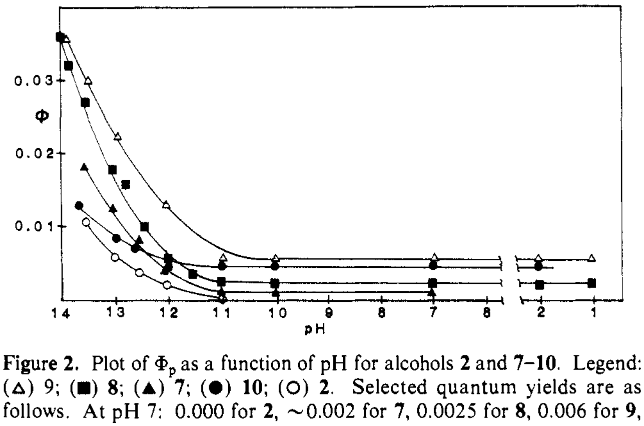


Figure 2. Plot of Φ_p as a function of pH for alcohols **2** and **7**–**10**. Legend: (△) **9**; (■) **8**; (▲) **7**; (●) **10**; (○) **2**. Selected quantum yields are as follows. At pH 7: 0.000 for **2**, ~0.002 for **7**, 0.0025 for **8**, 0.006 for **9**, 0.0057 for **10**. At pH 12: 0.003 for **2**, 0.005 for **7**, 0.007 for **8**, 0.014 for **9**, 0.0062 for **10**. At pH 13: 0.007 for **2**, 0.013 for **7**, 0.018 for **8**, 0.022 for **9**, 0.0091 for **10**. At pH 14: 0.036 for **8** and **9**.

Quantum Yields and pH Effects. The efficiency of the photo-retro-aldol reaction for alcohols **8**–**10** was studied as a function of pH by measuring the quantum yield of benzaldehyde formation (Φ_p) at 252 nm via UV spectrophotometry using potassium ferrioxalate actinometry (λ_{excit} 254 nm). For alcohols **2** and **7**, where UV spectrophotometry cannot be employed, quantum yields for product formation (nitrotoluene, dinitrobibenzyl) were estimated via small-scale preparative photolysis, using **8**–**10** as secondary actinometric references. The results are plotted as a function of pH in Figure 2. All of **2** and **7**–**10** displayed base catalysis of reaction above pH 11. Alcohol **2** showed no measurable reactivity below this pH. It is interesting to note that both meta-substituted nitro derivatives **7** and **9** have higher quantum yields of reaction than their corresponding para isomers. In addition, the α-methyl-substituted compound **10** has higher quantum yields of reaction than **8** at pH <12. Furthermore, **10** is the only compound that showed thermal retro-aldol reaction at high pH (pH ~14), with a half-life of several hours at pH 14 (25 °C). Additional studies are required before one can delineate the exact effect of α-methyl substitution (to nitrophenyl), but steric congestion resulting from replacing α-H by α-CH_3 should weaken the benzylic C–C bond, and hence the observed lability.

The base catalysis observed in all of these systems is not due to a simple "salt" effect, since we have found that the presence of salt (e.g., NaCl) increases the quantum yield by at most 20% at 0.3 M but quenches the reaction at higher concentrations. However, the small salt effect observed at low salt concentrations does lend support for a mechanism involving charged intermediates. The possibility that the observed base catalysis is due to direct excitation of the alkoxide ion of the substrate can be reasonably ruled out by noting that the pK_a of the hydroxyl group of these substrates (which are secondary alcohols) should be about 16.5. Thus at pH 13, only about 0.01% of the alcohol exists as the alkoxide, and at pH 12, only 0.001%. Additionally, a mechanism involving direct excitation of the alkoxide should result in 10-fold increases in Φ_p with the increase of each pH value. However, this effect is clearly not observed (Figure 2). The possibility that a small contributing portion of the observed base catalysis is due to direct excitation of the alkoxide cannot be rigorously ruled out at this time. Attempts to detect general-base catalysis were unsuccessful. We used HPO_4^- as the general base in pH 10 since it is essentially UV transparent and readily soluble at high concentrations. Concentrations of up to 0.8 M general base were used and compared with a solution without general base, but with the same salt concentration (NaCl), and showed no measurable enhancement of reaction quantum yield. We presume

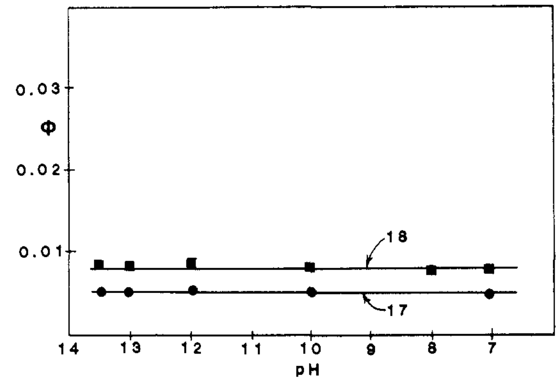


Figure 3. Plot of Φ_p as a function of pH for ketals **17** and **18**. Quantum yields at all measured pHs are 0.005 ± 0.002 for **17** and 0.008 ± 0.003 for **18**.

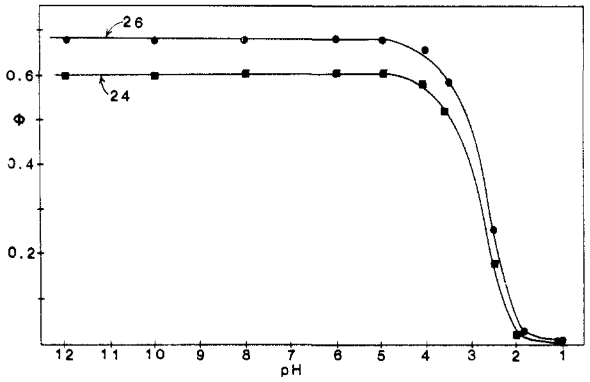


Figure 4. Plot of Φ_p as a function of pH for acetic acids **24** and **26**. The plot for **25** is nearly identical with that of **24**. Quantum yields at pH 12 are 0.6 for **24** and **25** and 0.68 for **26**.

that the reason for not observing general-base catalysis here is because the concentration of general acid used was insufficient to compete with solvent water (acting as the competing general base). Higher concentrations of HPO_4^- could not be used due to solubility problems.

Alcohols **7–10** are also reactive in the pH 1–11 region, although the quantum yields are depressed compared with the high-pH region. They are also reactive below pH 1 and in the H_0 acidity region. However, the mechanism in moderately strong acid appears to be different from that observed in the pH 1–14 region (new products derived from the nitrobenzyl fragment are isolated). We hope to report on the mechanism of reaction in this region of acidity in a later paper.

Quantum yields for formation of hydroxy ester **20** (Φ_p) were measured for ketals **17** and **18** via UV spectrophotometry (λ_{max} of **20** is at 235 nm) as a function of pH (pH 14–7). The results are plotted in Figure 3. In contrast to alcohols **2** and **7–10**, no base catalysis of reaction is observed. Instead, the quantum yields are essentially invariant with pH. As ketals are thermally unstable in dilute acid, quantum yield measurements were not carried out below pH 7.

Margerum and Petrusis[5a] have reported a quantum yield of 0.6 for product formation in the photodecarboxylation of **24** and **25** when pH > pK_a. With this value as reference, quantum yields for reaction (product formation) (Φ_p) were measured for **24–26** as a function of pH via small-scale preparative photolyses. The results are shown in Figure 4, which shows that when pH < pK_a, photodecarboxylation does not occur. At pH > pK_a, the efficiency of reaction reaches a pH-independent value; the overall plot resembles a titration curve for the acids (pK_a ~3.9),[12] which indicates that only the carboxylate ion is photoreactive.

Medium and Isotope Effects. That water is essential for photoreaction of these compounds is demonstrated by a plot of quantum yield of benzaldehyde formation (Φ_p) for alcohol **9** as water is depleted from a CH_3CN/H_2O (pH 7) mixture (Figure 5). Thus, below ~80 mol % water, the reaction becomes very sluggish and is essentially not observed below 60 mol %. A similar effect is observed when CH_3OH replaces CH_3CN as the organic cosolvent and when other substrates are used.

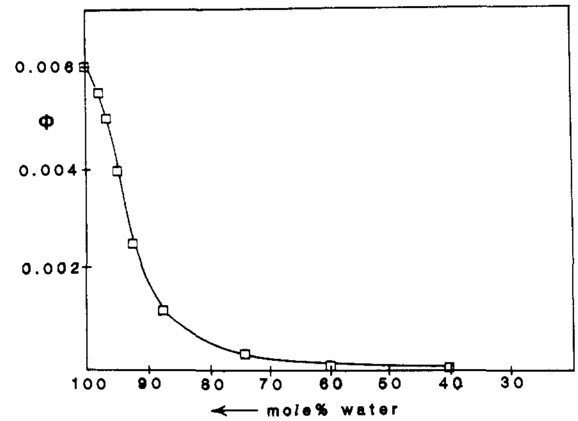


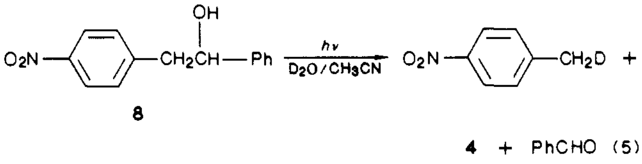
Figure 5. Plot of Φ_p for alcohol **9** as a function of mole percent H_2O (pH 7) in aqueous CH_3CN.

Table III. Solvent Isotope Effects on Quantum Yield for Photo-Retro-Aldol Reaction[a]

compd	$(\Phi_{H_2O}/\Phi_{D_2O})^b$	compd	$(\Phi_{H_2O}/\Phi_{D_2O})^b$
8	1.31 ± 0.05	**18**	1.34 ± 0.05
9	1.15 ± 0.03	**25**	1.43 ± 0.10
17	1.20 ± 0.03		

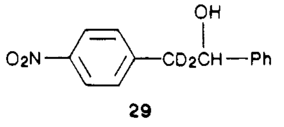
[a] Determined via UV spectrophotometry, except for **25** where small-scale preparative photolyses were used. [b] Relative quantum yield of product formation in H_2O vs D_2O.

Solvent isotope effects for photo-retro-aldol reaction were measured by comparing the reactivity of several substrates in H_2O vs D_2O (neutral solutions), via UV spectrophotometry for **8**, **9**, **17**, and **18** and via small-scale preparative photolyses for **25**. The results (Table III) show that these compounds are more reactive in H_2O than in D_2O. Deuterium is incorporated into only the nitrotoluene products and not into benzaldehyde or dinitrobibenzyls, as indicated by ^{1}H NMR and mass spectrometry of the isolated products (as shown in eq 5 for **8**). Additionally, there



is a higher relative yield of dinitrobibenzyl compared with nitrotoluene in D_2O than in H_2O. For example, *m*-nitrophenylacetic acid (**25**) gives ≤5% 3,3′-dinitrobibenzyl (**12**) and 95% *m*-nitrotoluene (**11**) on photolysis at pH 7 (H_2O), but in D_2O (pD ~7), the relative yield of **12** increases to 20% and that of *m*-nitrotoluene-α-*d* decreases to 80%. More dramatically, *p*-nitrophenylacetic acid (**24**) gives a 70% relative yield of **3** and a 30% yield of **4** at pH 7 (H_2O) but changes to >95% of **4** and only a trace of *p*-nitrotoluene-α-*d* in D_2O (pD ~7).

α-Deuterium isotope effects were measured for alcohols **8** and **9**. In this experiment, the relative reactivities of **8** and **9** were compared with **29** and **30**, respectively, in neutral water. This



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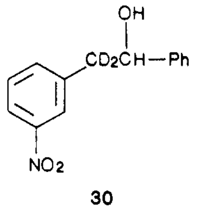

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secondary isotope effect may be used as a probe of the change

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(12) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 64th ed.; CRC: Boca Raton, FL, 1983; p D168.

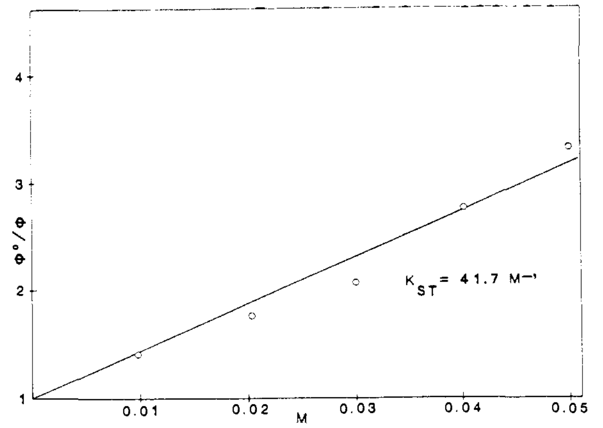
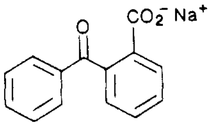


Figure 6. Stern–Volmer plot of quenching of photo-retro-aldol reaction of **9** by **32** at pH 12.

in hybridization at the α-carbon (to nitrophenyl) in the transition state of the primary photochemical step of the photo-retro-aldol reaction. The results are $\Phi_H/\Phi_D = 1.16 \pm 0.05$ for **8** and **29** and 0.95 ± 0.05 for **9** and **30**, where Φ_H and Φ_D are the quantum yields for benzaldehyde formation for the nondeuteriated and the deuteriated substrates, respectively. In product studies it is found that the proton from solvent water is incorporated into only the corresponding nitrotoluene products of **29** and **30**.

Triplet Sensitization and Quenching. The photoretro-aldol reactions of several derivatives can be sensitized by sodium benzophenone-2-carboxylate (**31**) ($E_T \approx 69$ kcal mol^{-1}, on the basis of the known triplet energies of benzophenone derivatives)[13] at pH 12, with 350-nm irradiation and at concentrations in which the sensitizer absorbed >95% of the exciting light. The estimated excited triplet-state energy of nitrobenzene derivatives is ≈60 kcal mol^{-1}.[14,15] The reaction of **8** and **9** can also be quenched (at pH 12) by 2,4-cyclohexadiene-1,6-dicarboxylic acid (monosodium salt, **32**) ($E_T \approx 50$ kcal mol^{-1}, on the basis of the known triplet energy of 1,3-cyclohexadiene).[13] Linear Stern–Volmer plots of quenching of reaction are observed (Figure 6). Assuming a quenching rate constant of 1×10^{10} M^{-1} s^{-1}, which is the diffusion-controlled rate in water at 25 °C,[13] a lifetime of 4.2 ns is calculated for **9** at pH 12. The very short reactive lifetime observed here for **9** appears to be the norm for many other nitroaromatic compounds reacting via the triplet state (typically 1–10 ns).[14,15] A similar calculation gives a lifetime of 6 ns for **8**.



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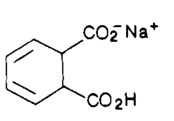

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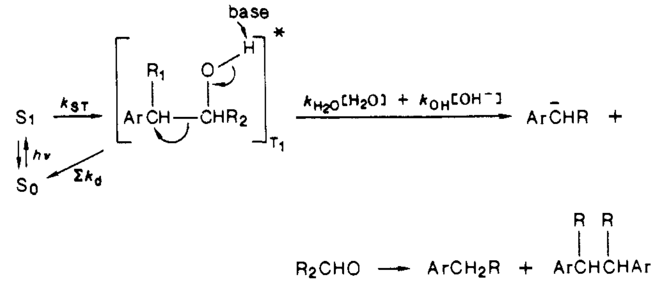
Discussion

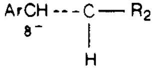
This study has shown that suitably substituted nitroaromatic derivatives can react via a photo-retro-aldol type pathway, in which the nitrobenzyl moiety may be regarded as a photolabile carbanion leaving group. The results presented also suggest that these compounds react via a common mechanism. Thus, the photodecarboxylation of nitrophenylacetates originally reported by Margerum and Petrusis[5a] is only one example of a general photochemical reaction of nitroaromatic compounds. The observations of base catalysis of reaction for the nitrophenethyl alcohols **2** and **7–10**, the pH-dependence behavior of reaction observed for nitrophenylacetates **24–26** and ketals **17–19**, the drastic water-dependent solvent effects observed for all substrates, and the α-deuterium isotope effects of reaction for **8** and **9** are consistent with a mechanism involving carbocation/carbanion intermediates derived from heterolytic cleavage of the benzylic C–C bond of these compounds.

Scheme I



The proposed mechanism[16] of reaction for nitrophenethyl alcohols **2** and **7–10** is shown in Scheme I, in which the reactive triplet state undergoes retro-aldol cleavage assisted by solvent water (or hydroxide ion) as the deprotonating base in the primary photochemical step. Consistent with this mechanism are the observations of base catalysis and the absence of reaction for derivatives **15** and **16**, which lack an abstractable proton at the β-position (to the nitrophenyl fragment). The photogenerated carbanion ($ArCHR^-$; Scheme I) subsequently reacts to give the observed products $ArCH_2R$ and ArCHRCHRAr in deaerated solution (vide infra) or reacts with molecular oxygen in aerated solution to give hydroperoxides as initial products. The mechanism for the oxygenation process is believed to resemble standard oxygenation reactions of carbanions and will not be discussed further.[10,11] The symbols k_{ST} and $\sum k_d$ represent the singlet–triplet intersystem-crossing rate constant and the sum of all nonproductive deactivational rate constants from T_1 to S_0, respectively. The overall pseudo-first-order rate constant (k_{obsd}) of the primary photochemical step is given by eq 6, where k_{H_2O} and k_{OH} are the water and hydroxide ion catalyzed pathways, respectively. The transition state for reaction at high pH (pH >12) may be depicted by structure **33** in which hydroxide ion deprotonation of the

$$k_{obsd} = k_{H_2O}[H_2O] + k_{OH}[OH^-] \qquad (6)$$



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(13) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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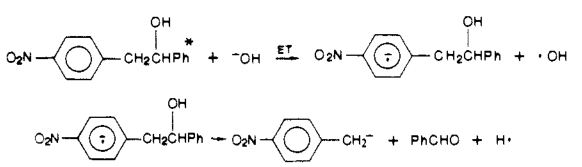
(15) Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 49.

(16) A reviewer has suggested the possibility of a competing pathway involving electron transfer (ET) from water (or hydroxide ion) to the triplet excited state of the nitroaromatic compound, to generate a nitroaromatic radical anion and water radical cation (or hydroxyl radical in the case of hydroxide ion as the electron donor). There is the possibility that this can be followed by benzylic C–C bond fission, to generate nitrobenzyl carbanion, a carbonyl compound, and a hydrogen atom and therefore provide an additional pathway for reaction:



Using electropotentials from Wubbels et al.[17] and an excitation energy of ca. 60 kcal mol^{-1}, we calculate $\Delta G°$ for electron transfer from water to the excited triplet state of nitroaromatic compound to be endothermic by about 30 kcal mol^{-1} and for hydroxide ion as the electron donor to be endothermic by about 5 kcal mol^{-1}. With the uncertainties inherent in these estimates, it is conceivable that electron transfer may be an important pathway in basic solution. We have recently shown[18] that radical anions of **8** and **10** have half-lives of several minutes at high pH. However, we have found no evidence to suggest that they fragment via the above pathway. Therefore, although electron transfer between hydroxide ion and nitroaromatic compound may well be substantial, it *does not* lead to photo-retro-aldol reaction.

(17) Wubbels, G. G.; Kalhorn, T. F.; Johnson, D. E.; Campbell, D. *J. Org. Chem.* **1982**, *47*, 4664.

(18) Muralidharan, S.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1142.

hydroxyl proton is concerted with benzylic C–C bond heterolysis. In lower pH, where the quantum yields are lower, a similar transition state for reaction can be visualized but with H_2O replacing OH^- as the deprotonating base (with presumably a less-developed transition state due to the lower basicity of H_2O). At pH <12, only alcohols **8**–**10** react with significant efficiency. This is presumably due to the extra stabilization of developing charges offered by the phenyl ring (at R_2) of these compounds in transition state **33**.

The results of the α-deuterium isotope studies at pH 7 for **8** and **9** may be interpreted if it is assumed that deuteriation at the α-carbon (to nitrophenyl) does not significantly alter the lifetime of the reactive triplet state. This is a reasonable assumption, since other workers have shown[19] that triplet lifetimes are lengthened appreciably only on *per*deuteriation. With this assumption, it is simple to show that $k_H/k_D \approx \Phi_H/\Phi_D$, where k_H and k_D are the primary rate constants for photoretro-aldol reaction for the parent and α-deuteriated compounds, respectively, and Φ_H and Φ_D are the corresponding quantum yields for photoreaction. A normal secondary isotope effect (typically $k_H/k_D \approx 1.3$)[20] will be expected if the reaction involves a change from sp^3 to sp^2 hybridization in the transition state and an inverse effect for the opposite situation. For the para isomer **8**, we find that $k_H/k_D \approx 1.16 \pm 0.05$, indicating a change from sp^3 to sp^2 hybridization in the transition state, whereas for the meta isomer **9**, $k_H/k_D \approx 0.95 \pm 0.05$, indicating essentially no change in hybridization. These observations are reasonable since the para isomer can react to give a resonance-stabilized *p*-nitrobenzyl carbanion (PNBC; **5**) (which has a half-life of ~50 s under dilute conditions, pH >6),[21,22] whereas the *m*-nitrobenzyl carbanion (MNBC) has so far eluded spectroscopic detection. It is reasonable to assume that MNBC is much less stable because of the lack of direct resonance stabilization and should be much shorter lived than PNBC.

Assuming the validity of the proposed mechanism (Scheme I) for the alcohols, the expression for quantum yield of formation of R_2CHO (or $ArCHR^-$) (Φ_p) may be derived. Applying steady-state assumptions for S_1 and T_1, the expression for Φ_p is given by eq 7, where Φ_{ST} is the singlet–triplet intersystem quantum

$$\Phi_p = \Phi_{ST}\left(\frac{k_{H_2O}[H_2O] + k_{OH}[OH^-]}{\sum k_d + k_{H_2O}[H_2O] + k_{OH}[OH^-]}\right) \qquad (7)$$

$$\Phi_p{}^0 = \Phi_{ST}[k_{OH}/(\textstyle\sum k_d + k_{OH})] \qquad (8)$$

$$\Phi_p{}^0/\Phi_p = \tau^0 k_{OH} + (\tau^0/\tau')[OH^-]^{-1} \qquad (9)$$

yield and the other quantities are as defined above. Equation 7 can be linearized as follows. We define $\Phi_p{}^0$ as the quantum yield for reaction at pH 14, given by eq 8. Dividing $\Phi_p{}^0$ by Φ_p and making the simplifying assumptions (1) $k_{OH}[OH^-] \gg k_{H_2O}[H_2O]$ at high pH and (2) $\sum k_d \approx (\sum k_d + k_{H_2O}[H_2O])$ gives the expression for $\Phi_p{}^0/\Phi_p$ (eq 9), where τ^0 and τ' are the triplet lifetimes in pH 14 and in neutral solution, respectively. The assumptions are reasonable since in the pH >12 region the contribution from the water reaction (k_{H_2O}) should not be significant compared with the hydroxide ion catalyzed pathway (k_{OH}); also, in neutral solution, the lifetime of τ_1 is essentially determined by $\sum k_d$ since the quantum yield for reaction in this pH region is quite low (i.e., assumption 2 above holds). A plot of $\Phi_p{}^0/\Phi_p$ vs $[OH^-]^{-1}$ for **8** and **9** gave good straight lines in the pH 12.5–14 region (Figure 7), with $\tau^0/\tau' = 0.087$ and 0.058 and $\tau^0 k_{OH} = 0.90$ and 0.94 M^{-1} for **8** and **9**, respectively. Triplet quenching results indicate a lifetime of ~4 ns at pH 12 for **9**. Assuming that $\tau^0 \approx 1$ ns (pH 14 value) for both **8** and **9**, we calculated that $k_{OH} \approx 1 \times 10^9$ M^{-1} s^{-1} for both **8** and **9** and $\tau' = 11$ and 17 ns for **8** and **9**, respectively. Since in pH 7, $\Phi = \tau'(k_{H_2O}[H_2O])$, we calculate that $k_{H_2O} \approx 4 \times 10^3$ and 6.5×10^3 M^{-1} s^{-1} for **8** and **9**, respectively.

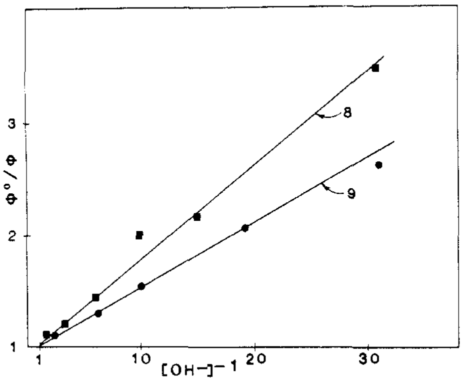
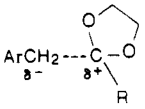


Figure 7. Plot of $\Phi_p{}^0/\Phi_p$ vs $[OH^-]^{-1}$ in the pH 12–14 region for alcohols **8** and **9**.

The lack of reactivity of derivatives **15** and **16** coupled with the observed reactivity of acetals **17**–**19** [with no observable pH effects (Figure 3)] suggests that formation of highly stabilized dioxocarbocations **22** and **23** facilitates the photoretro-aldol process. Compounds **15** and **16** do not react because the incipient carbocations are not sufficiently stabilized. It is therefore proposed that the mechanism for ketals **17**–**19** differs from Scheme I in that the primary step has only the $k_{H_2O}[H_2O]$ term. In other words, unimolecular heterolytic cleavage of the benzylic C–C bond of the ketals is implied, as shown by transition state **34**, which is presumed to be extensively water-solvated. We do not favor a mechanism involving attack of water at the developing oxocarbocationic center concerted with C–C bond cleavage, thus bypassing the discrete oxocarbocation intermediate. It is well-known[23] that many dioxocarbocations can be observed as discrete intermediates in aqueous solution. For example, they may be generated via unimolecular C–O bond heterolysis of ortho esters[23] to give observable dioxocarbocation intermediates. These points argue for the proposed unimolecular retroaldol process to give a discrete carbocation intermediate. Future studies will be directed at spectroscopic detection of these carbocations as direct evidence for the proposed mechanism.



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The mechanism of photodecarboxylation of *p*-nitrophenylacetate anion (**24**) has recently been studied in detail via both picosecond and nanosecond laser flash photolysis.[24] An important conclusion of this recent study is that PNBC may be formed in its triplet excited state (τ ~90 ns) from the T_1 precursor of **24** (i.e., an adiabatic process). The results of our study indicate that the mechanism for reaction of nitrophenylacetates **24**–**26** resembles the mechanism proposed for the alcohols and acetals; that is, loss of CO_2 is concerted with benzylic C–C bond heterolysis. The overall process can still be formally regarded as being a retroaldol reaction. This mechanism is not inconsistent with that proposed by Craig et al.,[24] although our study does not address the possibility of adiabaticity of reaction or the sequence of events leading to ground-state nitrobenzyl carbanion from T_1, as we have no probe of such details via the steady-state techniques used.

Buncel et al.[25] studied the thermal decarboxylation of *p*-nitrophenylacetate anion (**24**) and other nitrophenylacetates in nonaqueous media and concluded that nitrobenzyl carbanions are formed as intermediates, based on UV–vis spectroscopic analyses.

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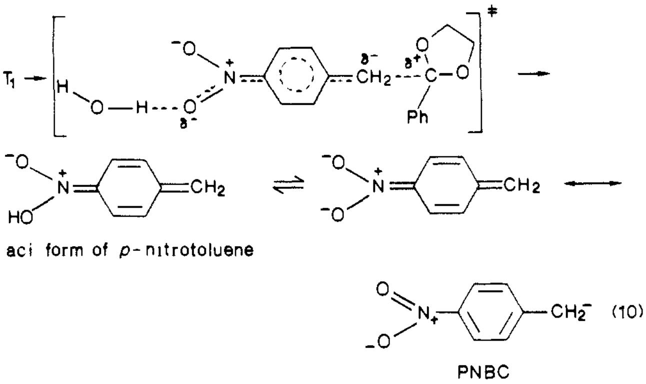
Because of the discrepancy in absorption spectra observed for PNBC with that reported by Margerum and Petrusis,[5a] Buncel et al.[25] made the suggestion that the photodecarboxylation mechanism may involve initial cleavage to give *p*-nitrobenzyl radical (along with CO_2 and solvated electron). This may be followed by recombination of the electron with radical to give PNBC, or the radical may escape to give 4,4′-dinitrobibenzyl (**4**) observed in the reaction. However, recent studies by McClelland and Steenken[26] and by Craig et al.[24] have shown that nitrobenzyl carbanions can suffer substantial solvent-induced spectral shifts. These recent studies appear to have resolved the above discrepancy in the observed absorption spectrum of PNBC generated via thermal and photochemical pathways. The alternative mechanism proposed[25] is therefore no longer warranted. Additionally, Craig et al.[24] have ruled out the possibility that the *p*-nitrobenzyl radical is a first-formed transient in laser flash experiments of **24**.

The mechanism of transformation of photogenerated nitrobenzyl carbanion ($ArCHR^-$ of Scheme I) to the observed products in deaerated solution ($ArCH_2R$ + ArCHRCHRAr of Scheme I) will now be addressed. Buncel and Russell and their respective co-workers[11,27,28] have shown that thermally generated PNBC [via deprotonation of *p*-nitrotoluene (**3**) with potassium *tert*-butoxide] gives 4,4′-dinitrobibenzyl (**4**) rapidly, with the production of nitroaromatic radical anions, as detected by ESR spectroscopy. The ESR signal observed can be assigned to the radical anion of **3** and implies that the mechanism of reaction involves overall electron loss from PNBC, followed by radical coupling to give **4**. We have observed strong ESR signals of the radical anions of the corresponding substrates on photolysis of para isomers **8**, **10**, **24**, **26**, and related compounds in the cavity of an ESR spectrometer.[18] Craig and Pace[22] have reported a similar observation in photolysis of **24**. The strongest signals are observed for those that have the higher quantum yields of photo-retro-aldol reaction. No ESR signals were observed under conditions in which the photoretro-aldol reaction does not take place. Additionally, all the meta isomers either failed to give any observable signal or gave only very weak signals, the assignment of which proved difficult. These observations indicate that photogenerated PNBC is a source of electrons that can be transferred to substrate molecule in the reaction. Loss of an electron from PNBC would give *p*-nitrobenzyl radical, which will dimerize to give **4**. On the other hand, the lack of an ESR signal for the meta isomers coupled with low yields of **12** indicates that MNBC is not a good source of electrons in the reaction. Protonation by solvent water is therefore the major reaction pathway for photogenerated MNBC. The mechanism of transformation of photogenerated PNBC to the observed products appears to be complicated. However, several pieces of data shed light on the general aspects of the mechanism. For example, it is observed (Tables I, II) that the yields of bibenzyl product (relative to simple protonation product) increase with increasing pH. In addition, increased yields of bibenzyl product are observed when photolysis of **8** and **9** is carried out in D_2O, compared with H_2O. Photolysis under aerated conditions results in overall "trapping" of PNBC by oxygen (to give hydroperoxide **27**) and decreased yields of *both* **3** and **4**. These observations are consistent with a mechanistic scheme in which PNBC (and to some extent for MNBC) may react via three competing pathways: (i) protonation by solvent to give **3**, (ii) reaction with oxygen to give **27**, and (iii) electron transfer to substrate, resulting in formation of **4**. In the absence of oxygen, only (i) and (iii) are important. Thus, as the pH of the solution is increased, the rate of protonation by solvent should decrease, thereby increasing the lifetime of PNBC, and hence allowing pathway iii to compete (which is visualized as a bimolecular process). This qualitatively explains the increased bibenzyl yields with increasing pH. It also offers an explanation for the increased bibenzyl yields observed in D_2O since protonation of PNBC by D_2O should be slower than by H_2O, resulting in a greater contribution from pathway iii. As to exactly how pathway iii operates, a simple bimolecular reaction between PNBC and substrate resulting in electron transfer would seem reasonable, but Craig et al.[22] have recently suggested the possibility of *dimerization* of PNBC (to give 4,4′-dinitrobibenzyl dianion) as being the only important bimolecular process available for PNBC. The 4,4′-dinitrobibenzyl dianion subsequently reacts with two substrate molecules to give **4** and two molecules of substrate radical anions (and hence the ESR signal).

The final fate of the "ejected" electron (from PNBC) has not been clearly established at this time. However, low yields (<10%) of reduced nitroaromatic compounds that have not been characterized, are observed under prolonged photolysis. It is also reasonable to assume that on high conversion the ejected electrons reside in product (in the form of the radical anion),[22] which may react further with electron scavengers in the system or be quenched during exposure to air on product isolation.

The solvent isotope effects for photo-retro-aldol reaction of several substrates (Table III) all indicate a preference for H_2O over D_2O in terms of relative reactivity. Although there are slight differences in physical properties between H_2O and D_2O,[12] the most important chemical difference is in terms of the relative rates of proton (deuteron) transfer from solvent. For alcohols **8** and **9**, exchange of the substrate hydroxyl proton with deuteron would be immediate and the observed "solvent isotope effect" can in fact be simply due to a primary isotope effect associated with cleavage of the O–H vs O–D bond in the substrate. However, for **17**, **18**, and **25**, the observed solvent isotope effects are also substantial and require a different rationalization. The observed effects suggest that solvent water is mediating the retro-aldol process by way of proton transfer. Previous studies from our laboratory[9a,b] have shown that solvent water is intimately involved in mediating the photoredox reactions of nitrobenzyl alcohols. Along the lines of these studies[9a,b] we propose that photo-retro-aldol reactions are mediated by water acting as a proton source. That is, formation of PNBC is proton-assisted, to generate initially the aci form of *p*-nitrotoluene, as shown in eq 10 for reaction of **17**. The pK_a (hydroxyl proton) of the aci form of *p*-nitrotoluene has been estimated to be 2–3,[24] so that in basic solution it will deprotonate quickly to give PNBC. In less basic solution, it may tautomerize to give *p*-nitrotoluene (**3**) without the intermediacy of PNBC or react via as yet unknown pathways. In the case of reaction of the meta isomers **18** and **25**, it is proposed that solvent water protonates the incipient benzylic carbanionic center rather than the nitro group, thus bypassing a discrete MNBC intermediate, and hence offers a rationalization for the observed solvent isotope effect. These proposals necessarily require additional studies before they can be substantiated.



Although simple nitrobenzenes have n,π* lowest triplets[15,29,30] in the common organic solvents, there is strong evidence to suggest that the nitroaromatic compounds studied in this work do not have an n,π* reactive triplet. It is clear that the nitro group activates the phenyl ring in these reactions via charge polarization in T_1.

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We feel that a π,π^* reactive triplet best accommodates the observed reactivity in these systems, since such a reactive configuration can activate the π system effectively. This proposal also explains the drastic solvent effects observed for these reactions, since polar solvents (e.g. water) can stabilize the reactive π,π^* state (and destabilize the n,π^* state).[8] Our study of photoredox chemistry of nitroaromatic compounds in aqueous solution also supports the intermediacy of π,π^* reactive triplets in simple nitrobenzenes in aqueous solution.[9] However, it is not clear at this time whether the π,π^* triplet is in fact lower in energy than the n,π^* state, but such a proposal would be consistent with the observed solvent dependence of the reaction.

In summary, we have documented general mechanistic aspects of a class of photo-retro-aldol type reactions initiated by the nitrobenzyl moiety in aqueous solution, in which the nitrobenzyl carbanion may be viewed simply as a photolabile leaving group. We have established the necessary structural and catalytic requirements for reaction, as well as giving insight into the nature of the primary photochemical step in the reaction mechanism. Additional studies in these and related areas are continuing.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 instrument in $CDCl_3$ (TMS internal standard) unless otherwise noted. UV spectra were taken on a Pye Unicam SP8-400 instrument. IR spectra were recorded on a Perkin-Elmer 283 instrument on NaCl disks. Mass spectra were taken on a Finnigan 3300 instrument. Melting points were taken on a Gallenkamp apparatus and are uncorrected. Microanalyses were performed by Canadian Microanalytical Service. Gas chromatography was carried out on a Varian 3700 instrument with a Hewlet-Packard 3390A integrator. Photolyses were carried out in Suprasil quartz cuvettes or 200-mL quartz tubes with a Rayonet RPR 100 photochemical reactor. pH solutions were made up with aqueous NaOH or aqueous H_2SO_4 and measured by a pH meter or were diluted from standardized stock solutions.

Materials. Acetic acids **24**–**26** and alcohol **6** were purchased from Aldrich and recrystallized in EtOH/water prior to use, except for **6**, which was used as received. Alcohols **2** and **7** were made via BH_3 reduction of the corresponding carboxylic acids. Alcohols **8**–**10** were made via $NaBH_4$ reduction of the corresponding ketones, which were obtained via Friedel–Crafts reaction of the corresponding nitrophenylacetyl chlorides with benzene, using $AlCl_3$ as catalyst, via a procedure similar to that of Fischer et al.[31] Compounds **15** and **16** were made via alkylation or acetylation of **8**.

2-(*p*-Nitrophenyl)-1-phenylethanol (8). To 5 g (0.020 mol) of **35** dissolved in 50 mL of cold MeOH was added 0.24 g of $NaBH_4$. After being stirred for 2 h, the solution was quenched with 30 mL of 10% HCl and extracted with CH_2Cl_2, which on evaporation gave a solid. Recrystallization from ligroin gave light yellow crystals: mp 84 °C; yield 4.3 g (85%); ^{1}H NMR δ 2.2 (br, 1 H), 3.15 (d, J = 8 Hz, 2 H), 4.9 (t, J = 8 Hz, 1 H), 7.2–7.4 (arom, 7 H), 8.15 (d, J = 9 Hz, arom, 2 H); IR, 3200–3600, 1520, 1335 cm^{-1}; mass spectrum (CI) m/z 244 (M^+ + 1).

2-(*m*-Nitrophenyl)-1-phenylethanol (9). Reduction of ketone **36** in a similar manner as for **8** gave **9**: 80% yield; mp 38–40 °C; ^{1}H NMR δ 2.3 (br, 1 H), 3.15 (d, J = 8 Hz, 2 H), 4.9 (t, J = 8 Hz, 1 H), 7.2–8.1 (arom, 9 H); IR, 3200–3600, 1520, 1330 cm^{-1}; mass spectrum (CI) m/z 244 (M^+ + 1).

2-(*p*-Nitrophenyl)-1-phenylpropanol (10). Reduction of ketone **37** in a similar manner as for **8** gave **10**: 85% yield; mp 88 °C; ^{1}H NMR δ 1.15 (d, J = 9 Hz, 3 H), 1.95 (br, 1 H), 3.1 (m, 1 H), 4.75 (d, J = 9 Hz, 1 H), 7.2–7.4 (arom, 7 H), 8.10 (d, J = 9 Hz, arom, 2 H); IR, 3200–3600, 1530, 1335 cm^{-1}; mass spectrum (CI) m/z 258 (M^+ + 1).

α-(*p*-Nitrophenyl)acetophenone (*p*-Nitrobenzyl Phenyl Ketone) (35). To 30 g of *p*-nitrophenylacetic acid (**24**) in a two-neck round-bottom flask was added 12 mL of redistilled thionyl chloride over several minutes. The mixture was warmed to ~55 °C for 20 min, and unreacted thionyl chloride was removed under vacuum. To this was added 150 mL of dry benzene followed by 28 g of $AlCl_3$ in small portions over a 20-min period. The mixture was then refluxed for 45 min and quenched by pouring into crushed ice. After acidification with 10% HCl, the mixture was extracted with 3 × 100 mL of CH_2Cl_2. Subsequent washing with saturated sodium bicarbonate solution and evaporation of the solvent gave a solid, which was recrystallized from 95% EtOH: yield 78%; mp 138 °C (lit.[31] mp 144 °C); ^{1}H NMR δ 4.3 (s, 2 H), 7.3–8.3 (arom, 9 H); IR, 1680, 1590, 1505, 1320 cm^{-1}; mass spectrum (EI) m/z 241 (M^+).

α-(*m*-Nitrophenyl)acetophenone (*m*-Nitrobenzyl Phenyl Ketone) (36). After reaction of *m*-nitrophenylacetic acid (**25**) in a similar manner as described for **24**, **36** was obtained in 80% yield after recrystallization from 95% EtOH: mp 80 °C (lit.[31] mp 82 °C); ^{1}H NMR δ 4.4 (s, 2 H), 7.4–8.2 (arom, 9 H); IR, 1670, 1585, 1510, 1320 cm^{-1}; mass spectrum (EI) m/z 241 (M^+).

α-(*p*-Nitrophenyl)propiophenone (37). After reaction of 2-(*p*-nitrophenyl)propionic acid (**26**) in a similar as described for **24**, **37** was obtained in 75% yield as an oil, which was used without further purification: ^{1}H NMR δ 1.55 (d, J = 8 Hz, 3 H), 4.8 (q, J = 8 Hz, 1 H), 7.3–8.0 (arom, 7 H), 8.15 (d, J = 9 Hz, arom, 2 H); IR, 1675, 1590, 1510, 1320 cm^{-1}; mass spectrum (EI) m/z 255 (M^+).

1-Methoxy-2-(*p*-nitrophenyl)-1-phenylethane (15). To a solution of 50 mL of dry DMSO, 0.10 g of metallic sodium spheres, and 1.75 g of methyl iodide in a 250-mL round-bottom flask was added 1 g of alcohol **8** over a period of 15 min with stirring. The resultant mixture was stirred overnight and quenched by diluting with water. The solution was subsequently acidified with 10% HCl and extracted with CH_2Cl_2. After evaporation of the solvent, the crude product mixture contained the expected methyl ether **15** (appearance of a methoxy singlet at δ 3.15) as well as starting material and *p*-nitrotoluene. The mixture was separated by column chromatography (silica/CH_2Cl_2) to give 140 mg of pure **15**: ^{1}H NMR δ 3.1 (d, J = 8 Hz, 2 H), 3.15 (s, 3 H), 4.3 (t, J = 8 Hz, 1 H), 7.1–7.3 (arom, 7 H), 8.05 (d, J = 9 Hz, arom, 2 H); IR, 1590, 1520, 1320 cm^{-1}; mass spectrum (CI) m/z 258 (M^+ + 1).

1-Acetoxy-2-(*p*-nitrophenyl)-1-phenylethane (16). To a solution of 1 g of alcohol **8** dissolved in 100 mL of CH_2Cl_2 in a 250-mL Erlenmeyer flask was cautiously added 0.5 mL of acetyl chloride. After being stirred overnight at room temperature, the solution was quenched by adding aqueous sodium bicarbonate. Extraction with CH_2Cl_2 followed by evaporation of the solvent gave a solid, which on recrystallization in aqueous EtOH yielded 85% **16**: mp 59–60 °C; ^{1}H NMR δ 2.0 (s, 3 H), 3.15 (d, J = 8 Hz, 1 H), 5.9 (t, J = 8 Hz), 7.1–7.3 (arom, 7 H), 8.05 (d, J = 8 Hz, arom, 2 H); IR, 1725, 1590, 1510, 1310 cm^{-1}; mass spectrum (CI) m/z 302 (M^+ + 1).

Ketals **17**–**19** were made from the corresponding ketones, via ketalization with ethylene glycol in toluene. For **19**, the corresponding ketone (*p*-nitrophenylacetone) was purchased from Aldrich. The dideuteriated derivatives **29** and **30** were made via simple deuterium exchange of the corresponding ketones **35** and **36** in 0.1 M NaOD/D_2O, followed by $NaBH_4$ reduction in MeOH.

α-(*p*-Nitrophenyl)acetophenone Ethylene Glycol Ketal (17). A solution of 3 g of ketone **35** and 4 g of ethylene glycol in 100 mL of toluene was refluxed for 3 h, using a Dean–Stark trap with 10 drops of concentrated H_2SO_4 as catalyst. After being cooled, the mixture was quenched with solid sodium bicarbonate and solvent removed on a rotary evaporator. The residue was taken up with 200 mL of CH_2Cl_2 and washed with aqueous sodium bicarbonate, which on evaporation gave 3.1 g of **17** (87% yield), which was further purified by recrystallization from 95% EtOH: mp 118–119 °C; ^{1}H NMR δ 3.3 (s, 2 H), 3.7–4.0 (m, 4 H), 7.3–7.5 (arom, 7 H), 8.1 (d, J = 8 Hz, arom, 2 H); IR, 1590, 1520, 1310 cm^{-1}; mass spectrum (CI) m/z 286 (M^+ + 1).

α-(*m*-Nitrophenyl)acetophenone Ethylene Glycol Ketal (18). By use of ketone **36** in a procedure similar to the one above, **18** was obtained in 80% yield: mp 92 °C; ^{1}H NMR δ 3.2 (s, 2 H), 3.7–4.0 (m, 4 H), 7.2–8.2 (arom, 9 H); IR, 1590, 1510, 1320 cm^{-1}; mass spectrum (CI) m/z 286 (M^+ + 1).

(*p*-Nitrophenyl)acetone Ethylene Glycol Ketal (19). By use of (*p*-nitrophenyl)acetone in a procedure similar to the one above, **19** was obtained as an oil: ^{1}H NMR δ 1.4 (s, 3 H), 3.0 (s, 2 H), 3.6–4.0 (m, 4 H), 7.4 (d, J = 9 Hz, arom, 2 H), 8.1 (d, J = 9 Hz, arom, 2 H); IR, 1590, 1530, 1320 cm^{-1}; mass spectrum (CI) m/z 224 (M^+ + 1).

2,2-Dideuterio-2-(*p*-nitrophenyl)-1-phenylethanol (29): mp 88 °C; ^{1}H NMR δ 2.3 (br, exchangeable, 1 H), 4.9 (br, 1 H), 7.2–7.4 (arom, 7 H), 8.1 (d, J = 9 Hz, arom, 2 H); mass spectrum (CI) m/z 246 (M^+ + 1).

2,2-Dideuterio-2-(*m*-nitrophenyl)-1-phenylethanol (30): mp 38 °C; ^{1}H NMR δ 2.3 (br, exchangeable, 1 H), 4.9 (br, 1 H), 7.2–8.1 (arom, 9 H); mass spectrum (CI) m/z 246 (M^+ + 1).

Product Studies (under Argon). Dark Reactions. The compounds studied in this work do not react in the dark in aqueous solution at the appropriate pH, with the exception of ketals **17**–**19**, which hydrolyze to the corresponding ketones in acidic solution, and alcohol **10** at pH >13.5, which showed thermal retro-aldol reaction. These compounds were not studied at these pHs. A typical experimental procedure for checking for dark reaction is described as follows. About 100 mg of the compound is dissolved in 60 mL of reagent-grade CH_3CN and added to 140 mL of water of the appropriate pH. The solution is then left in the dark under an atmosphere of argon for several hours. The solution is then extracted with CH_2Cl_2 after addition of NaCl (to saturate the aqueous solution

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[31] Fischer, A.; Grigor, B. A.; Packer, J.; Vaughan, J. *J. Am. Chem. Soc.* **1961**, *83*, 4208.

with salt). The isolated material is then analyzed by ^{1}H NMR. In those cases where UV spectrophotometry could be used to monitor reaction, solutions were prepared in cuvettes and monitored for the appropriate length of time in a UV spectrophotometer.

Preparatory Photolysis of 8–10. In a general procedure, 100 mg of the compound is dissolved in 40 mL of CH_3CN and added to 160 mL of distilled water at the appropriate pH. The solution is then transferred to a quartz vessel and photolyzed at 300 nm (254- or 350-nm lamps can also be used) with cooling by a cold finger and continuous purging by a stream of argon through the solution. After photolysis, the solution is first saturated with NaCl and then extracted with 2×100 mL of CH_2Cl_2. On evaporation of the solvent, the photolysate is analyzed by ^{1}H NMR from which the identity and the corresponding yields of the products may be obtained. The products benzaldehyde, **3**, **4**, and **11–13** were identified by comparison of the NMR signals with authentic samples. 2,3-Bis(*p*-nitrophenyl)butane (**14**) was a mixture of (*R*,*R*) and (*S*,*S*) and meso forms, as indicated by two sets of methyl doublets at δ 1.1 and 1.4, as well as two sets of aromatic AA′BB′ signals. Complete spectroscopic characterization of **14** (after separation from the product mixture by simple filtration of the photolysate—since it is insoluble in the reaction solvent—followed by recrystallization from hexanes) is as follows: mp 127–140 °C (mixture of diastereomers); ^{1}H NMR δ 1.1 (d, $J = 8$ Hz, 6 H), 1.4 (d, $J = 8$ Hz, 6 H), 3.05 (m, 4 H), 7.15 (d, $J = 9$ Hz, arom, 4 H), 7.35 (d, $J = 9$ Hz, arom, 4 H), 8.05 (d, $J = 9$ Hz, arom, 4 H), 8.20 (d, $J = 9$ Hz, arom, 4 H); the ratio of the two methyl doublets (relative ratio of the two diastereomers) (δ 1.1 to δ 1.4) is ~30:70; IR 1605, 1595, 1510, 1340 cm^{-1}; mass spectrum (CI) *m/z* 301 ($M^+ + 1$). Anal. Calcd for $C_8H_8NO_2$: C, 63.99; H, 5.37; N, 9.33%. Found: C, 64.10; H, 5.47; N, 9.30.

Preparatory Photolysis of 17–19. These were photolyzed in a similar manner as for alcohols **8–10** except that the volume of CH_3CN cosolvent was increased to 60 mL and the volume of water reduced to 140 mL, due to lower solubility of the ketals. The esters **20** and **21** were identified by their characteristic NMR and IR spectra (after separation on preparative TLC on silica/CH_2Cl_2) as follows. 2-Hydroxyethyl benzoate (**20**): ^{1}H NMR δ 2.5 (s, 1 H), 3.9 (t, $J = 6$ Hz, 2 H), 4.4 (t, $J = 6$ Hz, 2 H), 7.4–8.2 (arom, 5 H); IR, 3200–3600, 1720, 1610 cm^{-1}. 2-Hydroxyethyl acetate (**21**): ^{1}H NMR δ 2.05 (s, 3 H), 3.1 (br, 1 H), 3.8 (m, 2 H), 4.2 (m, 2 H); IR, 3200–3600, 1740 cm^{-1}.

Preparatory Photolysis of 24–26. These were photolyzed in a similar manner as for alcohols **8–10** except that the pH of the solution was checked after addition of the acid and readjusted to the desired value as required.

Product Studies (under Oxygen). Dark Reactions. None of the compounds studied in this work react in the dark under an atmosphere of oxygen at any pH for an extended period (typically several hours), except as previously noted for **10** at pH >13.5 and the ketals at pH <7.

Preparatory Photolysis of 8 and 9 under Oxygen. The procedure is identical with that described above for photolysis under argon except that a stream of oxygen was sent through the photolysis vessel. After workup (as described above) the extent of conversion and yields of the products can be calculated by ^{1}H NMR integration. Typical yields of hydroperoxides **27** and **28** were ~60–70%, with conversions of >80% in the pH 1–12 region. In addition, about 5% yield of *m*- or *p*-nitrobenzaldehyde and ~15% yield of the corresponding nitrotoluenes and dinitrobibenzyls are observed. Hydroperoxides **27** and **28** were separated from the reaction mixture by preparative TLC (silica/CH_2Cl_2). *p*-Nitrobenzyl hydroperoxide (**27**): mp 63–64 °C; ^{1}H NMR ($CDCl_3$, acetone-d_6) δ 5.1 (s, 2 H), 7.6 (d, $J = 9$ Hz, arom, 2 H), 8.1 (d, $J = 9$ Hz, arom, 2 H), 11.65 (s, exchangeable, 1 H); IR, 3200–3600, 1530, 1350 cm^{-1}; mass spectrum (EI) *m/z* 191 (M^+), 151 ($M^+ - H_2O$). *m*-Nitrobenzyl hydroperoxide (**28**) (viscous oil): ^{1}H NMR δ 5.05 (s, 2 H), 7.4–8.2 (arom, 4 H), 8.7 (s, exchangeable, 1 H); IR, 3200–3600, 1530, 1350 cm^{-1}; mass spectrum (EI) *m/z* 191 (M^+), 151 ($M^+ - H_2O$). Due to the lability of **27** and **28**, microanalyses were not attempted. However, additional confirming evidence of their assigned structure is that they can both be reduced cleanly to the corresponding nitrobenzyl alcohols (which are known compounds) with aqueous KI or Na_2SO_3. When photolyses are carried out at pH >12, *p*- and *m*-nitrobenzoic acids are formed, in addition to **27** and **28**, respectively. No attempts were made to calculate relative yields of hydroperoxides and benzoic acids observed in this pH range.

Preparatory Photolysis of 24–26 under Oxygen. As a typical example of a preparative run, 500 mg of **24** was dissolved in a solution consisting of 25 mL of CH_3CN and 175 mL of water. The pH of the solution was checked with a pH meter and adjusted to pH ~12 by addition of small aliquots of 1 M NaOH. The solution was transferred to a 200-mL quartz tube. A cold finger was placed inside the vessel, and a stream of oxygen (via a long metal syringe needle) was sent through the solution for 5 min. The solution was subsequently photolyzed (at 254 or 300 nm) for 60 min inside the Rayonet reaction chamber with continuous purging by oxygen. After photolysis, the solution showed only a residual amount of precipitate, whereas when photolysis was carried out under argon, large quantities of precipitate can be observed [due to 4,4′-dinitrobibenzyl (**4**)]. The photolyzed solution was extracted with 2×100 mL of CH_2Cl_2 after addition of NaCl. Evaporation of the solvent gave a solid (crude yield ~85%), which was dissolved in $CDCl_3$/acetone-d_6 for NMR analysis. The ^{1}H NMR spectrum of the photolysate showed 67% *p*-nitrobenzyl hydroperoxide (**27**) and about 15% total yield of **3** and **4**; the remainder was starting material and a trace of *p*-nitrobenzaldehyde. When photolysis is carried out under argon, no trace of **27** is observed. Compound **25** showed nearly identical behavior. Compound **26** gave α-methyl-*p*-nitrobenzyl hydroperoxide as the major product at pH <12: ^{1}H NMR δ 1.45 (d, $J = 8$ Hz, 3 H), 5.15 (q, $J = 8$ Hz, 1 H), 7.55 (d, $J = 9$ Hz, arom, 2 H), 8.20 (d, $J = 9$ Hz, arom, 2 H), 8.4 (s, exchangeable, 1 H); IR 3200–3600, 1600, 1520, 1340 cm^{-1}; mass spectrum (EI) *m/z* 187 (M^+), 165 ($M^+ - H_2O$). Reduction with aqueous Na_2SO_3 gave 1-(*p*-nitrophenyl)-1-ethanol. At pH >13, the major product of the photolysis is *p*-nitroacetophenone.

Quantum Yields and pH Effects. Quantum yields for product (benzaldehyde) formation for alcohols **8–10** were measured in quartz cuvettes at 254-nm irradiation by monitoring for the formation of benzaldehyde at 252 nm with potassium ferrioxalate actinometry.[13,32] For ketals **17** and **18**, quantum yields for formation of hydroxy ester **20** were measured by following its absorption maximum at 232 nm. Solutions in quartz cuvettes (10^{-4} M substrate) were photolyzed alongside the actinometer solution in a merry-go-round apparatus at 254 nm inside a Rayonet photochemical reactor. To confirm the observed pH effects, small-scale (typically 50–100 mg) photolyses were carried out and the extent of conversion was calculated by ^{1}H NMR, the results of which agreed with the pH behavior obtained by UV spectrophotometry. For alcohols **2** and **7**, quantum yields for reaction were estimated, with either **7** or **8** as a secondary actinometric reference, by small-scale preparative photolyses. Quantum yields for photodecarboxylation of **24–26** were measured, with the known quantum yield of reaction of **24** in pH 7 as the secondary actinometric reference ($\Phi = 0.6$),[5a] via small-scale preparative photolyses.

Medium and Isotope Effects. Quantum yields for reaction of **9** as a function of water content were measured via UV spectrophotometry in quartz cuvettes and varying the water content of the solution. The results were confirmed by preparative photolyses. Solvent isotope effects for **7**, **8**, **17**, and **18** were measured in a similar manner. For **25**, small-scale preparative photolyses were used, and the solvent isotope effect (Table III) was calculated by taking the ratio of conversion of reaction in H_2O vs D_2O. α-Deuterium isotope effects for **29** and **30** were measured by UV spectrophotometry as described above, by monitoring for the formation of benzaldehyde and compared with solutions of the nondeuteriated compounds.

Triplet Sensitization and Quenching Studies. Triplet sensitization of reaction of alcohols **8–10**, **24**, and **25** were carried out by using 2–5 g of sodium benzophenone-2-carboxylate as the triplet sensitizer with 100 mg of the substrate, all dissolved in 200 mL of 30% aqueous CH_3CN (pH 12) in a 200-mL Pyrex tube. The sensitizer absorbed >95% of the light under these conditions. Photolyses were carried out with 350-nm lamps in a Rayonet photochemical reactor. Triplet quenching of reaction for **8** and **9** were carried out with 20-mL quartz tubes using **32** as the triplet quencher and employing a merry-go-round apparatus. Although relatively high concentrations (10^{-2} M) of quencher **32** were used, photolyses were carried out at 350 nm where only **8** and **9** have significant absorption. After photolysis, the samples were extracted with CH_2Cl_2 and were analyzed by gas chromatography, by monitoring for formation of benzaldehyde.

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