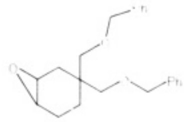
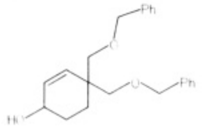
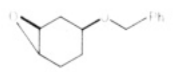
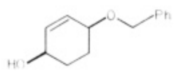
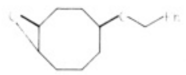
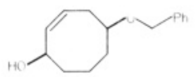
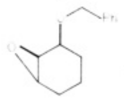
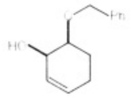
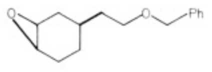
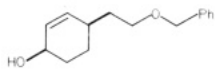
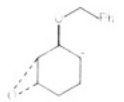
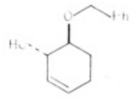
Table II

entry	epoxides	rctn times, h	products	% yield
1		12		82
2		2		87
3		12		71
4		12[a]		60
5		3[a]		81[b]
6		12[a]		47

[a] No HMPA. [b] The *trans*-epoxide isomer is recovered unchanged.

ship of epoxide and benzyloxy substituent led to deprotonation at the benzylic position and nucleophilic opening of epoxides to afford oxetanes, tetrahydrofurans, and tetrahydropyrans with considerable stereocontrol observed at the new asymmetric benzylic carbon. The phenyl ring prefers orientations that minimize steric interactions. Closure to oxetanes is especially facile, even in cases where displacement is directed at a fully substituted carbon (entry 6). Formation of allylic alcohols could not be confirmed under these conditions. The cis isomers generally led to complete destruction of starting material without isolable products.[14]

A different reaction pathway is available by use of lithium diethylamide as illustrated in Table II.[5] In these cases cyclizations were generally not observed.[12] Clean transformations to allylic alcohols were obtained from cis isomers (entries 1–5), whereas trans compounds usually gave very poor yields of allylic alcohols with numerous side products and decomposition. In cases where cyclization is not feasible (entry 5: *trans*-epoxide gave a complex mixture upon treatment with lithio-2,6-dimethylpiperidide) allylic alcohols may be obtained in good yield from the cis isomer. High regioselectivity is a notable characteristic in each isomerization with the new double bond formed upon site-selective deprotonation apparently directed by base chelation with the benzylic ether.[15]

Further applications of these results for stereocontrolled syntheses of heterocyclic natural products are under investigation.

Acknowledgment. We thank the National Institutes of Health (AI-17674) for their generous support and gratefully acknowledge assistance of the National Science Foundation (CHE 81-05004) for purchase of high-field NMR instrumentation.

Supplementary Material Available: A listing of ^{1}H NMR data for the products (4 pages). Ordering information is given on any current masthead page.

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[14] In all cases, our results provide the "favored" exo–tet mode of ring closure as summarized by Baldwin's observations (Baldwin, J. E. *Chem. Commun.* **1976**, 734, 738).

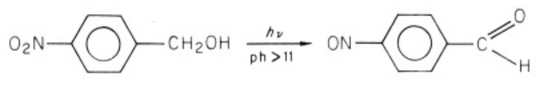
[15] For other examples: Still, W. C.; Lewis, A. J.; Goldsmith, D. *Tetrahedron Lett.* **1971**, 1421. Teutsch, G.; Bucourt, R. *Chem. Commun.* **1974**, 763.

Photoredox Chemistry of *m*- and *p*-Nitrobenzyl Alcohols in Aqueous Solution. Observation of Novel Catalysis by the Hydronium and Hydroxide Ions in These Photoreactions

Summary: *p*-Nitrobenzyl alcohol is found to undergo a hydroxide ion catalyzed photoredox reaction (eq 1), while *m*-nitrobenzyl alcohol undergoes a water and hydronium ion catalyzed process (eq 3).

Sir: A recent report by Wubbels and Celander[1] on the specific- and general-base catalysis in a photochemical Smiles rearrangement prompts us to present our results on the observed catalytic phenomena in the aqueous solution photochemistry of *m*- and *p*-nitrobenzyl alcohols. We employ the definition of a photochemical catalyst (as defined by Wubbels)[1] as being a substance that appears in the quantum yield expression to a power higher than it appears in the stoichiometry.[2]

Irradiation[3] of *p*-nitrobenzyl alcohol (**1**) in aqueous sodium hydroxide at a pH >11 resulted in the formation of *p*-nitrosobenzaldehyde (**2**; eq 1) as the only observed product in low-conversion experiments (i.e., <30% loss of the substrate). No reaction was observed when an identical solution was kept in the dark at room temperature. All spectroscopic data[4] (UV, ^{1}H NMR, IR, and MS) are consistent with the proposed structure of the product, which exists as its nitroso dimer.[5]



(1)

1 **2**

Relative quantum yields (Φ/Φ^0), where Φ^0 is the yield in 1.0 M (pH 14) NaOH, were measured as a function of pH. The results are shown in Figure 1. The efficiency of the photoreaction was found to depend strongly on the hydroxide ion concentration. Thus, under the above definition, this photoreaction is hydroxide ion catalyzed.

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[1] Wubbels, G. G.; Celander, D. W. *J. Am. chem. Soc.* **1981**, *103*, 7669.

[2] As noted by Wubbels,[1] the definition could be qualified by specifying a particular reactive state as the starting state. This would exclude sensitizers as being "catalysts" in photochemical reactions.

[3] A typical experiment involves dissolving 100 mg of the substrate in 140 mL of aqueous sodium hydroxide (~6% CH_3CN, v/v) and irradiating in a Rayonet RPR 100 reactor (254- or 300-nm lamps) for 6 h, with internal cooling and continuous purging of the solution with a stream of argon. Workup involves saturating the solution with NaCl before CH_2Cl_2 extraction. The extent of conversion of the substrate to **2** could be monitored by integrating the aldehyde proton of **2** relative to the methylene protons of **1** in the ^{1}H NMR spectrum.

[4] Yellow solid, mp 185–187 °C; UV (95% EtOH) λ_{max} 340 nm (log ϵ 4.08); ^{1}H NMR ($CDCl_3$) δ 7.9–8.6 (two sets of superimposed AA′BB′ protons, 8 H), 10.1, 10.2 (two nonequivalent formyl protons, 2 H); IR ($CHCl_3$) 2740 (w), 2840 (w), 1710 (s), 1600 (m), 1460 (m), 1230 (m), 1180 cm^{-1}(s); mass spectrum, m/e 254 ($M^+ - 16$).

[5] A large number of nitroso compounds are known to exist as their nitroso dimers. See, for example: Luttke, W.; Gowenlock, B. G. *Q. Rev., Chem. Soc.* **1958**, *12*, 321.

0022-3263/83/1948-0136$01.50/0

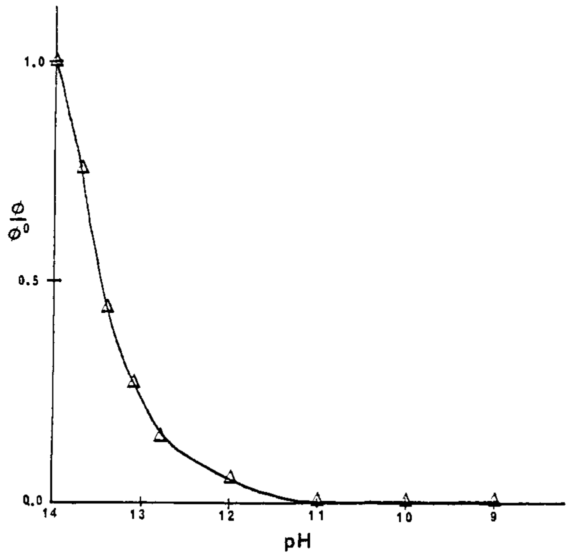
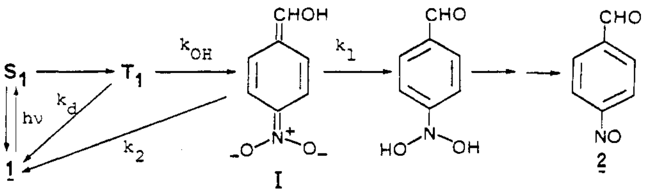


Figure 1. Variation of Φ/Φ^0 as a function of pH for the photoredox reaction of *p*-nitrobenzyl alcohol (1).

Scheme I



No photoreaction was observed at hydroxide ion concentrations of less than 0.001 M (pH 11), or in neutral and acidic media. When irradiated in 0.1 M $NaOCH_3$ in methanol, or in pure organic solvents (e.g., CH_3CN, ethanol or benzene), the reaction was not observed. We have eliminated the possibility of "salt catalysis" by showing that the presence of 0.1 M NaCl did not enhance the efficiency of the photoreaction at pH 13, relative to a solution of the same pH but without added salt. That there is no observable reaction at pH values lower than 11 indicates the absence of a water-catalyzed process: water is ineffective as a catalyzing base. Wubbels et al.[6] have reported the photoisomerization of *p*-nitrobenzaldehyde in aqueous solution to give *p*-nitrosobenzoic acid, which can be viewed as a similar reaction. However, as far as we are aware, their reaction is not subject to catalysis by hydroxide ions.

Irradiation of α,α-dideuterio-*p*-nitrobenzyl alcohol at pH 14 under identical conditions as for **1** resulted in no observable reaction. A conversion of ca. 5% or greater can be readily detected via our technique.[3] Since irradiation of **1** under identical conditions resulted in 54% conversion to **2**, we estimate that the α-deuterium isotope effect on the quantum yield (Φ_H/Φ_D) is approximately 10. This result strongly implies that hydroxide removal of the α-hydrogen is involved in the product-forming step in the mechanism.

Triplet sensitization of the reaction was effected by sodium benzophenone-4-carboxylate ($E_T \sim 69$ kcal mol^{-1}; $\lambda_{excit} = 350$ nm). The reaction could be quenched by 3,5-cyclohexadiene-1,2-dicarboxylic acid (monosodium salt). These results implicate a triplet reactive state, which adds to the large number of known nitroaromatic compounds reacting via this state.[7]

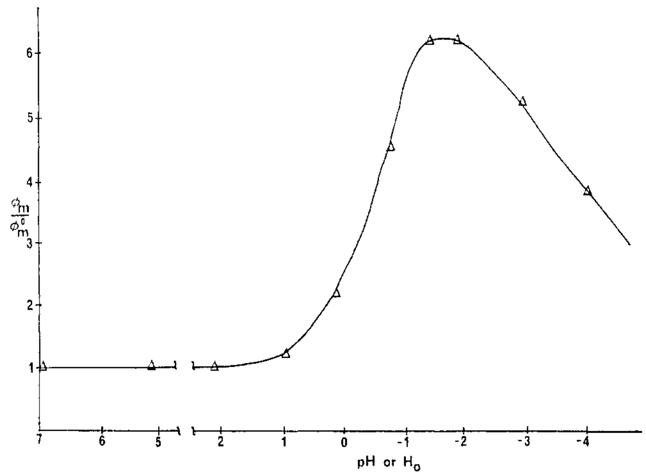


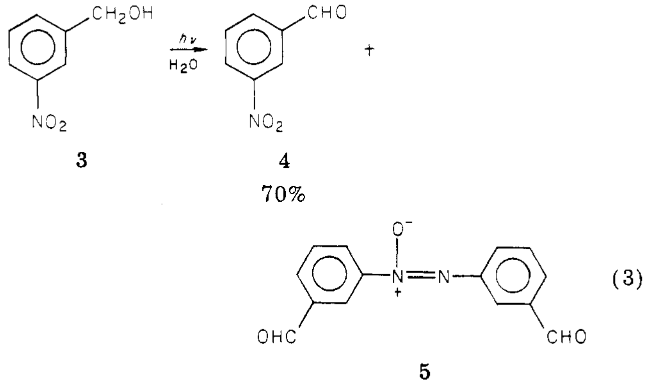
Figure 2. Variation of $\Phi_m/\Phi_m{}^0$ as a function of medium acidity for the photoredox reaction of *m*-nitrobenzyl alcohol (**3**). At pH 9, $\Phi_m/\Phi_m{}^0 = 0.82$. Above this pH the aldehyde products are significantly hydrated and relative yield experiments were not performed.

Our proposed mechanism, which is consistent with all the experimental results, is shown in Scheme I. By assuming a steady state for intermediate I, the expression for Φ^0/Φ is given by eq 2, where Φ^0 is the yield in 1.0 M

$$\frac{\Phi^0}{\Phi} = \left(\frac{1}{k_d + k_{OH}}\right)\left(k_{OH} + k_d\frac{1}{[OH^-]}\right) = \tau^0 k_{OH} + \frac{\tau^0}{\tau'}\frac{1}{[OH^-]} \qquad (2)$$

NaOH and τ^0 and τ' are the lifetimes of the triplet in 1.0 M NaOH and in neutral water, respectively. A good linear plot of Φ^0/Φ vs. $[OH^-]^{-1}$ was obtained (slope = 0.42, correlation coefficient = 0.998), which gives additional support for the proposed mechanism. Simple nitrobenzenes are known to have characteristically short triplet lifetimes of ~1 ns.[8] Assuming that $\tau' = 1 \times 10^{-9}$ s, we calculate that $\tau^0 = 0.42$ ns and $k_{OH} = 1 \times 10^9$ M^{-1} s^{-1}.

We next turned our attention to the aqueous photochemistry of the meta isomer. We had recently reported[9] a preliminary study that showed that photolysis of *m*-nitrobenzyl alcohol (**3**) in neutral water gave the compounds shown in eq 3 (an additional minor product pre-



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(6) (a) Wubbels, G. G.; Hautala, R. R.; Letsinger, R. L. *Tetrahedron Lett.* **1970**, 1689. (b) Wubbels, G. G.; Kalhorn, T. F.; Johnson, D. E.; Campbell, D. *J. Org. Chem.* **1982**, *47*, 4664.

(7) For reviews, see: (a) Morrison, H. A. In "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Wiley: New York, 1969; Chapter 4. (b) Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 49. (c) Frolov, A. N.; Kuznetsova, N. A.; E'tsov, A. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1976**, *45*, 1024.

(8) The short triplet lifetime has been attributed to rapid radiationless decay ($k_d \sim 10^9$ s^{-1}): (a) Hurley, R.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 1949. (b) Trotter, W.; Testa, A. C. *Ibid.* **1968**, *89*, 6917.

(9) Wan, P.; Yates, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1023.

viously reported for us for this reaction,[9] 3-[3-(hydroxymethyl)phenyl]-*NNO*-azoxybenzaldehyde, has been withdrawn; it is not produced in the photoreaction). We now report that this photoreaction is catalyzed by the hydronium ion. The effect of medium acidity (aqueous H_2SO_4) on Φ_m/Φ_m^0, where Φ_m^0 is the quantum yield for the formation of 4 in water at pH 7, was determined by monitoring the increase in optical density at 233 nm due to the formation of product 4, using a merry-go-round apparatus, with 254-nm irradiation. The results are shown in Figure 2. Identical results for Φ_m/Φ_m^0 were obtained by preparative irradiation experiments. The efficiency of the photoreaction is observed to depend strongly on the medium acidity.[10] In addition, Φ_{H_2O}/Φ_{D_2O} (both solutions of pH 7) was found to be 1.30 ± 0.10, thus indicating that proton transfer from the solvent occurs in the product-forming process.

The quantum yield (absolute yield at pH 7, $\Phi_m^0 = 0.055$) was found not to depend on the substrate concentration from 10^{-4} and 10^{-3} M. This strongly suggests that a unimolecular process occurs, leading up to the product-forming step, which is inconsistent with the previously proposed mechanism.[9] Additional support for a unimolecular process is the observation that irradiation of an equimolar (10^{-4} M) mixture of nitrobenzene and benzyl alcohol in aqueous solution does not result in an analogous reaction.

α,α-Dideuterio-*m*-nitrobenzyl alcohol was synthesized and the isotope effect on quantum yield (Φ_m^H/Φ_m^D), where Φ_m^H and Φ_m^D represent the quantum efficiency for *m*-nitrobenzaldehyde formation for the undeuterated and deuterated alcohols, respectively, was measured. It gave 2.4 ± 0.1 in water at pH 7. A lower value (1.3 ± 0.1) was observed in 15% H_2SO_4. The observed isotope effect indicates that abstraction of the α-hydrogen is involved in the product-forming process.

It is clear from the results presented for the meta isomer that the mechanism of this reaction is more complex than for the para isomer: the meta isomer does not react via a simple intramolecular reduction–oxidation process. The fact that water is *essential* for the reaction, and that added hydronium ions can increase the efficiency of the photoreaction, suggests that protons, either donated from water or H_2SO_4, are required to "trap" the reactive triplet state, possibly via protonation of the nitro group. It is not clear at this time why the para isomer does not react in an analogous reaction under these conditions.

At acidities greater than $H_0 = -2$, Φ_m/Φ_m^0 decreases dramatically. Since the estimated pK_{SH^+} of the CH_2OH group[11] is approximately −3 to −6, we propose that the protonated molecule (on the hydroxyl group) is less reactive than the free molecule in the photoreaction. However, we cannot as yet eliminate the possibility of nonproductive photophysical quenching processes at these acidities.

To summarize, we have uncovered a meta/para dichotomy in catalytic effects in the aqueous photochemistry of *m*- and *p*-nitrobenzyl alcohols: the meta isomer exhibits proton-catalyzed redox photochemistry, while, on the other hand, the para isomer exhibits hydroxide-catalyzed redox photochemistry. Neither photoreactions occur in organic media; hence both could be described as "water-catalyzed".[12] We are presently studying these and related reactions in detail, the results of which will be reported in due course.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support of this research, and for a postgraduate scholarship to one of us (P.W.).

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[10] The possibility that these observations are due to a salt effect was eliminated since the presence of up to 3 M NaCl or $LiClO_4$ failed to enhance Φ_m/Φ_m^0 to the extent observed in Figure 2. Typically we find $\Phi(2\ M\ NaCl)/\Phi(0\ M\ NaCl) \approx 1-2$. However, the observation of a salt effect implicates the possible existence of polarized intermediates on the reaction pathway.

[11] Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223.

[12] Preliminary results show that the photochemistry of the ortho isomer (to give *o*-nitrosobenzaldehyde) is not subject to catalysis by proton or hydroxide ions. It reacts equally efficiently in water and in organic media.

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Methyl 5-(Triphenylphosphoranylidene)levulinate: A Reagent for Homologation of Aldehydes to δ-Ene γ-Keto Esters

Summary: Methyl 5-(triphenylphosphoranylidene)levulinate has been synthesized and shown to condense with aldehydes to afford *E* δ-ene γ-keto esters in good yield.

Sir: γ-Keto esters are useful as synthetic intermediates, and subsequently a number of synthetic sequences for their production have been developed.[1] In the course of a natural product synthesis we wished to homologate an aldehyde to the corresponding *E* δ-ene γ-keto ester. To our knowledge no methodology had been reported to effect this transformation in a single synthetic operation.

We have developed two syntheses of ylide **1** and herein report its reaction with aldehydes in DMF proceeds in good to excellent yield. Ketones appear to be unreactive toward the reagent, though an exhaustive study has not been undertaken.

Ylide **1** may be prepared either by condensation of 2 equiv of methylenetriphenylphosphorane with 3-carbomethoxypropionyl chloride in THF at −78 °C or by condensation of triphenylphosphine with methyl 5-bromolevulinate[2] in refluxing benzene, followed by deprotonation with aqueous sodium carbonate (Scheme I).[3]

Ylide **1** is a stable crystalline solid, readily soluble in DMF, and condenses with aldehydes under mild conditions (Table I).[3] Products (as determined by ^{1}H NMR) are generally greater than 95% "*E*", with the exception of the homatropaldehyde adduct **4d**, which is approximately 85% "*E*".

A total synthesis of (±)-γ-dodecanolide (**3**), sex pheremone of the Rove beetle, has been completed in 68% overall yield from heptanal (Scheme II) to demonstrate the viability of the reagent for production of γ-lactones.

Though compound **3** has been previously synthesized in optically active form,[4] this synthesis illustrates the po-

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[1] (a) Woessner, W. D.; Solera, P. S. *Synth. Commun.* **1978**, *8*, 279–283. (b) Ryu, I.; Matusumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283–4286. (c) Miyashita, M.; Kumazawa, T.; Yoshikoshi, A. *Chem. Lett.* **1980**, 1043–1044 and references therein.

[2] For preparation, see: MacDonald, S. F. *Can. J. Chem.* **1974**, *52*, 3257–3258.

[3] See paragraph at the end of paper concerning supplementary material. The ^{1}H NMR spectra of ylide 1 is noteworthy in that the α- and β-carbomethoxy protons appear magnetically equivalent, registering as a 4-proton singlet (δ 2.55) even at 200 MHz.

[4] Pirkle, W. H.; Adams, P. E. *J. Org. Chem.* **1979**, 2169–2175. Alternate syntheses are referenced by Pirkle and Adams.

0022-3263/83/1948-0138$01.50/0