1354 *J. Org. Chem.* **1989**, *54*, 1354–1359

Photoaddition of Water and Alcohols to 3-Nitrostyrenes. Structure–Reactivity and Solvent Effects

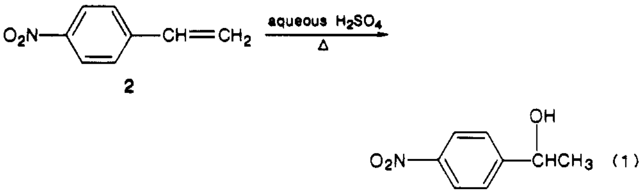
Peter Wan,*[1] Michael J. Davis, and Mary-Anne Teo

Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Received August 3, 1988

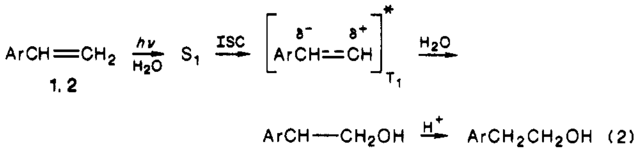
The photoadditions of water and several alcohols to the triplet excited states of 3-nitrostyrenes **1**, **3–5**, and **8** to give the corresponding anti-Markovnikov addition products are reported. Both 3- and 4-nitrostilbenes (**6** and **7**, respectively) do not undergo photoaddition on direct or sensitized irradiation in aqueous or alcohol solutions; only trans to cis photoisomerization is observed. It is proposed that for the nitrostilbenes, efficient twisting of the alkene in the triplet excited state competes favorably with photoaddition. The efficient photoaddition of water and methanol observed for 5-nitroindene (**8**)—the alkene moiety of which cannot attain an orthogonal ("twisted") state—is taken as additional evidence that these photoadditions probably occur via the planar triplet state and that twisting results in only deactivation to the ground state. The use of cosolvents (CH_3CN and $HCONH_2$) on several photoadditions is also reported. For example, use of CH_3CN cosolvent in aqueous solution decreases the efficiency of photohydration in the parent 3-nitrostyrene (**1**) but is observed to enhance the efficiency of reaction (until about 40–70 mol % CH_3CN, depending on the substrate) for **3**, **4**, and **8**. Quantum yields for photohydration and photoaddition of alcohols are reported for several systems.

The ethylene moieties of both 3- and 4-nitrostyrenes (**1** and **2**, respectively) are highly deactivated in the ground state compared to other styrenes lacking the nitro substituent. The strongly electron withdrawing character of the nitro group ($\sigma_p = +0.78$; $\sigma_m = +0.71$)[2] in the ground state is responsible for the low reactivity of **1** and **2** toward electrophilic addition. Thus the hydration of **2** in aqueous sulfuric acid is slow, but does give rise to the Markovnikov alcohol in sufficiently strong acid (eq 1).[3] Both bromination and epoxidation of **1** and **2** are usually not successful under normal reaction conditions. However, sufficiently electron poor alkenes are susceptible to nucleophilic attack, as opposed to their inertness to electrophilic attack.[4-6] For example, alkenes conjugated with strongly electron withdrawing groups such as carbonyl (or those to which highly electronegative atoms are attached, such as fluorine) undergo nucleophilic attack,[4-6] which results in 1,4-addition overall. Many of these conjugate additions have great synthetic utility.[4] However, **1** and **2** are not known to be susceptible to such nucleophilic attack in the ground state, apparently due to the fact that the nitro group, although strongly electron withdrawing, is not sufficiently so when attached to phenyl and hence does not activate the alkene moiety for such a process. Thus, nitrostyrenes are relatively stable styrenes in the ground state; they are not affected by many reagents.



(1)

Several years ago we reported the facile photochemical addition of water to both **1** and **2**, which gives rise to the anti-Markovnikov alcohols with high quantum yields ($\Phi = 0.1–0.4$).[7] The photoreaction was found to proceed via the triplet excited state. The data[7] suggested a mechanism involving initial formation of a nitrobenzyl carbanion intermediate via nucleophilic attack of water at the β-carbon of T_1 (eq 2). The driving force of the reaction was rationalized as being due to the *enhanced* electron-withdrawing character of aromatic nitro groups (3-nitro more so than 4-nitro) in T_1, thus facilitating the nucleophilic attack. This reaction was mechanistically interesting considering the relative inertness of nitrostyrenes to such attacks in the ground state. Hence, additional study of the nitrostyrene system was warranted. In this paper we report a study of the photoaddition of water and alcohols to several 3-nitrostyrenes, the results of which give additional insights into the mechanism and generality of the reaction.



$$\underset{\mathbf{1},\,\mathbf{2}}{ArCH{=}CH_2} \xrightarrow[H_2O]{h\nu} S_1 \xrightarrow{ISC} \left[\overset{\delta^-}{Ar}CH{=}\overset{\delta^+}{CH}\right]^*_{T_1} \xrightarrow{H_2O} Ar\overset{-}{C}H{-}CH_2OH \xrightarrow{H^+} ArCH_2CH_2OH \quad (2)$$

Results

Product Studies. Our experience with nitrostyrene photohydration has shown that the 3-nitro isomers react more cleanly and with much higher quantum yields than the corresponding 4-nitro isomers.[7,8] This is also true in studies of the photo-retro-aldol type reactions of nitrobenzyl derivatives, in which the 4-nitro isomers have more complicated mechanistic behavior than the corresponding 3-nitro isomers.[9,10] For these reasons, we have restricted the present study mostly to 3-nitrostyrenes. Compounds **1–8** were made via standard procedures (see the Experimental Section) and were distilled or recrystallized before use. The photoaddition of water (photohydration) was studied by photolyzing (Rayonet RPR 100 photochemical reactor; 254-, 300-, or 350-nm lamps; typical photolysis times 5–30 min) 10^{-3} M solutions of the substrates in $CH_3CN–H_2O$ mixtures, typically 30% (v/v) CH_3CN except for the less soluble materials (**5–7**), where 50% CH_3CN had

---

[1] Natural Sciences and Engineering Research Council (NSERC) of Canada University Research Fellow, 1984–89.

[2] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

[3] (a) Schubert, W. M.; Keeffe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559. (b) Durand, J.-P.; Davidson, M.; Hellin, M.; Coussemant, F. *Bull. Soc. Chim. Fr.* **1966**, 43.

[4] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 664.

[5] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; p 620.

[6] Sykes, P. *A Guidebook to Mechanism in Organic Chemistry*, 6th ed.; Longman: Harlow, Essex, 1986; p 198.

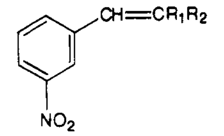
[7] Wan, P.; Culshaw, S.; Yates, K. *J. Am. Chem. Soc.* **1982**, *104*, 2509.

[8] Wan, P.; Teo, M.-A., unpublished results.

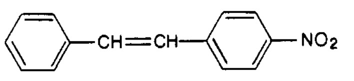
[9] Wan, P.; Muralidharan, S. *Can. J. Chem.* **1986**, *64*, 1949.

[10] (a) Wan, P.; Muralidharan, S. *J. Am. Chem. Soc.* **1988**, *110*, 4336. (b) Okamoto, Y.; Iwamoto, N.; Toki, S.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 277.

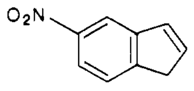
0022-3263/89/1954-1354$01.50/0 © 1989 American Chemical Society



1: $R_1 = R_2 = H$
3: $R_1 = CH_3$; $R_2 = H$
4: $R_1 = CH_2CH_3$; $R_2 = H$
5: $R_1 = R_2 = CH_3$
6: $R_1 = Ph$; $R_2 = H$ (trans)



7 (trans)



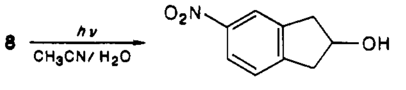
8

to be used. In all of 1, 3–5, and 8, nearly quantitative conversion to the corresponding alcohols was possible, all with respectable quantum yields (vide infra) (eq 3 and 4).

$$\mathrm{ArCH{=}CR_1R_2} \xrightarrow[\mathrm{CH_3CN/H_2O}]{h\nu} \mathrm{ArCH_2CR_1R_2OH} \qquad (3)$$

1, 3-5

9: $R_1 = R_2 = H$
10: $R_1 = CH_3$; $R_2 = H$
11: $R_1 = CH_2CH_3$; $R_2 = H$
12: $R_1 = R_2 = CH_3$



(4)

13

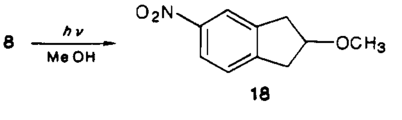
The photoproducts 9–13 were readily characterized as the anti-Markovnikov addition products by standard spectroscopic techniques. Both of the nitrostilbenes 6 and 7 gave only trans to cis photoisomerization with almost identical efficiencies, based on ^{1}H NMR data; no trace of photoaddition products was observed even under prolonged irradiation (several hours). The photostationary trans to cis ratio of 6 was ≈72:28 and ≈52:48 at 254- and 350-nm excitation wavelengths, respectively, as calculated by ^{1}H NMR integration using the resonances of the vinyl protons, which were readily assignable by high field NMR (see the Experimental Section). Similar photostationary ratios were observed for 7. 5-Nitroindene (8), with its "locked" alkene moiety, reacts as efficiently as any of 1 and 3–5 to give 13, with yields of up to 80%.

According to the N_+ scale developed by Ritchie,[11] methanol is slightly more nucleophilic than water. Therefore, it was of interest to see whether MeOH would add to nitrostyrenes on photolysis. Surprisingly, 1 gave only low yields (<10%) of the photoaddition product with MeOH, which cannot readily be accounted for based on the difference in solvent nucleophilicity between H_2O and MeOH. However, all of 3–5 and 8 gave high yields (>60%) of the corresponding methyl ethers on photolysis in pure MeOH (eq 5 and 6). Again, both of the nitrostilbenes (6

$$\mathrm{ArCH{=}CR_1R_2} \xrightarrow[\mathrm{MeOH}]{h\nu} \mathrm{ArCH_2CR_1R_2OMe} \qquad (5)$$

1, 3-5

14: $R_1 = R_2 = H$
15: $R_1 = CH_3$; $R_2 = H$
16: $R_1 = CH_2CH_3$; $R_2 = H$
17: $R_1 = R_2 = CH_3$



(6)

18

and 7) gave only trans to cis photoisomerization on photolysis in MeOH. The low reactivity of 1 with MeOH was curious considering that all of 3–5 and 8 gave high yields of the corresponding methyl ether product. The lack of reactivity of 6 and 7 in MeOH is understandable since these stilbenes have already been found not to undergo photohydration. However, clearly 1 does not have any deactivational pathways that are not already apparent in any of 3–5. We postulated that the low polarity of MeOH, as measured by its dielectric constant ($\epsilon = 33^2$ compared to H_2O ($\epsilon = 80$))[2] was a possible cause for the low reactivity in 1. Indeed, photolysis of 1 at 300 nm in a 50% (v/v) solvent mixture of MeOH and $HCONH_2$ ($\epsilon = 111$)[2] gave >40% yields of the corresponding methyl ether 14. When dimethylformamide (DMF) ($\epsilon = 37$)[2] was used in place of $HCONH_2$, essentially no photoaddition was observed (<5% yield), and 1 could be recovered unchanged. Whereas the photoadditions of EtOH ($\epsilon = 25$),[2] i-PrOH ($\epsilon = 20$),[2] and t-BuOH ($\epsilon = 12.5$)[2] to 1 gave barely detectable amounts of the corresponding 3-nitrobenzyl ethers when photolyzed in the pure alcohol, photolysis in a 50% (v/v) mixture of the alcohol and $HCONH_2$ resulted in a much higher yielding reaction (yields in the range 20–60%). Interestingly, use of AcOH ($\epsilon = 6$)[2] as pure solvent or in $HCONH_2$ failed to give any reaction.

Table I. Product Quantum Yields for the Photoaddition of Water (Φ_{OH}) and Methanol (Φ_{OMe}) to 3-Nitrostyrenes 1, 3-5, and 8

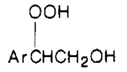
compd	Φ_{OH}[a,b]	Φ_{OMe}[b]
1	0.32	≈0.005
3	0.22	0.27
4	0.21	0.17
5	0.18	0.07
8	0.17	0.40

[a] Essentially wholly aqueous solution at pH 7 (<2% CH_3CN cosolvent) except for 4, 5, and 8, which were measured in 96 mol % H_2O-CH_3CN. [b] For loss of substrate, by UV spectrophotometry at a substrate concentration of 10^{-4} M. Since the reactions gave only one product cleanly, the measured quantum yields may be taken as product quantum yields (λ_{excit} = 254 nm; potassium ferrioxalate actinometry). Estimated errors ±10% of quoted value.

Photolysis of 1 in 50% D_2O/CH_3CN and in 50% $MeOD/HCONH_2$ gave the corresponding α-deuteriated products 19 and 20, respectively. In addition, we have found[12] that photolysis of 1, 3, and 4 in oxygenated aqueous solution results in formation of β-hydroxy α-hydroperoxides (e.g., 21 from 1) instead of the simple photohydration products. The above results support a mechanism involving 3-nitrobenzyl carbanions as intermediates in these photoadditions: protonation of the carbanion would give the usual photoaddition products whereas in the presence of oxygen, oxygenation of the α-carbanion[13-15] would give β-hydroxy α-hydroperoxides.

ArCHDCH₂OH 19

ArCHDCH₂OCH₃ 20



$\mathrm{ArCH(OOH)CH_2OH}$

21

(Ar = 3-nitrophenyl)

Quantum Yields. Product quantum yields for loss of substrate (Φ_L) in H_2O and MeOH for 3-nitrostyrenes 1, 3–5, and 8 were measured by UV spectrophotometry (λ_{excit} = 254 nm), by following the loss of OD at λ_{max} of the compounds. Potassium ferrioxalate actinometry[27] was used

---

(11) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.

(12) Wan, P.; Davis, M. J., manuscript in preparation.

(13) Stowell, J. C. *Carbanions in Organic Synthesis*; Wiley: New York, 1979.

(14) Jones, J. R. *The Ionisation of Carbon Acids*; Academic Press: London, 1973.

(15) Russell, G. A.; Moye, A. J.; Janzen, E. G.; Mak, S.; Talaty, E. R. *J. Org. Chem.* **1979**, *32*, 137.

(16) Wan, P.; Yates, K. *Can. J. Chem.* **1986**, *64*, 2076.

(17) Based on the known E_T of similar compounds.[2]

Table II. Product Quantum Yields (Φ_{OH}) for the Photoaddition of Water and Alcohols to 1 in 50% (v/v) $HCONH_2$-ROH Mixtures

solvent[a]	Φ_{OH}[b]	solvent[a]	Φ_{OH}[b]
H_2O[c]	0.038	*i*-PrOH	0.003
H_2O[d]	0.045	*t*-BuOH	≈0.001
MeOH[e]	0.015	AcOH	0.000[f]
EtOH	0.011		

[a] Solvent consists of 50% (v/v) of either water, alcohol, or acetic acid with $HCONH_2$ as the cosolvent. Photolyses in the pure alcohols gave only low yields (<10%) of addition product (extended photolysis runs). [b] Quantum yield for photoaddition product estimated from semipreparative experiments using the run in 50% H_2O-CH_3CN (entry 2) as the reference (λ_{excit} = 300 nm). Estimated errors ±10% of the quoted value. [c] Equivalent to 65 mol % H_2O-$HCONH_2$. [d] In 50% (v/v) H_2O-CH_3CN (74 mol % H_2O-CH_3CN). [e] Equivalent to 57 mol % MeOH-$NCONH_2$. [f] No photoaddition product observed.

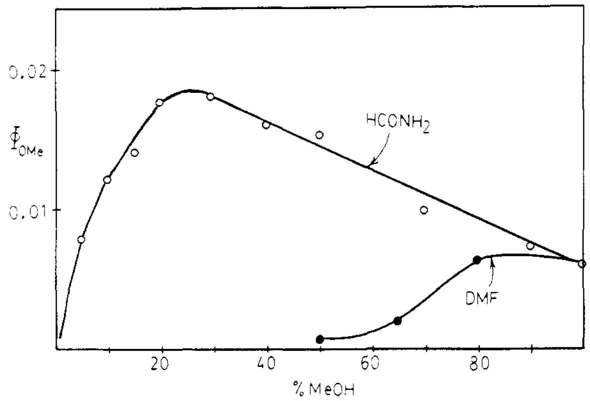


Figure 1. Photoaddition quantum yields in MeOH (Φ_{OMe}) for 1 as a function of percent MeOH (v/v) in $HCONH_2$ and DMF cosolvents.

for measurement of incident light intensity. Since the only products observed in H_2O and MeOH are the corresponding photoaddition products (the reactions are very clean), Φ_L may be equated to Φ_{OH} (photohydration quantum yield) in H_2O, and to Φ_{OMe} (quantum yield for methyl

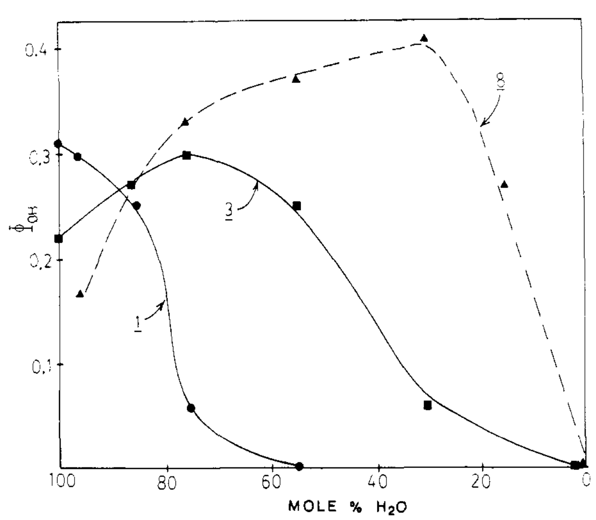


Figure 2. Photohydration quantum yields (Φ_{OH}) for 1, 3, and 8 as a function of mole percent H_2O in CH_3CN cosolvent. The behavior observed for 4 is similar to that of 3, except that the maximum Φ_{OH} (in ≈75 mol % H_2O) is 0.45.

ether formation) in MeOH (Table I). The value of 0.32 for photohydration of 1 is identical within experimental error with the value reported previously[7] using Malachite green leucocyanide actinometry. This value for the photohydration quantum yield of 1 did not change appreciably at different pH's (range of 1–14) and indicates lack of competing hydroxide ion attack in the mechanism. When MeOH (no cosolvent) was used as the solvent, 1 hardly reacts (Φ_{OMe} ≈ 0.005) while all of 3–5 and 8 remain quite reactive. Quantum yields for photoaddition of several alcohols and acetic acid to 1 were measured in 50% (v/v) ROH (or AcOH)-$HCONH_2$ mixtures since the quantum yields in pure alcohol (or pure AcOH) are exceptionally low. The results are shown in Table II. Use of $HCONH_2$ cosolvent for H_2O results in a drastic drop in Φ_{OH} (from 0.32 in pure water to 0.038), whereas its use enhances the quantum yield for all the alcohols used (e.g., for MeOH, Φ_{OMe} increases to 0.015 from ≈0.005). This effect is illustrated in more detail in Figure 1 where a plot of Φ_{OMe} vs percent (v/v) MeOH in $HCONH_2$ and DMF for reaction of 1 is shown. Use of $HCONH_2$ enhances the addition until about 75% $HCONH_2$ when it begins to drop off due to the low concentration of MeOH available in the mixture. The same results are also observed when EtOH is used in place of MeOH. Use of DMF at any concentration decreases the already low quantum efficiency in pure MeOH. These effects appear to be attributable to the polarity of the cosolvent used, $HCONH_2$ being much more polar than DMF (ϵ = 111 compared to ϵ = 37).[2] Otherwise, there appears to be no simple explanation for these observations since the chemical and UV absorption characteristics of these two cosolvents are essentially identical.

The somewhat unexpected effects observed for $HCONH_2$ cosolvent with 1 in MeOH prompted us to investigate the effect of CH_3CN cosolvent concentration in photohydration efficiency since CH_3CN has been, for the most part, the standard cosolvent in many of our studies of nitroaromatic photochemistry. It has been assumed for the most part that use of CH_3CN does not interfere with the photochemistry, but only decreases the quantum efficiency of reaction by decreasing the polarity of the medium.[10,16] Quantum yields for photohydration (Φ_{OH}) of 1, 3, 4, and 8 as a function of mole percent of CH_3CN cosolvent were measured by using UV spectrophotometry. The results are plotted in Figure 2. The photohydration efficiency was observed to decrease at all CH_3CN con-

---

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

(19) Yip, R. W.; Sharma, D. K.; Giasson, R.; Gravel, D. *J. Phys. Chem.* **1984**, *88*, 5770.

(20) See for example: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, 1978.

(21) Schulte-Frohlinde, D.; Görner, H. *Pure Appl. Chem.* **1979**, *51*, 279.

(22) A reviewer has suggested that other possibilities exist to account for the lack of photoaddition of the nitrostilbenes besides the simple competing isomerization pathway. For example, perhaps nitrostilbenes have different charge distribution compared to simple nitrostyrenes in T_1. The reviewer also indicated that it was not clear why the simple nitrostyrenes (3–5) do not undergo facile isomerization also. We point out that it is well known that stilbenes have much higher quantum yields for twisting than simple styrenes,[20] which can be easily accounted for by the size of the introduced phenyl substituent. In "locked" stilbenes (i.e., those stilbenes that are structurally modified to prevent twisting), fluorescence *and* photoaddition of methanol (via the singlet state) have been observed.[20] Although a similar study has not been done for the nitrostilbenes in this work, the results already available suggests the operation of the above. However, in order to demonstrate it directly, a "locked" nitrostilbene derivative needs to be studied. This is presently under way in our laboratory.

(23) An additional possibility for the "anomalous" behavior of 1 is that its triplet lifetime is very sensitive to solvent polarity. That is, as the polarity of the solvent decreases, its lifetime also decreases. This may account for the reduced reactivity of 1 with increasing CH_3CN content. However, it would be difficult to distinguish between this possibility and the explanation offered in the text without direct spectroscopic studies.

(24) (a) Steenken, S.; McClelland, R. A., submitted to *J. Am. Chem. Soc.* (b) McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S., submitted to *J. Am. Chem. Soc.*

(25) Ingold, C. K.; Pigott, H. A. *J. Chem. Soc.* **1923**, 1469.

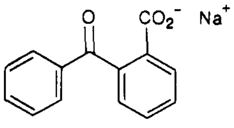
(26) Haworth, R. D.; Woodcock, D. *J. Chem. Soc.* **1947**, 95.

(27) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

centrations for 1 until the reaction is no longer observed at ≈60 mol % water. However, all of 3, 4, and 8 showed *increasing* Φ_{OH}'s in this same region of CH_3CN concentration. Only at rather high CH_3CN concentrations (e.g., ≈70 mol % CH_3CN for 8) does Φ_{OH} begin to fall off, presumably to the low water content available in the mixture. These observations from UV data have been confirmed by semipreparative studies. For example, product studies by ^1H NMR show that 8 photohydrates as efficiently in 80 mol % CH_3CN–H_2O as in 20 mol % CH_3CN–H_2O! The reactions in high CH_3CN content are also clean, with no new photochemistry being observed, and hence ruling out the possibility of artifacts in the UV technique for measuring Φ_{OH}. The above observations suggest that the photochemical behavior of 1 is not the norm for 3-nitrostyrenes and that "normal" behavior is exemplified by the more highly substituted 3-nitrostyrenes (i.e., **3**–**5** and **8**, but not the nitrostilbenes).

Solvent Isotope Effects. The solvent isotope effect for photohydration of 1 (Φ_H/Φ_D), where Φ_H and Φ_D are the quantum yields for photohydration in H_2O and D_2O, respectively, was reported to be 1.00 ± 0.05,[7] as measured by UV spectrophotometry. In this study, the same value is also observed for the photohydration of **3**–**5** and **8**. In addition, a value of 1.0 ± 0.1 for 1 was calculated for Φ_H/Φ_D from semipreparative scale experiments using ^1H NMR for analysis, corroborating the results obtained from the UV technique. Also using semipreparative experiments, we have determined that $\Phi_H/\Phi_D = 1.0 \pm 0.1$ for the photoaddition of MeOD to 1 in 50% (v/v) MeOH (MeOD)–$HCONH_2$.

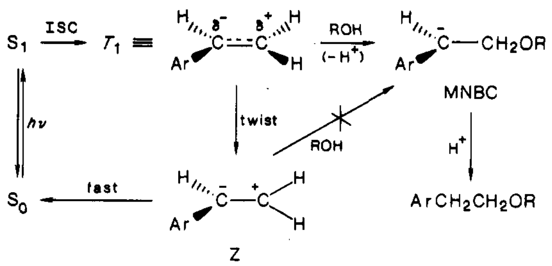
Triplet Sensitization. In these experiments, the sensitizer used was sodium benzophenone-2-carboxylate ($E_T \approx 70$ kcal mol^{-1}),[17] which is water soluble above pH ≈ 5 and can be excited at 350 nm. The energy of nitrobenzene triplets has been estimated to be ≈60 kcal mol^{-1} [18,19] making **22** a useful sensitizer for nitroaromatic compounds in aqueous solution. As expected, the photohydrations of all of **3**–**5** and **8** can be sensitized by **22**. However, triplet sensitization of both **7** and **8** resulted in only trans to cis isomerization, as was observed on direct irradiation. The possibility that **7** and **8** do not photohydrate on direct irradiation because of facile twisting (isomerization) from the singlet state (and hence insignificant population of the triplet manifold where photohydration is believed to take place) can therefore be excluded. The high singlet to triplet intersystem crossing yields (typically ≈ 0.7)[18] of nitrobenzenes would suggest that the only important reactive state in these photoadditions is the triplet, as determined for other photoreactions of nitroaromatic compounds studied in our laboratory.[7,10a,16]



22

Discussion

Scheme I



An important aspect of the mechanism of photohydration not addressed in the original study[7] was whether reaction took place via the planar or orthogonal ("twisted") state or via both species. Alkenes in both the singlet and triplet excited states are known to undergo a facile twisting motion, resulting in the corresponding orthogonal state, which subsequently can deactivate to the ground state via internal conversion from the singlet or intersystem crossing from the triplet.[20] Both of these deactivational pathways to the ground state from the corresponding orthogonal state are believed to be very fast. Polarized singlet alkenes twist to give zwitterionic orthogonal states and diradicaloid triplet alkenes give diradicaloid orthogonal states. The results of this study support a mechnism of photohydration (or photoaddition in general) of 3-nitrostyrenes in which the initially populated planar triplet excited state (assumed to be T_1 for discussion purposes and also polarized) undergoes photoaddition, via nucleophilic attack of H_2O (or ROH) at the β-carbon, to generate a 3-nitrobenzyl carbanion (MNBC) intermediate (Scheme I). Subsequent protonation of this intermediate gives the observed anti-Markovnikov addition product. A competing process from the planar T_1 state is twisting about the alkene moiety to give the orthogonal zwitterionic state (Z), which deactivates to S_0 without addition of ROH. These proposals are supported by the following results and observations: (i) 5-Nitroindene (**8**)—with an alkene moiety that cannot attain an orthogonal ("twisted") state—reacts relatively efficiently (compared to the 3-nitro styrenes **3**–**5**) in photohydration and much more so in the photoaddition of MeOH. This strongly suggests that for these simple 3-nitro styrenes reaction occurs mostly (if not all) from the planar polarized triplet state. (ii) It is known[21] that 4-nitrostilbene (**7**) and other nitrostilbenes have high quantum yields for trans–cis photoisomerization in a number of solvents (typically Φ ≈ 0.3–0.5).[21] In addition, it has been shown that the trans to cis photoisomerization mechanism for **7** occurs exclusively via the triplet state.[21] In this study, we have shown that 3-nitrostilbene (**6**) undergoes photoisomerization as efficiently as **7**. It is reasonable to assume that the trans to cis photoisomerization mechanism for **7** also occurs exclusively via the triplet state. Hence, we propose that the observed lack of photoaddition for both of **6** and **7** is due to facile deactivation to the ground state by twisting in these substrates.[22]

Triplet excited states are formally "diradicaloid" in electronic character.[20] However, the photoadditions of 3-nitrostyrenes clearly involve excited triplet states, which have significant charge transfer character. The photochemistry of several other nitroaromatic compounds studied in our laboratory[9,10,16] are also best rationalized as from a strongly polarized T_1 state, giving rise to charged intermediates. Thus, it seems clear that the classical "diradicaloid" picture of triplets do not apply to these nitroaromatic compounds. They might be better represented as triplet states, which have a high degree of charge transfer character due to the enhanced electron-withdrawing character of the nitro group. However, a detailed characterization of the reactive triplet state would require spectroscopic studies, which are beyond the scope of the present work.

The effects of cosolvent (CH_3CN and $HCONH_2$) on quantum efficiency of photoaddition for the nitrostyrenes can be explained by the following working hypothesis: the degree of charge transfer character of the reactive state of the parent 3-nitrostyrene (1) is strongly dependent on solvent polarity. That is, the photochemical behavior of 1 is actually anomalous compared to 3–5 and 8. As observed in Figures 1 and 2, 1 reacts efficiently only when the solvent is sufficiently polar whereas 3–5 and 8 behave differently. One simple explanation for the effects observed for 1 is that there are two close-lying triplets, only one of which is reactive (e.g., a π,π^* as opposed to an n,π^* state). It is well established that a change in solvent polarity can change the ordering of π,π^* and n,π^* energy levels.[20] Thus a slight change in solvent polarity can have a substantial effect on reactivity of 1 if there are indeed two close-lying triplets. For the more heavily substituted 3-nitrostyrenes 3–5 and 8, the energy gap between these two triplets is much larger, with the reactive state (presumably π,π^*) lower in energy. For these substrates, depleting the amount of CH_3CN in solution (Figure 2) initially enhances the photohydration.[23] With the assumption that this effect is not due to a change in reactive state, the observation implies that water is more nucleophilic in mixtures of H_2O–CH_3CN rather than in pure H_2O, at least to ≈60 mol % water. Direct kinetic support of this phenomenon is in the measured rates of nucleophilic attack of photogenerated carbocations by water, which have been found to remain constant and in some cases increase substantially with increasing CH_3CN content.[24]

In summary, we have shown that the photohydration and photoadditions in general of 3-nitrostyrenes occur via the planar excited triplet state (probably π,π^* in configuration). Twisting of the alkene moiety in T_1 results in only deactivation to the ground state. The photobehavior of the parent 3-nitrostyrene (1) is anomalous with respect to its dependence on cosolvent polarity, the observations of which can be rationalized by proposing the existence of two close-lying triplets, only one of which is reactive. The behavior of 3, 4, and 8 toward CH_3CN as cosolvent suggests that these substrates may be used as a photochemical probe of water nucleophilicity in aqueous solution.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on Perkin-Elmer R32 or Bruker WM250 instruments, in $CDCl_3$ with TMS as internal standard. UV spectra were recorded on a Pye Unicam SP8-400 instrument. IR spectra were recored on a Perkin-Elmer 283 instrument with use of NaCl plates. Mass spectra were taken on a Finnigan 3300 instrument. Microanalysis were performed by Canadian Microanalytical Service, New Westminster, British Columbia, Canada. Preparative photolyses were carried out in 200-mL quartz tubes in a Rayonet RPR 100 photochemical reactor equipped with 254-, 300-, or 350-nm lamps. Quantum yield measurements were carried out in 1.00-cm Suprasil quartz cuvettes with an Oriel 200-W Xe–Hg light source filtered through distilled water and a Corning 7-54 bandpass filter before further filtration through an Applied Physics monochromator set at 254 nm.

Materials. *m*-Nitrostyrenes 1 and 3 and nitrostilbenes 6 and 7 were prepared via dehydration of the corresponding benzyl alcohols, which were obtained from $NaBH_4$ reduction of the corresponding ketones.

***m*-Nitrostyrene (1)** was prepared from 3-nitroacetophenone by $NaBH_4$ reduction and subsequent dehydration over 85% H_3PO_4. The sample obtained was identical with authentic material (from Aldrich).

β-Methyl-3-nitrostyrene (1-(3′-nitrophenyl)propene) (3) was prepared from 3-nitropropiophenone: bp 104–105 °C (2 mmHg); ^1H NMR δ 1.9 (m, 3 H), 6.4 (m, 2 H), 7.3–8.2 (m, 4 H).

***trans-m*-Nitrostilbene (6)** was prepared from *m*-nitrobenzyl phenyl ketone:[10] mp 102–105 °C; ^1H NMR (250 MHz) δ 7.15 (AB quartet, *J* = 16 Hz, 2 H, trans vinyl H), 7.25–7.55 (m, 6 H), 7.73–7.8 (m, 1 H), 8.05–8.10 (m, 1 H), 8.3–8.35 (m, 1 H).

***trans-p*-Nitrostilbene (7)** was prepared from *p*-nitrobenzyl phenyl ketone:[10] mp 150–155 °C; ^1H NMR δ 7.3–7.55 (m, 9 H), 7.6 (d, *J* = 9 Hz, 2 H), 8.2 (*J* = 9 Hz, 2 H).

β-Ethyl-3-nitrostyrene (1-(3′-nitrophenyl)-1-butene) (4) was prepared from a Wittig reaction of *n*-propyltriphenylphosphonium bromide with 3-nitrobenzaldehyde (*n*-BuLi/THF): bp 120 °C (2 mmHg); ^1H NMR (250 MHz) δ 1.05 (m, 3 H), 2.25 (m, 2 H), 5.75 (m, 1 H), 6.35 (m, 1 H), 7.3–8.2 (m, 4 H).

β,β-Dimethyl-3-nitrostyrene (2-methyl-1-(3′-nitrophenyl)-1-propene) (5) was prepared from a Wittig reaction of isopropyltriphenylphosphonium bromide with 3-nitrobenzaldehyde (*n*-BuLi/THF): ^1H NMR δ 1.9 (d, *J* = 8 Hz, 6 H), 6.3 (m, 1 H), 7.3–8.2 (m, 4 H).

5-Nitroindene (8) was prepared from nitration of 1-indanone followed by reduction and dehydration. The nitration of 1-indanone was adapted from Ingold and Pigott:[25] To a 250-mL round-bottom flask equipped with a magnetic stirring bar was charged 50 mL of concentrated H_2SO_4 and cooled to 0 °C in a ice/salt bath. 1-Indanone (Aldrich) (6 g; 0.045 mol) was added with stirring. To this solution was added dropwise 5 g of KNO_3 dissolved in 15 mL of concentrated H_2SO_4 via a dropping funnel, making sure that the temperature of the solution does not rise above 15 °C. After addition, the solution was stirred for 1 h and then poured into crushed ice. The precipitate was filtered and washed with distilled water and left to dry. The yield of crude nitroindanone (believed to be mixture of isomers) was ≈8 g. The crude solid was divided up into several portions and each fractionally recrystallized from boiling hexanes containing ≈10% $CHCl_3$. Two kinds of crystals separated out on crystallization: yellow needles on the bottom and side of the flask and an almost colorless fluffy material in the bulk solvent. The colorless fluffy material was decanted and filtered, which proved to be pure 6-nitro-1-indanone: ^1H NMR δ 2.8 (m, 2 H), 3.3 (m, 2 H), 7.65 (d, *J* = 9 Hz, 1 H), 8.45 (dd, *J* = 9 and 3 Hz, 1 H), 8.55 (d, *J* = 3 Hz, 1 H). The other possible isomeric nitroindanones would give a different splitting pattern for the aromatic protons: IR (cm^{-1}) 1710 (s), 1600 (m), 1530 (m), 1350 (s). Reduction of 6-nitro-1-indanone with $NaBH_4$ gave 6-nitro-1-indanol: ^1H NMR δ 1.8–3.3 (m, 5 H), 5.3 (m, 1 H), 7.35 (d, *J* = 9 Hz, 1 H), 8.1 (dd, *J* = 9 and 3 Hz, 1 H), 8.2 (d, *J* = 3 Hz, 1 H). Subsequent dehydration in toluene with several drops of concentrated H_2SO_4 as catalyst using a Dean–Stark trap gave the crude 5-nitroindene, which was further purified by crystallization from MeOH to give rosettes of yellow needles: mp 80 °C (lit.[26] mp 82–83 °C), ^1H NMR δ 3.45 (s, 2 H), 6.7 (m, 1 H), 6.95 (m, 1 H), 7.55 (d, *J* = 9 Hz, 1 H), 8.05 (dd, *J* = 9 and 3 Hz, 1 H), 8.2 (d, *J* = 3 Hz, 1 H).

Photohydration of 1. In a typical experiment, 100 mg of the substrate was dissolved in 50 mL of CH_3CN and added to 150 mL of distilled water. The solution was then placed into a 200-mL quartz vessel containing a water-cooled cold finger. The solution was purged with argon (Linde, 99.9%) for 5–10 min prior to photolysis and irradiatd for ≈10 min with a continuous stream of argon purging through the solution. After photolysis, the solution was extracted with 2 × 100 mL of CH_2Cl_2. The product observed was 3-nitrophenethyl alcohol (9) in quantitative yield. The ^1H NMR of 9 was identical with an authentic sample from a previous study.[10a]

Photohydration of 1 in D_2O. By use of the same procedure as above but with D_2O instead of H_2O, 19 was obtained after back exchange of the hydroxyl deuteron for proton with H_2O: ^1H NMR (250 MHz) δ 1.7 (broad, exchangeable, 1 H), 2.95 (tt, *J* = 7 and 2 Hz, 1 H), 3.9 (d, *J* = 7 Hz, 2 H), 7.4–8.2 (m, 4 H); mass spectrum (CI), *m/z* 169 (M^+ + 1).

Photohydration of 3. Under the same procedure as above, 3 gave 1-(3′-nitrophenyl)-2-propanol (10) in quantitative yield: ^1H NMR (250 MHz) δ 1.35 (d, *J* = 7 Hz, 3 H), 2.85 (m, 2 H), 4.08 (m, 1 H), 7.4–8.1 (m, 4 H); IR (cm^{-1}) 3200–2500 (broad), 1520 (s), 1340 (m); mass spectrum (CI), *m/z* 181 (M^+ + 1).

Photohydration of 4. Under the same procedure as above, 4 gave 11 in quantitative yield: ^1H NMR (250 MHz) δ 0.97 (t, *J* = 7 Hz, 3 H), 1.53 (m, 2 H), 1.6 (broad, exchangeable, 1 H), 2.7–2.95 (m, 2 H), 3.78 (m, 1 H), 7.4–8.1 (m, 4 H); IR (cm^{-1}) 3200–3500 (broad), 1520 (s), 1350 (s); mass spectrum (CI), *m/z* 196 (M^+ + 1).

Photohydration of 5. Under the same procedure as above, 5 gave 12 in quantitative yield: ^1H NMR (250 MHz) δ 1.24 (s, 6 H), 2.85 (s, 2 H), 7.4–8.15 (m, 4 H); IR (cm^{-1}) 3200–3500 (broad), 1530 (s), 1350 (s); mass spectrum (CI), *m/z* 196 (M^+ + 1).

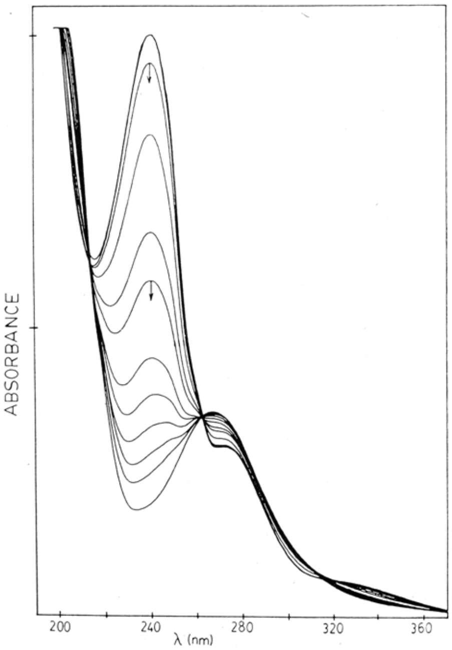


Figure 3. Photohydration of **1** as followed by UV spectrophotometry. Each trace represents ≈10–60-s photolysis on a merry-go-round apparatus at 254 nm.

Photohydration of 6 and 7. Photolysis of either **6** or **7** in 50% H_2O–CH_3CN at 254, 300, or 350 nm gave only the corresponding cis isomer, as identified by the growth of a new AB quartet at δ 6.7 (J = 12 Hz) (compared to the AB quartet of the trans isomer at δ 7.2).

Photohydration of 8. Photolysis of **8** under the conditions described for **1** gave **13** in nearly quantitative yield, which was first purified by preparative TLC (silica/CH_2Cl_2) and subsequently by crystallization from ligroin: mp 90–91 °C; ^{1}H NMR δ 2.25 (broad, exchangeable, 1 H), 2.75–3.4 (m, 4 H), 4.75 (m, 1 H), 7.35 (d, J = 9 Hz, 1 H), 7.85–8.1 (m, 2 H); IR (cm^{-1}) 3100–3500 (s), 1590 (w), 1520 (s), 1350 (s); mass spectrum (CI), m/z 180 (M$^+$ + 1). Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 59.81; H, 5.16; N, 7.82.

Photoaddition of MeOH to 1. In a typical experiment, 100 mg of the substrate was dissolved in 100 mL of MeOH and added to 100 mL of $HCONH_2$. The solution was transferred to a 200-mL quartz tube, purged with argon, and photolyzed for 60 min at 300 nm. After photolysis, 200 mL of water and NaCl were added followed by extraction with CH_2Cl_2. Typical conversion to **14** was 30–50%: ^{1}H NMR δ 2.95 (t, J = 7 Hz, 2 H), 3.3 (s, 3 H), 3.65 (t, J = 7 Hz, 2 H), 7.4–8.2 (m, 4 H).

Photoaddition of EtOH to 1. Via the above procedure, use of EtOH gave 3-nitrophenethyl ethyl ether: ^{1}H NMR δ 1.2 (t, J = 7 Hz, 3 H), 2.95 (t, J = 7 Hz, 2 H), 3.5 (q, J = 7 Hz, 2 H), 3.7 (t, J = 7 Hz, 2 H), 7.4–8.2 (m, 4 H).

Photoaddition of i-PrOH to 1. Via the above procedure, use of i-PrOH gave 3-nitrophenethyl isopropyl ether: ^{1}H NMR δ 1.15 (d, J = 7 Hz, 6 H), 2.95 (t, J = 7 Hz, 2 H), 3.5–3.8 (m, 3 H), 7.4–8.2 (m, 4 H).

Photoaddition of t-BuOH to 1. Via the above procedure, use of t-BuOH gave 3-nitrophenethyl *tert*-butyl ether: ^{1}H NMR δ 1.12 (s, 9 H), 2.9 (t, J = 7 Hz, 2 H), 3.6 (t, J = 7 Hz, 2 H), 7.4–8.2 (m, 4 H).

Photoaddition of MeOD to 1. Via the above procedure, use of MeOD gave **20**: ^{1}H NMR δ 2.8–3.05 (m, 1 H), 3.3 (s, 3 H), 3.65 (d, J = 7 Hz, 2 H), 7.4–8.2 (m, 4 H).

Photoaddition of MeOH to 3. In the product studies below, $HCONH_2$ was not used. Instead, the substrate was dissolved in pure MeOH and irradiated at 254 nm for 30–60 min, after which the solvent was evaporated and the product was separated by preparative TLC (silica/CH_2Cl_2–hexanes), to give 1-(3′-nitrophenyl)-2-methoxypropane (**15**): ^{1}H NMR δ 1.15 (d, J = 7 Hz, 3 H), 2.9 (m, 2 H), 3.3 (s, 3 H), 3.5–3.7 (m, 1 H), 7.4–8.2 (m, 4 H); IR (cm^{-1}) 1580 (m), 1530 (s), 1350 (s); mass spectrum (CI), m/z 164 (M$^+$ + 1 − MeOH).

Photoaddition of MeOH to 4. Via the above procedure, **4** gave 2-methoxy-1-(3′-nitrophenyl)butane (**16**): ^{1}H NMR δ 1.0 (t, J = 7 Hz, 3 H), 1.55 (m, 2 H), 2.85 (d, J = 7 Hz, 2 H), 3.3 (s, 3 H), 3.5 (m, 1 H), 7.4–8.2 (m, 4 H); IR (cm^{-1}) 1610 (m), 1530 (s), 1350 (s); mass spectrum (CI), m/z 178 (M$^+$ + 1 − MeOH).

Photoaddition of MeOH to 5. Via the above procedure, **5** gave 2-methoxy-2-methyl-1-(3′-nitrophenyl)propane (**17**): ^{1}H NMR δ 1.15 (s, 6 H), 2.85 (s, 2 H), 3.25 (s, 3 H), 7.4–8.2 (m, 4 H); IR (cm^{-1}) 1610 (m), 1530 (s), 1350 (s); mass spectrum (CI), m/z 178 (M$^+$ + 1 − MeOH).

Photoaddition of MeOH to 8. Via the above procedure, **8** gave 2-methoxy-5-nitroindane (**18**): ^{1}H NMR δ 3.15 (m, 4 H), 3.35 (s, 3 H), 4.3 (m, 1 H), 7.25–8.2 (m, 4 H); IR (cm^{-1}) 1590 (m), 1525 (s), 1350 (s); mass spectrum (CI), m/z 162 (M$^+$ + 1 − MeOH).

Triplet Sensitization. In a typical experiment, 2–5 g of **22** was dissolved in 150 mL of H_2O, and the pH was adjusted to ≈7–9. The substrate (50–100 mg) in 50 mL of CH_3CN was then added. Photolysis under argon was carried out at 350 nm where the sensitizer absorbs strongly. The solution was worked up by extracting with CH_2Cl_2 followed by washing of the organic extract with a sodium bicarbonate solution to remove residual sensitizer. ^{1}H NMr analysis was used to determine the extent of reaction, if any.

Quantum Yield Measurements. Quantum yields for loss of substrate were measured by UV spectrophotometry, by following the loss in optical density of the 3-nitrostyrenes, as shown in Figure 3 for the photohydration of **1**. The substrate 3-nitrostyrenes have much larger values of ϵ compared to the photoaddition products. In all cases, the conversions were very clean, as exhibited by good isosbestic points. Quantum yields were calculated via the procedures described in a previous work.[7] Substrates (10^{-5} M) were prepared in 3.0-mL quartz cuvettes and purged with argon prior to photolysis on an optical bench set up at λ_{excit} = 254 nm. Potassium ferrioxalate[27] was used for chemical actinometry.

Acknowledgment. Financial support of this work was provided by the Natural Sciences and Engineering Research Council of Canada and in part by the University of Victoria. We thank Steven Hodges for carrying out some preliminary experiments.