1500 *J. Org. Chem.* **1984**, *49*, 1500–1506

Photochemical and Thermal Hydrations of Aromatic Allenes. Evidence for Allyl and Vinyl Cation Intermediates

Karim Rafizadeh and Keith Yates*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 1A1

Received August 30, 1983

The photohydration of aromatic allenes has been studied in water and in dilute aqueous sulfuric acid (0–25% H_2SO_4). It was found that phenylallene (**2a**) and α-methylphenylallene (**2b**) undergo photohydration to give the corresponding cinnamyl alcohol derivatives. The proposed mechanism involves protonation of the central carbon of phenylallenes in their singlet excited state (S_1). In contrast, (*p*-nitrophenyl)allene (**2g**) and (*m*-nitrophenyl)allene (**2h**) gave the corresponding (nitrophenyl)acetones. The mechanism for the formation of these ketones is believed to be due to initial protonation of the α- or γ-carbon atom of the (nitrophenyl)allene in the triplet excited state (T_1). Phenylallenes with CN, CF_3, and F substituents failed to photohydrate. The results of these photohydrations were compared with those of the much slower thermal hydrations in 70–83% H_2SO_4. Phenylallenes **2a** and **2b** cyclized to the corresponding indene derivatives in 70% H_2SO_4. Phenylallenes with NO_2 substituents (**2g**–**2h**) underwent hydration to give the corresponding (nitrophenyl)acetones (expected products) and (nitrophenyl)-1-propanones (unexpected products) in 83% H_2SO_4. Similar results were obtained with (*m*-cyanophenyl)allene. The formation of both types of ketone is discussed in terms of the intermediacy of a common vinyl cation intermediate.

The photohydration of aromatic alkenes and alkynes[1,2] in aqueous sulfuric acid has been previously investigated. In general, these photohydrations are acid catalyzed and lead via the S_1 state to products which are formed regiospecifically in the Markovnikov sense, as do the analogous thermal hydration reactions. Exceptions are the *m*- and *p*-nitro derivatives, which add water via the T_1 state in the anti-Markovnikov direction.[2]

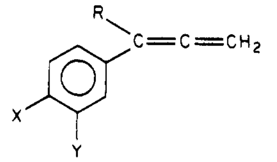
Our interest in the systematic study of photoaddition of water to aromatic alkenes and alkynes[1,2] led us to explore the photohydration of aromatic allenes. To our knowledge there are no previous studies on the photohydration of either aliphatic- or aromatic-substituted allenes. However, other photoaddition reactions are known. The first reported photoassisted polar addition of acetic acid[3] to phenylallenes gave exclusively enol acetates, which shows reversed regioselectivity to that found in the corresponding thermal additions, which have been shown to yield allyl acetates. The reaction was reported to proceed via the triplet excited state. Recently, the photoaddition of methanol to di-, tri-, and tetraphenylallenes, in the absence of acid catalysts, was shown to give the corresponding allylic methyl ethers,[4a] and involvement of singlet excited states was proposed. Apparently, both the regioselectivity of the addition of methanol and multiplicity of the reactive state are in contrast to that of the acetic acid additions.

In this paper we report our exploratory investigations of the photohydration of aromatic allenes in comparison with their thermal hydrations, which significantly extends our understanding of the chemistry of addition reactions of this functional group in the excited and ground states.

The thermal hydration of alkyl-substituted allenes has been the subject of numerous studies.[5] Relatively little attention has been paid to the thermal hydration of aromatic allenes.[6,8b]

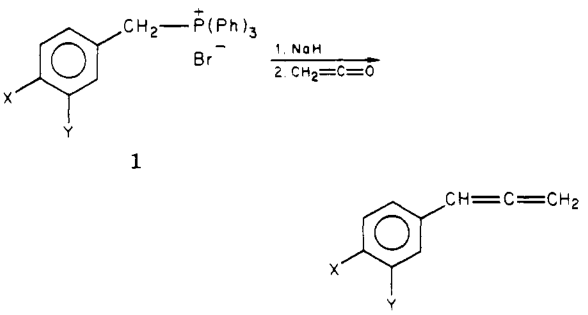
Results

Synthesis. The substrates chosen for this study (**2a**–**2h**) were not commercially available and were synthesized by the reaction of phenyldibromocyclopropane derivatives with methyllithium according to a general procedure described by Skattebol[7] for phenylallenes **2a**–**2b**. The



	X	Y	R
2a,	H	H	H
b,	H	H	CH_3
c,	CN	H	H
d,	H	CN	H
e,	H	F	H
f,	H	CF_3	H
g,	NO_2	H	H
h,	N	NO_2	H

substrates **2c**–**2h** were prepared in good yields by a modified literature method[8] which was developed in our laboratories. The method involves the reaction of ketene with unstabilized ylids which were produced in situ from the reaction of the corresponding benzyltriphenylphosphonium halides **1** and sodium hydride (eq 1).



1

2

(1)

---

(1) Wan, P.; Yates, K. *J. Org. Chem.* **1983**, *48*, 869 and references therein.

(2) Wan, P.; Culshaw, S.; Yates K. *J. Am. Chem. Soc.* **1982**, *104*, 2509.

(3) Fujita, K.; Matsui, K.; Shono, T. *J. Am. Chem. Soc.* **1975**, *97*, 6256.

(4) (a) Klett. M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107. (b) Steinmetz, M. G.; Mayes, R. T.; Yang, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3518.

(5) Jacobs, T. L. In "The Chemistry of the Allenes"; Landor, S. R., Ed.; Academic Press: New York, 1982; Chapter 5.4.

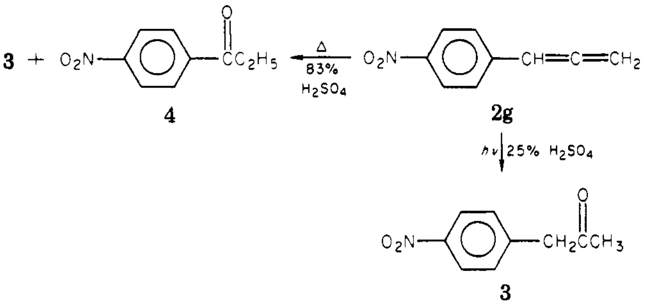
(6) For a kinetic study of the hydration of aromatic allenes, see: Long, G. W., M.A. Thesis, The College of William and Mary, Williamsburg, VA, 1981.

(7) Skattebol, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

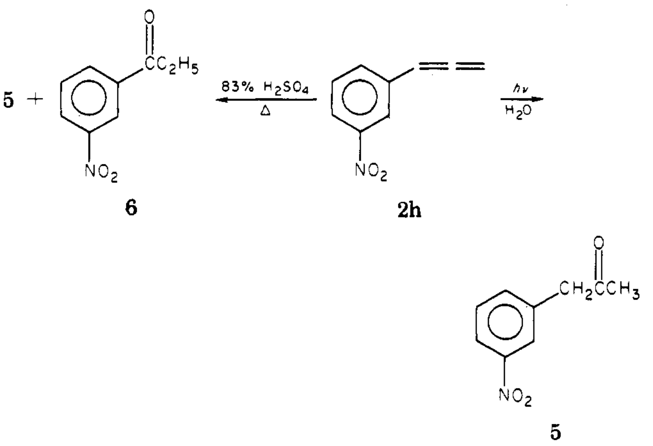
(8) (a) The reaction of stable ylids with ketene has been reported: Hamlet, Z.; Barker, W. D. *Synthesis* **1970**, 544. (b) The reaction of aromatic ketenes with ylides is also known: Aksens, G.; Froyen, P. *Acta Chem. Scand.* **1968**, *22*, 2347.

Product Studies. A 10^{-3} M solution of phenylallenes **2a** or **2b** in outgassed 20% aqueous sulfuric acid-acetonitrile[9] (5:1 v/v) was irradiated (254 nm) for 12 h with cooling. The major product[10] was found to be the corresponding cinnamyl alcohol derivative as a mixture of the cis and trans isomers.[11] The structures of these products were confirmed by comparison with authentic samples after separation of the products by preparative TLC. NMR, IR, and GC were routinely used for product analyses. Under these conditions, the ground-state (thermal) hydration was insignificant, as indicated by dark control experiments. However, these phenylallenes are not stable thermally under more acidic conditions. A 10^{-3} M solution of each of these compounds upon treatment with 70% H_2SO_4 resulted in formation of the corresponding indene derivatives.[8b,12] No hydration products were observed in these thermal reactions.

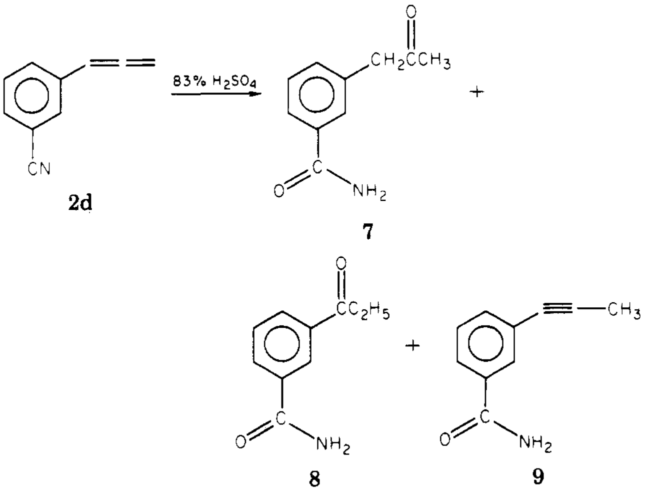
In contrast to the photohydrations of **2a** and **2b**, direct irradiation (350 nm) of a solution of 10^{-3} M (*p*-nitrophenyl)allene (**2g**) in 25% H_2SO_4 for 12 h gave (*p*-nitrophenyl)acetone (**3**) as the only photohydration product.[13a] At low acidity or in pure water, the formation of this product is inefficient. For example in 12 h most of the starting material was recovered along with some polymeric material, and only a trace amount of the photohydration product was identified. Since this phenylallene is thermally quite stable in 25% H_2SO_4, a concentration of 83% sulfuric acid was used for its thermal hydration. Upon heating this solution the hydration products **3** and **4** were obtained in a 70:30 ratio as determined by NMR spectroscopy based on integration of the methyl group of **4** (δ 1.25, t, J = 7 Hz) and methyl group of **3** (δ 2.25, s).



Direct irradiation (300 nm) of (*m*-nitrophenyl)allene **2h** gave (*m*-nitrophenyl)acetone[13a] as the only isolable product in weakly acidic solutions at pH > 2 (and even in water at pH 7). At higher acid concentrations (4–25% H_2SO_4) a dramatic change was observed in the rate of product formation and side reactions became significant.[13b] It was noted that this substrate is about 30 times more reactive than its para isomer upon irradiation in water. A control experiment in the dark was carried out at 25% H_2SO_4. No change was observed for this substrate thermally. This compound, upon treatment with 83% H_2SO_4, like its para isomer gave two isomeric ketones **5** and **6** in 70:30 ratio as determined by NMR spectroscopy of the crude reaction material.



Irradiation of the other phenylallenes **2c**–**2f** under varying acidic conditions (0–25% H_2SO_4) did not give any photohydration products. These substrates polymerized upon prolonged irradiation, and some unreacted material was recovered together with polymers, at shorter irradiation times. These photochemical reactions are not acid dependent as determined by a study of relative quantum efficiency against acid concentration (vide infra). These substrates are also thermally resistant towards acid concentrations below 70% H_2SO_4 at room temperature. Treatment of substrate **2d** with 83% H_2SO_4 upon heating gave products **7**, **8**, and **9**. Their ratio was obtained from the NMR spectrum of the crude material, as calculated from the integration of the methyl group signals for **7** (δ 2.08, s), **8** (δ 1.10, t, J = 7 Hz), and **9** (δ 2.13, s). The NH protons of all these primary amides appeared together at δ 6.17 as a broad peak which disappeared upon addition of D_2O.



Quantum Yields. The photohydration of phenylallenes is generally an inefficient process ($\Phi \simeq 0.01$) except for (*m*-nitrophenyl)allene (**2h**) ($\Phi \simeq 0.30$). The relative quantum yields (Φ/Φ_0, where Φ_0 is the quantum yield at pH 7) for these photohydration reactions were measured as a function of medium acidity for substrates **2c**–**2h** at a substrate concentration of 10^{-5} M. This was done by following the course of the reaction based on the loss of substrate, using UV spectrophotometry, since the substrate and product absorption characteristics were sufficiently different for these compounds. For substrates **2a**–**2b** the relative quantum efficiency of product formation was also measured as a function of increased medium acidity. The

---

[9] The cosolvent was necessary in most cases for solubility reasons.

[10] There are minor products under the reaction conditions such as carbonyl compounds and traces of corresponding indene derivatives. In addition, cinnamyl alcohol derivatives are not photostationary compounds, and therefore, the irradiation time was adjusted for 20–30% conversion by monitoring the aliquots of sample by GC during irradiation.

[11] The proportion of *cis*- and *trans*-cinnamyl alcohols formed depended strongly on the irradiation time used. At short irradiation times the product mixture contained approximately equal amounts of each isomer. At longer irradiations times the cis isomer predominated and some byproducts were observed upon prolonged irradiation since cinnamyl alcohols were found to be photolabile.

[12] (a) Maitland, P.; Mills, W. H. *J. Chem. Soc.* **1936**, 987. (b) Vorander, D.; Siebert, C. *Chem. Ber.* **1906**, *39*, 1024.

[13] (a) (Nitrophenyl)acetones are photostationary compounds under the reaction conditions. (b) In acidity greater than 4% H_2SO_4, *m*-nitrobenzaldehyde was isolated (30%) in addition to two unknown products.

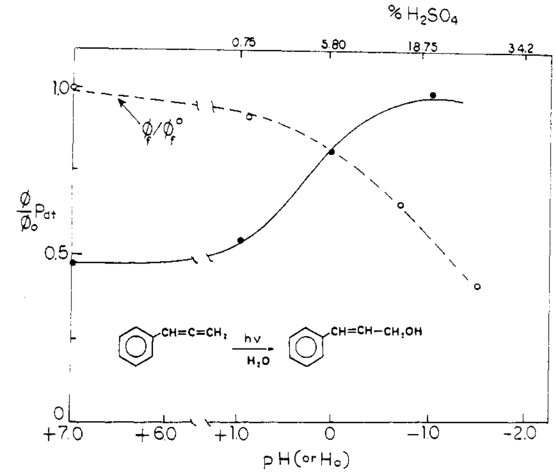


Figure 1. Relative quantum efficiency of product formation (Φ/Φ_0 Pdt) and fluorescence quenching (Φ_f/Φ_f^0) as a function of acidity for phenylallene (**2a**). The initial (Φ_f/Φ_f^0) value has been set arbitrarily at the maximum observed product quantum yield.

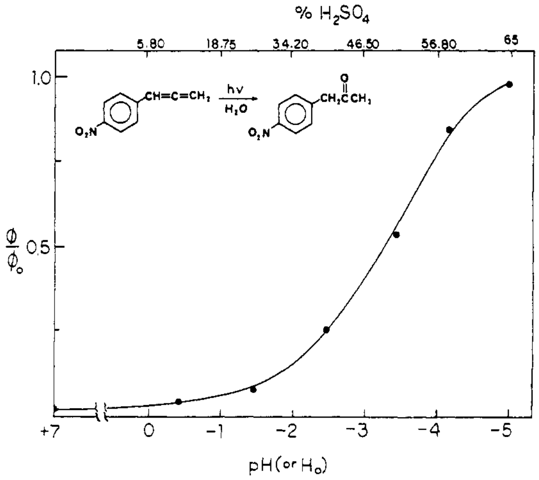


Figure 2. Relative quantum efficiency (Φ/Φ_0) as a function of acidity for (*p*-nitrophenyl)allene (**2g**).

formation of product in these cases was measured by gas chromatography. Plots of relative quantum efficiency for substrates **2a**–**2b** and **2g** vs. increasing medium acidity are sigmoid curves (Figure 1, for **2a** and Figure 2 for **2g**). The photohydration of **2h** is not acid dependent. For substrates **2c**–**2f** the relative quantum efficiency did not change significantly with medium acidity and no sigmoid curve was observed for these substrates.

Fluorescence Quenching Studies. Substrates **2a** and **2b** exhibited very weak fluorescence emission. Compound **2a** had a maximum at λ^f = 298 nm and **2b** at λ^f = 312 nm when samples of these substrates in water–acetonitrile (10:1 v/v) were excited at 270 nm. Plots of the relative fluorescence quantum yield (Φ_f/Φ_f^0 where Φ_f^0 is the fluorescence quantum yield at pH 7) vs. added sulfuric acid show quenching of the singlet excited state (Figure 1). Plots of Φ_f/Φ_f^0 for these substrates show sigmoid behavior which is complementary to that observed for the relative quantum efficiencies for photohydration.[14]

This is a strong indication that for these substrates S_1 is the reactive state, with protonation simultaneously leading to product formation and fluorescence quenching. Similar complementarity was observed in the acid-catalyzed photohydrations of styrenes and phenylacetylenes.[1,2]

No fluorescence emission was detected for substrates **2c**–**2h**.

Triplet Sensitization Studies. In order to investigate the possible involvement of triplet excited states in the photohydration of these compounds, triplet sensitization experiments were carried out with water soluble triplet sensitizers *o*-benzoylbenzoic acid (sodium salt), $E_t \simeq 69$ kcal mol^{-1} and acetone $E_t \simeq 79$ kcal mol^{-1}. In a typical experiment, 30–40 mg of substrate was dissolved in aqueous acetonitrile (10:1 v/v) and enough sensitizer was added (5–10 g) to ensure that the sensitizer absorbed at least 95% of the incident light. In the case of acetone, the cosolvent (acetonitrile) was not needed. The triplet energy of phenylallenes should not be significantly different from that of tetraphenylallene[15] (E_t = 57.4 kcal mol^{-1}) and should be low enough for efficient energy transfer. It was found that the photohydration of **2a** and **2b** could not be sensitized by *o*-benzoylbenzoic acid and the substrates were almost quantitatively recovered. The use of acetone as a sensitizer failed since it was found that acetone reacted with these allenes. No photohydration products were detected. The reported reaction of some excited carbonyl compounds such as xanthone, benzophenone, and acetophenone with alkyl-substituted allenes[16] may explain this failure. For *m*-nitrophenylallene **2h** the same photohydration product as previously obtained was found using the *o*-benzoylbenzoic acid salt as sensitizer. The formation of the same photohydration product for **2h** via a triplet sensitizer suggests involvement of the triplet excited state for this compound. Also, nitroaromatics are known to intersystem cross with high efficiency.[17] The use of acetone was again a failure for this substrate, since no photohydration products were observed.

Discussion

In previously studied photohydration reactions[2] the singlet excited states of non-nitro-substituted aromatic alkenes and alkynes have been shown to behave as strongly polarized species, with the β-carbon bearing a negative charge. Protonation of the S_1 state occurs readily on this carbon, followed by nucleophilic trapping of water at the α-carbon to give products which are formed regiospecifically in the Markovnikov sense. On the other hand, nitro-substituted analogues, which react via T_1, show a reversed polarization, so that nucleophilic trapping of water occurs exclusively at the β-carbon, with or without prior protonation at C_α. Hence these products are formed regiospecifically, but in the anti-Markovnikov sense. There are relatively few reports in the literature concerning the nature of the corresponding excited states of allenes.[18] There is some evidence [4a,b] to show that singlet states are involved in the photochemical reactions of phenylallenes, although the original report by Fujita et al.[3] proposed the involvement of a triplet excited state in the photoaddition of acetic acid to allenes, based on the use of the triplet sensitizer xanthone in these reactions. This apparent contradiction was later clarified by Johnson et al.,[4a] who suggested an electron transfer process for the involvement

---

[14] Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. Lahiri, S. C. *J. Sci. Ind. Res.* **1979**, *38*, 492.

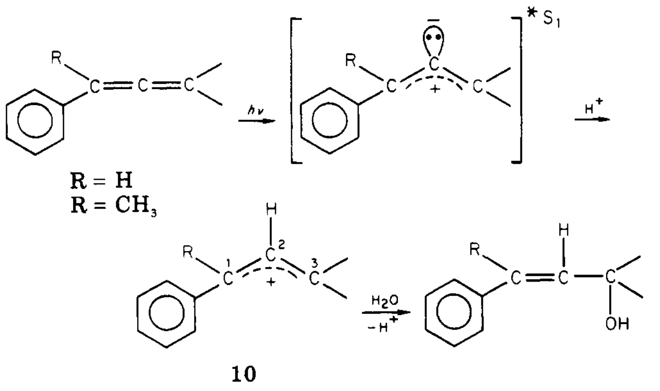
[15] Ullman, E. F.; Henderson, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 4390.

[16] Gotthardt, H.; Steinmetz, R.; Hammond G. S. *J. Org. Chem.* **1968**, *33*, 2774.

[17] 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.

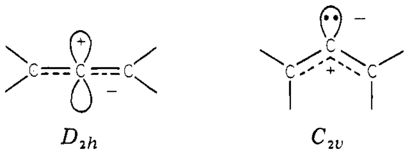
[18] (a) Bordern, W. T. *J. Chem. Phys.* **1966**, *45*, 2512. (b) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

Scheme I. Mechanism of Photohydration of Phenylallenes



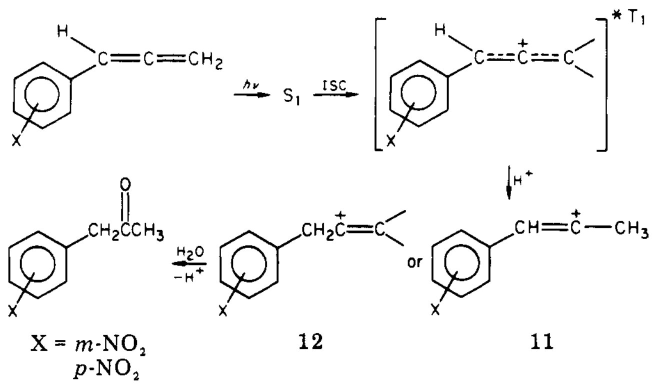
of xanthone rather than triplet energy transfer by the sensitizer. In this work we present additional evidence in support of singlet excited states in the photochemical reactions of phenylallenes **2a** and **2b**. Concurrent quenching of the fluorescence emission of these phenylallenes by added sulfuric acid (Figure 1) and the lack of photohydration products when a triplet sensitizer was used are in agreement with a proposed S_1 reactive state. In contrast, a triplet excited state is the most likely reactive species in the photohydration of (nitrophenyl)allenes based on the evidence of photohydration products in the triplet-sensitized reaction of **2h** and the different regioselectivity found.[1,2]

Allenes, like other alkenes, can twist to nonvertical geometries in their lowest excited states to result in polarized species.[19] Recent theoretical calculations[20] have suggested two closely lying ionic states (D_{2h} and C_{2v}) for the allene



singlet excited states. The proposed geometries for polarized excited states of allenes were supported by the same authors' experimental study of the addition of methanol to di-, tri-, and tetraphenylallenes, to produce the corresponding allylic methyl ethers.[4a] It was suggested that in these photochemical addition reactions, the phenylallenes favor the C_{2v} geometry. In our investigation, formation of the cinnamyl alcohol derivatives as the photohydration products from phenylallenes **2a** and **2b** is in good agreement with involvement of C_{2v} geometry in terms of the polarization calculated by Johnson[20] for this state. This geometry and polarization permits protonation of the singlet excited state of the allenes at the central carbon atom in acidic solution (pH <0) to form a resonance stabilized allylic cation of type **10** (Scheme I) followed by addition of a molecule of water to form cinnamyl alcohol derivatives. The presence of sigmoid quantum yield curves (Figure 1 shown for **2a**) strongly suggests that protonation of the singlet excited states of phenylallenes **2a** and **2b** is the rate-limiting step in their photohydrations. The fluorescence-quenching curves which are also sigmoid, (Figure 1 shown for **2a**) intersect the quantum efficiency curves of these phenylallenes at $H_0 = -0.10$ to -0.20. This is in agreement with the expectation of increased basicity of the singlet excited state.[14]

Scheme II. Mechanism of Photohydration of (Nitroaromatic)allenes



There are two possibilities for addition of a molecule of water to the allyl cation **10** (on C_1 and C_3). In the photohydration of phenylallenes **2a** and **2b** to give cinnamyl alcohols, no addition of water at C_1 to produce the isomeric alcohols was observed. This was determined by comparison of the crude reaction mixture with authentic samples synthesized independently.[21] The absence of products derived from addition of water to C_1 might indicate the inequality of charge distribution between C_1 and C_3. The terminal carbon atom (C_3) of this resonance stabilized allyl cation is probably more electron deficient than C_1 due to relative localization of positive charge on C_3, whereas the charge on C_1 can be delocalized into the phenyl ring. Also C_3 is relatively less hindered than C_1 toward the approach of a molecule of water. The proposed mechanism of photohydration is shown in Scheme I.

To be able to compare the photohydration of these phenylallenes with the corresponding thermal hydrations, we have studied product formation from the thermal reactions of phenylallenes **2a** and **2b** in higher concentrations of sulfuric acid. These phenylallenes cyclize *intra*molecularly to give the corresponding indene derivatives when they are treated with 70% H_2SO_4 upon heating. Such cyclizations have previously been observed for other phenylallenes.[8b,12] Contrary to the reaction of alkyl-substituted allenes[5] the initial protonation of these substrates has taken place on the *central* carbon atom. Upon protonation, the orthogonal double bond (C_2–C_3) rotates, presumably without a large energy barrier, to form the more stable conjugated cation **10**.[22] Obviously, both the photochemical and thermal reactions of these phenylallenes proceed via a common cation **10**, but the lack of formation of hydration product in the thermal reaction may be due to the relatively low concentration of water in the solvating cage at such high acidities and may also be due to the short life time of these cations.[23]

The photohydration of **2g** is acid dependent, as shown by the increasing quantum efficiency for formation of product vs. increasing the medium acidity (Figure 2). The presence of a sigmoid type quantum yield curve for photohydration of this compound suggests that protonation of the excited state (T_1) of this substrate on C_1 or C_3 is the rate-limiting step. On the other hand, (*m*-nitrophenyl)allene **2h** also gave the corresponding photohydration product **5**. In contrast the photohydration of this com-

---

[19] This phenomenon has been termed "sudden polarization" by Salem, L. (*Acc. Chem. Res.* **1979**, *12*, 87).

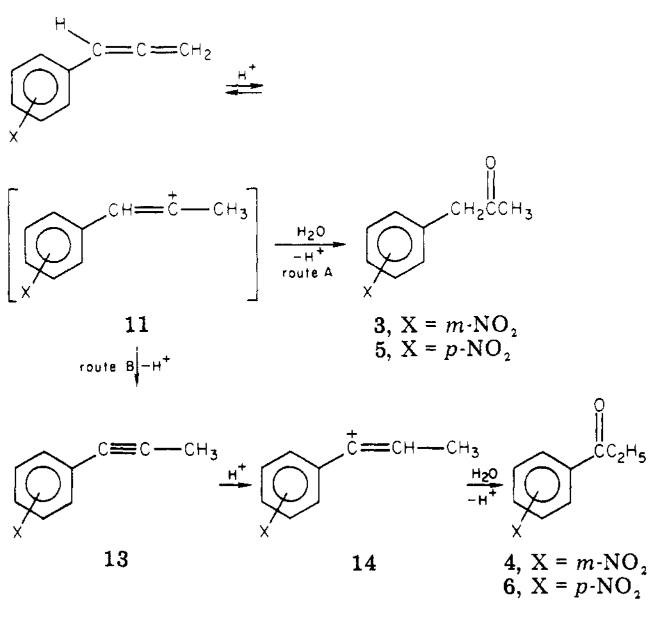
[20] Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *26*, 7479.

[21] 1-Phenyl-2-propen-1-ol (bp 63–65 °C (0.8 mmHg)) was prepared in 70% yield by the reaction of magnesium vinyl bromide and benzaldehyde in dry THF, and 2-phenyl-3-butene-2-ol (bp 54–55 °C (1 mmHg)) was also prepared by the reaction of magnesium vinyl bromide with acetophenone (60% yield).

[22] Okuyama, T.; Izawa, K.; Fueno, T. *J. Am. Chem. Soc.* **1973**, *95*, 6749.

[23] Pittman, C. U.; Miller, W. G. *J. Am. Chem. Soc.* **1973**, *95*, 2947.

Scheme III. Mechanism of Thermal Hydration of (Nitrophenyl)allenes



pound is not acid dependent. The quantum efficiency of this compound does not show a sigmoid type curve and at pH 7 is essentially the same as in 25% H_2SO_4 solution. The nondependency of quantum efficiency on acid concentration indicates that the protonation of the triplet excited state is not the rate-limiting step in its photohydration. The suggested mechanism for the photohydration of nitroaromatic allenes is shown in Scheme II. Due to the formation of (nitrophenyl)acetones **3** and **5**, a reversed polarization must be considered for the triplet excited state of (nitrophenyl)allenes. This reversed polarization and considerable charge separation in the excited state is enhanced by the strongly electron-withdrawing effect of the nitro group in the excited state.[24] The reversed polarization may favor D_{2h} geometry, although Johnson's calculations[20] predicted polarized species for the S_1 states only. However, these calculations were based on the allene system itself and would necessarily lead to nonpolarized T_1 states whether of D_{2h} or C_{2v} geometry. It is quite possible that a polarized triplet of D_{2h} type could be produced by the strongly electron-withdrawing effect of the nitro group in the excited state, especially for (*m*-nitrophenyl)allene. It is difficult to explain the reversed regiospecificity and acid catalysis observed in photohydrations of nitro-substituted styrenes, phenylacetylenes, and phenylallenes if only nonpolarized T_1 states are involved.[25] Such geometry and polarization would permit protonation of the excited state at C_1 or C_3 to form vinyl cations of type **11** or **12**, although addition of water to both intermediates would yield the same observed (nitrophenyl)acetone.

For comparison, the thermal hydration of (nitrophenyl)allenes **2g** and **2h** was carried out at 83% H_2SO_4 since these allenes are thermally quite unreactive at lower acidity. The thermal hydration of both (nitrophenyl)allenes resulted in formation of the corresponding expected (nitrophenyl)acetones **3** and **5**, in addition to the unexpected (nitrophenyl)-1-propanones **4** and **6**. Formation of both expected and unexpected ketones can be explained via a common vinyl cation of type **11** as shown in Scheme III. In the ground state, protonation at C_3 may be favored over C_1 since the nitro function can withdraw electrons from the conjugated C_1–C_2 double bond and C_3 may become relatively electron rich with respect to C_1 and thus more prone to protonation in the rate-limiting step to form the vinyl cation **11**. The vinyl cations **11** have two competing routes available to form the observed products, i.e., (route A) addition of water, loss of proton, and tautomerization of the resulted enol to the corresponding nitrophenylacetones **3** and **5** and (route B) direct loss of a proton from **11** to give acetylenic homologues **13** which can further protonate to form the isomeric vinyl cations **14**. Addition of a molecule of water to **14** and loss of a proton finally results in formation of the unexpected ketones **4** and **6** (Scheme III). Although base-catalyzed isomerizations of aromatic[7] and aliphatic[26] substituted allenes to give their acetylenic homologues are known, to our knowledge this is the first observation of acid-catalyzed isomerization of aromatic allenes to the acetylenic homologues. However, acid-catalyzed isomerization of aliphatic-substituted allenes has been previously reported.[27]

Contrary to the photohydration of the above (nitrophenyl)allenes no photohydration products were isolated for phenylallenes **2c**–**2f**. The relative quantum efficiency for these substrates, based only on the loss of the substrate, did not show a sigmoid type curve with added acidity. This indicates a lack of sufficient polarization of their excited states to give protonation of these substrates in the excited state. The absence of photohydration products may suggest that either more radicaloid type excited states (T_1) are involved for these substrates, or nonpolarized S_1 excited states are involved, due to the cancellation of the normal direction of polarization by the electron-withdrawing effect of the CF_3,CN, or F substituents.[28] This leads to the conclusion that the electron-withdrawing effect of these substituents in the excited state is located between that of the H and NO_2 groups, by analogy with the previous reported photobehavior of substituted styrenes and phenylacetylenes.

Thermal hydration of phenylallene **2d** in 83% sulfuric acid, like that of **2g** and **2h**, gave the corresponding expected (**7**) and unexpected (**8**) ketones. The formation of amide **9** is additional evidence for the correctness of the mechanistic scheme shown in Scheme III. By prolongation of the reaction time for this allene (**2d**) the amount of **9** is reduced and the amount of **8** is increased, which is obviously due to the further thermal hydration of **9**.

In summary, the photobehavior of aromatic allenes in dilute aqueous acids can be divided into three types, in the same way as the analogous reactions of aromatic alkenes and alkynes reported previously.[2] These three types of behavior are illustrated in Scheme IV. The parent compounds (and presumably those with electron-releasing substituents)[29] photohydrate via protonation of S_1 at C_β

---

[24] Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922.

[25] A referee has suggested that the best structure for a twisted allene triplet[18b] would be a C_{2v} biradical structure. However, it is not clear that such a biradical would react in the simple manner observed for the nitrophenylallenes.

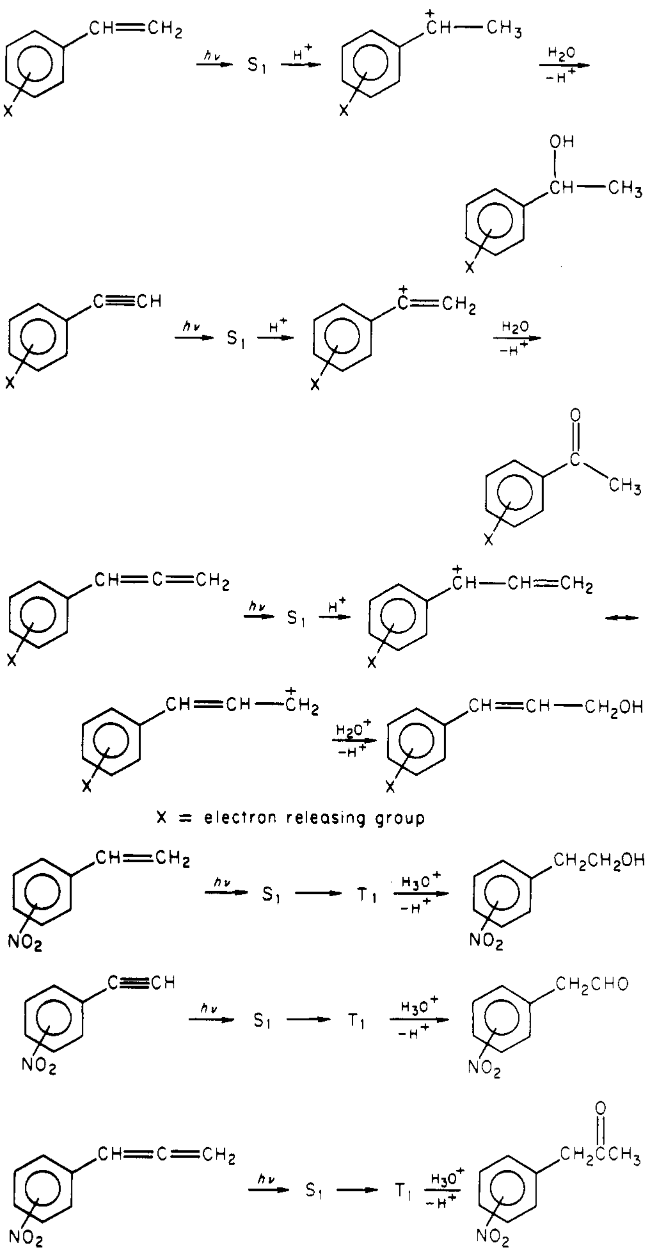
[26] Brandsma, L. "Synthesis of Acetylenes, Allenes and Cumulenes, a laboratory manual"; Elsevier Scientific Publishing Co.: New York, 1981.

[27] Barry, B. J.; Beale, W. J.; Carr, M. D.; Hei, S. K.; Reid, I. *J. Chem. Soc., Chem. Commun.* **1973**, 177.

[28] An alternative explanation is that protonation of the presumed S_1 reactive states for these substrates would lead to destabilized allyl cations.

[29] This has been shown to be the case for styrenes and phenylacetylenes[1,2] containing electron-releasing groups in the aromatic ring. This is much more difficult to establish for the phenylallenes since thermal hydrations are more rapid when electron-releasing groups are present in the ring, and interfere seriously with any photochemical studies of the hydration reaction. However, α-methylphenylallene, which is the only example with an electron-releasing group we have been able to study, does photohydrate.

Scheme IV. Summary of the Photobehavior of Aromatic Alkenes, Alkynes, and Allenes



exclusively, followed by nucleophilic addition of water to the resulting cation at C_α, or C_γ in the case of phenylallenes **2a–2b**. The efficiency of these reactions depends on medium acidity in sigmoid fashion. These substrates with nitro groups photohydrate via T_1, in which water attack takes place exclusively at C_β, with or without prior protonation at C_α (or C_γ). The dependence of quantum efficiency on medium acidity for the nitro compounds in some cases is sigmoid and in other cases is absent. Those with electron-withdrawing groups (other than nitro) do not photohydrate at all, and their photochemical behavior is complex and appears not to be acid catalyzed.

Experimental Section

General Remarks. All melting points and boiling points reported are uncorrected. Melting points were measured with a Gallenkamp MF-370 instrument. Dry column chromatography was accomplished by the technique described by Loev and Goodman.[30] Baker Silica Gel 3405 (60–200 mesh) was generally used as the adsorbent. A ratio of 1 g of the reaction mixture to 25 g of adsorbent was usually used. Fractions of 10 mL were collected and monitored by TLC using a UV lamp (254 nm). A Chromatotron Model 7929 was also used for separation of fractions. Infrared spectra were routinely recorded with a Unicam SP 1025 Infrared Spectrophotometer. ^{1}H NMR were recorded with a Varian T-60 Spectrometer, on undegassed samples in $CDCl_3$ or CCl_4 with Me_4Si as internal standard. UV Spectra were recorded on a Unicam SP 1800 instrument. GC analyses were performed on a Varian Aerograph series 2700 instrument on a 5% QF-1 on Chrom. GHP (mesh 80/100), 6 ft x $^1/_4$ in. OD, 2mm ID glass column. Integrated peak areas were calculated by using a Varian CDS 111 processor. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrophotometer at room temperature.

Materials. All substituted benzyl bromides and chlorides were purchased from Aldrich Chemical Co. All substituted phenylallenes were prepared following the general procedure outlined below, except for **2a–2b** which were synthesized using literature methods.[7]

Irradiations. Preparatory irradiations were carried out by using a Rayonet RPR-100 reactor at 254, 300, 350 nm. Solutions were purged with argon for 30 min before irradiation. Stirring during irradiation was accomplished by a magnetic stirring bar or by continuous argon bubbles. All samples were cooled by a cold finger during the irradiation time.

General Procedure for the Preparation of Substituted Benzyltriphenylphosphonium Bromides (1c–1h). The reported procedure was followed with minor modifications.[31] An equimolar mixture of substituted benzyl halide and triphenylphosphine was refluxed in toluene for 6 h. The white precipitate was filtered and washed several times with toluene and dried. These salts are usually pure enough to be used in the next step, but for analysis they were recrystallyzed from $CHCl_3$–toluene.

General Procedure for the Preparation of Aromatic Allenes. This procedure is described on a 10^{-2} M scale. In a 500-mL three-necked round-bottom flask equipped with a gas inlet, condenser, and gas outlet was placed the required amount (usually a 20% excess) of NaH (50% oil suspension) previously washed three times with dry hexane. To this was added 200–300 mL of dry ether. The required amount of the appropriate benzyltriphenylphosphonium halide was then added under N_2 and the reaction mixture was placed in an ultrasonic bath for two days. The resulting colored solution was transferred to another three-necked flask by using a double headed needle, leaving NaH and unreacted phosphonium salt behind. Enough ketene was bubbled into the colored solution until the color disappeared (10–15 min). Rotary evaporation of this solution resulted in a mixture of allene and triphenylphosphine oxide. Dry column chromatography on silica gel using appropriate proportions of hexanes–CH_2Cl_2 gave the allene as the first fraction. To the remaining unreacted phosphonium salt (original three-necked flask) was added 200–300 mL of dry ether and the procedure was repeated until a higher yield of allene was obtained (usually 70–75%). All of phenylallenes were kept cool and under an inert atmosphere except (nitrophenyl)allenes.

Thermal Hydrations. A solution of 100–150 mg of phenylallene in 10 mL of acetonitrile was added dropwise to 200–300 mL of 70–83% H_2SO_4 (depending upon substrate, substrates with electron-withdrawing groups required 83% H_2SO_4) with rapid stirring. The solution was then heated on a steam bath to about 60 °C for 30 min. A colored solution was usually obtained and poured onto sufficient ice, saturated with salt, extracted with CH_2Cl_2, washed, dried, and evaporated to get the crude product. Routine analyses were then carried out on this crude product.

(*p*-Cyanobenzyl)triphenylphosphonium Bromide (1c). When the general procedure for preparation of phosphonium salts was followed, this compound was obtained in 96% yield as a white powder: mp 315–316 °C; NMR ($CDCl_3$) δ 5.89 (2 H, d, CH_2, J = 15.5 Hz), 7.33–8.0 (19 H, m, Ph); IR ($CHCl_3$) 3550, 3080, 2210, 1010 cm^{-1}.

(*m*-Cyanobenzyl)triphenylphosphonium Bromide (1d). When the general procedure for preparation or phosphonium salts was followed, this compound was obtained in 90% yield as a white

---

[30] Loev, B.; Goodman, M. M. *Intra.-Sci. Chem. Rep.* **1970**, *4*, 283.

[31] Johnson, A. W.; Kyllingstad, V. L. *J. Org. Chem.* **1966**, *31*, 334.

[32] Naso, F.; Ronzini, L. *J. Chem. Soc., Perkin Trans 1* 1974 [3], 340.

powder: mp 313–314 °C; NMR (Me_2SO-d_6) δ 5.25 (2 H, d, CH_2, J = 15.5 Hz), 7.50–7.85 (19 H, m, Ph); IR (KBr) 2950, 2850, 2780, 2220, 830 cm^{-1}.

(*m*-Fluorobenzyl)triphenylphosphonium Bromide (1e). When the general procedure for preparation of phosphonium salts was followed, this compound was obtained in 95% yield as a white solid: mp 309–310 °C; NMR ($CDCl_3$) δ 5.58 (2 H, d, CH_2, J = 15 Hz), 6.66–7.96 (19 H, m, Ph); IR (KBr), 2980, 2900, 2830, 2512, 1625 (w), 1600 (m), 1147, 1120 (s), 1010, 960, cm^{-1}.

(*m*-(Trifluoromethyl)benzyl)triphenylphosphonium Chloride (1f). The general procedure was followed by using (trifluoromethyl)benzyl chloride. A white powder was obtained in 90% yield: mp 283–284 °C; NMR ($CDCl_3$) δ 5.86 (2 H, d, CH_2; J = 15 Hz), 7.03–8.0 (19 H, m, Ph); IR ($CHCl_3$) 2960, 2910, 2830, 2512, 1630, 1603, 1503, 1461, 1420, 1340, 1330, 1130, 1010, 910 cm^{-1}.

(*p*-Nitrobenzyl)triphenylphosphonium Bromide (1g). The general procedure was followed and a white powder was obtained in 92% yield: mp 269–270 °C dec (lit.[31] 269–270 °C); NMR ($CDCl_3$) δ 5.93 (2 H, d, CH_2, J = 15.5 Hz), 7.40–8.0 (19 H, m, Ph); IR ($CHCl_3$) 2980, 2900, 2810, 1610, 1550, 1350, 1110, 1000, 860 cm^{-1}.

(*m*-Nitrobenzyl)triphenylphosphonium Bromide (1h). When the general procedure of preparation of phosphonium salt was followed, this compound was obtained in 98% yield as a white solid: mp 290 °C; NMR ($CDCl_3$) δ 5.87 (2 H, d, CH_2, J = 15.5 Hz), 7.17–8.07 (19 H, m, Ph); IR ($CHCl_3$) 2980, 2900, 2830, 2015, 1630, 1600 (m), 1500 (w), 1475, 1360 (s), 1325, 1120, 911 cm^{-1}.

(*p*-Cyanophenyl)allene (2c). This compound was prepared according to the described general procedure. A colorless oil was obtained after column chromatography using pentanes–CH_2Cl_2 (2:1 v/v): 65% yield; NMR (CCl_4) δ 5.13 (2 H, d, CH_2, J = 7 Hz), 6.06 (1 H, t, CH=, J = 7 Hz), 7.20, 7.46 (centers of doublets of a quartet, 4 H, Ph, J = 8 Hz); IR (neat) 2980, 2220, 1945, 1600 cm^{-1}.

(*m*-Cyanophenyl)allene (2d). When the general procedure for preparation of phenylallenes was followed a colorless oil was obtained after column chromatography using pentanes–CH_2Cl_2 (2:1 v/v): 70% yield; NMR (CCl_4) δ 5.17 (2 H, d, CH_2, J = 7 Hz), 6.08 (1 H, t, CH=, J = 7 Hz), 7.43 (center of a multiplet, 4 H, Ph); IR neat 3080, 2980, 2900, 2220, 1945, 1600, 1485, 900, 853, 800, 700 cm^{-1}.

(*m*-Fluorophenyl)allene (2e). When the general procedure for preparation of aromatic allenes was followed, a colorless oil was obtained after a dry column chromatography on silica gel using hexanes: 60% yield; NMR (CCl_4) δ 5.12 (2 H, d, CH_2, J = 7Hz), 5.95 (1 H, t, CH=, J = 7 Hz), 6.62–7.33 (4 H, complex m, Ph); IR (neat) 2950, 1947, 1640, 1150, 940, 880 cm^{-1}.

(*m*-(Trifluoromethyl)phenyl)allene[3] (2f). The general procedure for preparation of aromatic allenes was followed. A white solid, mp 108–110 °C, was obtained after chromatography using hexanes–CH_2Cl_2 (5:1 v/v): 65% yield; NMR (CCl_4) δ 5.22 (2 H, d, CH_2, J = 7 Hz), 6.12 (1 H, t, CH=, J = m Hz), 7.18–7.46 (4 H, complex 7, Ph); IR (neat) 1950, 1600, 1445, 1360, 1120, 1075, 752, 730, 705 cm^{-1}.

(*p*-Nitrophenyl)allene (2g). When the general procedure for preparation of aromatic allenes was used, a needle-shaped pale yellow crystalline material was obtained: mp 66–67 °C (sublimed or hexanes) [lit.[32] mp 66–67 °C (ethanol)]; 78% yield; NMR (CCl_4) δ 5.26 (2 H, d, CH_2, J = 7 Hz), 6.20 (1 H, t, CH=, J = 7 Hz), 7.42, 8.07 (centers of doublets of a quartet, 4 H, Ph, J = 9 Hz); IR ($CHCl_3$) 3560, 1940, 1600, 1520 (s), 1350 (s), 1270 (s), 853, 785, 700 cm^{-1}.

(*m*-Nitrophenyl)allene (2h). When the general procedure for preparation of aromatic allenes was followed, a pale yellowish solid was obtained after chromatography using hexanes–CH_2Cl_2 (1:1 v/v): mp 53–55 °C (also sublimed); yield 76%; NMR (CCl_4) δ 5.25 (2 H, d, CH_2, J = 7 Hz), 6.17 (1 H, t, CH=, J = 7 Hz), 7.33–8.03 (4 H, m, Ph); IR ($CHCl_3$) 1960, 1550, 1363, 1100, 915, 870, 820, 742, 700 cm^{-1}.

Anal. Calcd for $C_9H_7NO_2$: C, 67.08; H, 4.38. Found: C, 67.22; H, 4.23.

Photolysis of Phenylallene (2a). A solution of 200 mg of **2a** (purified by column chromatography on silica gel using hexanes) in 500 mL of 20% H_2SO_4 and 100 mL of MeCN in a quartz tube was outgassed with argon for 30 min. It was irradiated at 254 nm (Rayonet) for 12 h with cooling. The solution was saturated with NaCl and extracted with 3 × 50 mL of CH_2Cl_2. The combined extracts were washed with saturated $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave 170 mg of a yellowish oil. The NMR of the isolated product showed the presence of unreacted material. TLC showed 2 major components. It was chromatographed on silica gel (hexane as the first eluent) to isolate unreacted material, 70 mg, and the column was further eluted by hexane–acetone (3:1 v/v) to obtain 60 mg of an oil which was identified as cinnamyl alcohol (cis and trans isomers) based on comparison with the spectral data of an authentic sample. Some polymeric material was further eluted from the column (MeOH) for which no attempt was made to determine its structure.

Photolysis of α-Methylphenylallene (2b). The procedure was identical with that of the photolysis of **2a**. From 250 mg of **2b** was isolated 210 mg of a crude oil after irradiation for 12 h. Chromatography on silica gel gave 80 mg of unreacted starting material and 110 mg of α-methylcinnamyl alcohol as identified by spectroscopic comparison with authentic material.

Photolysis of 2c–2f. When the procedure described for photolysis of **2a** was followed a solution of 150–200 mg of purified (chromatography) samples were irradiated for 12 h. In all cases unreacted material along with a considerable amount of polymeric material was isolated after the usual workup. In the case of **2c** no unreacted material was isolated.

Photolysis of (*p*-Nitrophenyl)allene (2g). Following the procedure described for the photolysis of **2a**, from irradiation (350 nm) of 250 mg of **2g** in 25% H_2SO_4 for the 12 h was isolated 240 mg of a brown oil. The fractions were separated on prep TLC on silica gel applying CH_2Cl_2. The first fraction was unreacted starting material, 150 mg, and the second fraction was 80 mg of a solid which was identified as (*p*-nitrophenyl)acetone (**3**) based on spectroscopic comparison with an authentic sample: NMR ($CDCl_3$) δ 2.25 (3 H, s, CH_3), 3.85 (2 H, s, CH_2). A trace amount of polymeric material was also isolated.

Photolysis of (*m*-Nitrophenyl)allene (2h). The procedure followed was identical with that of photolysis of **2a** with minor differences. A solution of 250 mg of **2h** in 450 mL of distilled water and 150 mL of MeCN was irradiated (300 nm) for 3 h. The usual workup gave 230 mg of an oil. The conversion was found to be 80% (NMR). Fractions were isolated on prep TLC on silica gel (CH_2Cl_2 as the eluent). The first fraction, 30 mg, was the unreacted material, the second, 20 mg, *m*-nitrobenzaldehyde, and the third, 165 mg, was identified as (*m*-nitrophenyl)acetone (**5**): NMR (CCl_4) δ 2.17 (3 H, s, CH_3), 3.73 (2 H, s, CH_2). Irradiation of this compound in 4% and 25% H_2SO_4 resulted in the formation of higher yields (30–40%) of *m*-nitrobenzaldehyde and two other unidentified minor products.

Acknowledgment. The continued financial assistance of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. **1c**, 26104-68-7; **1d**, 24722-19-8; **1e**, 89302-81-8; **1f**, 35675-77-5; **1g**, 2767-70-6; **1h**, 1530-41-2; **2a**, 2327-99-3; **2b**, 22433-39-2; **2c**, 89302-78-3; **2d**, 89302-79-4; **2e**, 70090-82-3; **2f**, 70090-81-2; **2g**, 38319-12-9; **2h**, 89302-80-7; CH_2=C=O, 463-51-4.