Via syringe techniques a solution of the ketene and diene (and, if necessary, of **15**) in acetonitrile was placed in the tube. Unless noted differently, a solution or a suspension of the one-electron oxidant was added dropwise at 0 °C within a maximum of 2 min. Thereupon, the reaction mixture was stirred for a total of 5 min. Finally, the reaction was quenched by the dropwise addition of a 2 N $NaOCH_3/CH_3OH$ solution. Within 60 s, 30 mL of brine was added, and the products were extracted three to five times using a total of 100 mL of methylene chloride. The combined organic layers were dried (sodium sulfate) and the solvent removed in vacuo. To the crude product mixture was added a known amount of *m*-nitroacetophenone, if necessary, and the mixture was analyzed by ^1H NMR and GC. When ET3 was used as the one-electron oxidant, then the reaction was quenched by addition of 0.50 mL methanol (stirred for 15 min). After removal of all volatile components, the remainder was extracted with benzene or ether to separate off the iron salts. After removal of the solvent, the crude mixture was analyzed as noted above. The results of the cycloadditions are provided in Tables I and II. Control experiments using Lewis acids were run following the above procedure, but the reactions were quenched by addition of water.

(d) Cycloaddition and Vinylcyclobutanone Rearrangement under PET Initiation. A solution of ketene **1** (0.2–0.5 mmol), diene **2**, and the acceptor/biphenyl system was prepared in 0.5 mL of argon-flushed acetonitrile (or d_3-acetonitrile). The mixture was irradiated in a Pyrex tube at $\lambda > 350$ nm for the indicated time periods. To quench the ketene several drops of methanol were added, and the volatile components were removed in vacuo. The mixture was analyzed by ^1H NMR (Table III). Similarly, the PET-induced vinylcyclobutanone rearrangement was performed, the results of which are presented in Table V.

(e) Vinylcyclobutanone Rearrangement in the Presence of One-Electron Oxidants. According to the conditions noted above under paragraph c, the solution of vinylcyclobutanone and **15** in acetonitrile was placed in a Schlenk tube, and a solution of the one-electron oxidant was added dropwise. After workup the mixture was analyzed by ^1H NMR (Table V). Control experiments to evaluate the configurational stability of **10a** and **12a** as well as of **3a–6a** were conducted under the above conditions (Table VII).

(f) Stoichiometric Oxidation of 7 in the Presence of Methanol. To a solution of ET2 (82.0 mg, 0.100 mmol) in acetonitrile (0.50 mL) was added a solution of **7** (11.4 mg, 0.050 mmol) dissolved in 0.3 mL of methanol and 0.1 mL of acetonitrile. After 15 min at room temperature the color of the mixture changed from blue to a turbid, gray bluish hue. The reaction mixture was stirred for another 10 min, and then it was quenched. After standard workup the mixture was analyzed by ^1H NMR, indicating recovery of 55% of **7**. The products were analyzed by GC/MS using cold-on-column techniques. Six products, a–f, could be identified by their MS data. Product a (55%) was identified as **7**. Product b (8%): MS *m/z* 258 (4, $M^{\cdot+}$), 244 (5, M − CH_2), 230 (5, M − CO), 215 (20, M − CO − CH_3), 199 (26, M − CO − OCH_3), 151 (44, M − An), 135 (49), 66 (33, Cp), 43 (54), 40 (100); MS (CI, NH_3) *m/z* 259 (3, M + H^+), 245 (24, M + H − CH_2), 227 (100, M − CH_3O). Product c (10%): MS *m/z* 165 (100, $C(An)(CH_3)(OCH_3)^+$), 135 (11), 43 (28); MS (CI, NH_3) *m/z* 259 (37, M + H^+), 227 (12), 199 (8), 165 (100), 151 (25). Product d (8%): MS *m/z* 165 (100, $C(An)(CH_3)(OCH_3)^+$), 135 (12), 43 (34); MS (CI, NH_3) *m/z* 259 (54, M + H^+), 227 (12), 199 (9), 165 (100), 151 (14). Product e (11%): MS *m/z* 165 (100, $C(An)(CH_3)(OCH_3)^+$), 135 (12), 43 (43); MS (CI, NH_3) *m/z* 259 (100, M + H^+), 227 (3), 199 (8), 165 (6), 151 (3). Product f (5%): MS *m/z* 165 (100, $C(An)(CH_3)(OCH_3)^+$), 135 (12), 43 (45); MS (CI, NH_3) *m/z* 259 (100, M + H^+), 227 (15), 199 (10), 165 (87), 151 (12).

Acknowledgment. For financial support we are indebted to the Deutsche Forschungsgemeinschaft, the Wissenschaftliche Gesellschaft Freiburg, the Fonds der Chemischen Industrie, and the Land Baden-Württemberg. H. v. Seggern thanks the Fonds der Chemischen Industrie for a scholarship. The X-ray analysis was done by Dr. M. Keller, to whom we are grateful. The authors thank Prof. Z. Rappoport for helpful discussions.

Cooperative Effect of Acid Sites in the Photocyclization of Azobenzene within the Zeolite Microenvironment

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Abstract: Photolysis of azobenzene in the presence of a series of acidic zeolites with different crystal size (0.8 and 0.3 μm), crystalline structure (Y, β, ZSM-5), and framework Si-to-Al ratio (Al/cage ranging from 4.6 to 0.25) gives rise to benzo[*c*]cinnoline and benzidine. The latter remains protonated within the zeolite cavities, as has been established by FT-IR spectroscopy of the hosts. The lack of influence of the crystallite size on the activity of the zeolite reveals that the reaction is mainly taking place on the internal surface of these microporous solids. Finally, the relationship between the activity of the zeolite and the number of Brönsted sites per α-cage indicates that only two H^+ per supercavity can participate in the photocyclization of azobenzene. This result agrees with the relative size of the zeolite cavities and the reactant molecules.

Introduction

The photochemistry of organic compounds within the voids and cavities of zeolites has recently emerged as one of the most promising tools to gain control of the different pathways undergone by the excited states.[1-3]

The main advantage of zeolites as "microscopic reactors" is that these photostable microporous solids can be synthesized in a large variety of crystalline structures and chemical compositions, thus providing a series of well-characterized isotropic materials with strictly regular properties.

Up to now, the majority of the photochemical studies within zeolites have made use of these materials just as a vessel of molecular dimensions to restrict the motions of the reaction intermediates (radicals). However, the possibilities of zeolites can be enlarged by making them directly intervene during the course of the photochemical reaction due to the presence in the internal voids of charge-compensating cations which can act as active sites.

In the present paper we describe the influence of the chemical environment of the zeolite host on the photocyclization of azobenzene (AB) to benzo[*c*]cinnoline (BC) adsorbed on a series of acid zeolites with different particle size, crystalline structure, and framework Si-to-Al ratio. To the best of our knowledge, this constitutes the first example where a cooperative contribution of

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(1) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* **1990**, *55*, 5269–5278 and references cited therein.

(2) Scaiano, J. C.; Casal, H. L.; Netto-Ferreira, J. C. *ACS Symp. Ser.* **1985**, *278*, 211–222.

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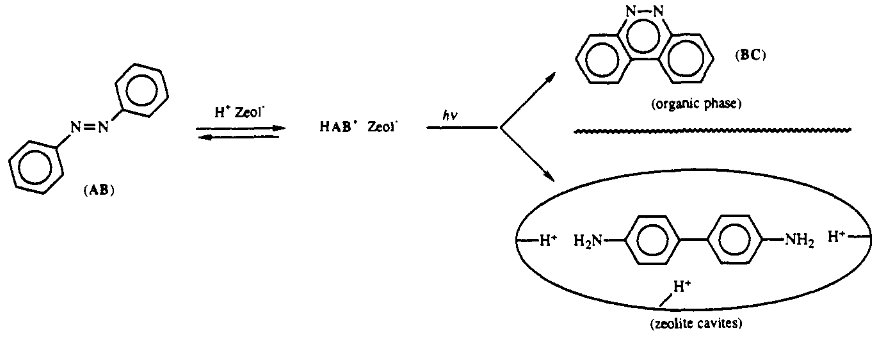
Scheme I



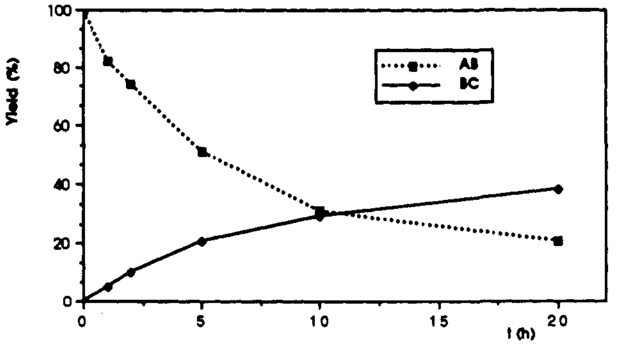


Figure 1. Plot of the product distribution versus the irradiation time for the photocyclization of AB adsorbed on HY-100.

the active sites is required in the course of a photochemical reaction performed within the voids of a zeolite.

The azobenzene system follows two different reaction pathways depending on the photolysis conditions.[4] Thus, if the irradiation is carried out in neutral medium, Z/E isomerization occurs and photostationary mixtures of both stereoisomers are obtained. However, when photolysis is performed in the presence of acids, azobenzene undergoes a photochemical cyclization through a disproportionation mechanism. In this process, it has been established that the conjugated acid of azobenzene (and not the neutral molecule) is the species which undergoes ring closure.[5]

Results and Discussion

In the first stage of our work, we investigated the photolysis of AB in hexane solution at reflux temperature in the presence of Y zeolites, using high-pressure mercury lamps through Pyrex walls. At the end of the irradiation, the organic solvent was filtered off, and the zeolite was submitted to continuous solid–liquid extraction using dichloromethane as solvent. When the photolysis of AB was carried out in the presence of the acidic HY-100 sample, it was noteworthy that while part of the recovered AB was present in the hexane solution, BC could be only recovered after extraction of the solid. This is in agreement with the known higher basicity of the aromatic heterocycle compared with the starting azo compound. By contrast, when a non-acidic NaY zeolite was used, no BC was formed and a complete recovering of the starting AB was achieved (Scheme I).

Since it was not possible to follow the course of the photocyclization by analyzing the organic phase, a series of experiments were carried out under the same conditions in order to establish the appropriate irradiation time. As it can be seen in Figure 1, a linear relationship between the yield of BC and the reaction time was found under our experimental conditions for conversions lower than 25%. In order to estimate the activity of the different samples, we choose 2 h as a convenient irradiation time. Using HY-100, the yield of BC was 10% for a AB conversion of 26%.

As can be seen in Figure 1, a linear correlation exists between a higher conversion of AB (long irradiation times) and a poorer recovering of the organic material. This could be due to the formation of other products strongly adsorbed on the acid zeolite and non-recoverable by solid–liquid extraction. In fact, taking into account that the reaction mechanism of AB photocyclization involves disproportionation, the formation of variable amounts of diphenylhydrazine, which usually rearranges to benzidine under the reaction conditions, was anticipated. In order to test this possibility, a FT-IR spectrum of the HY-100 sample used to perform the photochemical reaction was recorded after submission of the solid to an exhaustive extraction and the spectrum was compared with those of pure commercial diphenylhydrazine or benzidine adsorbed on HY-100. As Figure 2 shows, a very good match was obtained for the latter indicating that benzidine is the irradiation product adsorbed on HY-100 non-recoverable by extraction. Moreover, a comparison between those spectra and the IR spectrum of benzidine dihydrochloride[6] suggests the structure of protonated benzidine for the species locked within the HY-100 supercavities. A calibration of the IR absorption by means of standards was used to estimate that the amount of benzidine adsorbed is equimolar with the BC formed, closing in all the experiments the mass balances up to more than 90% of the starting material.

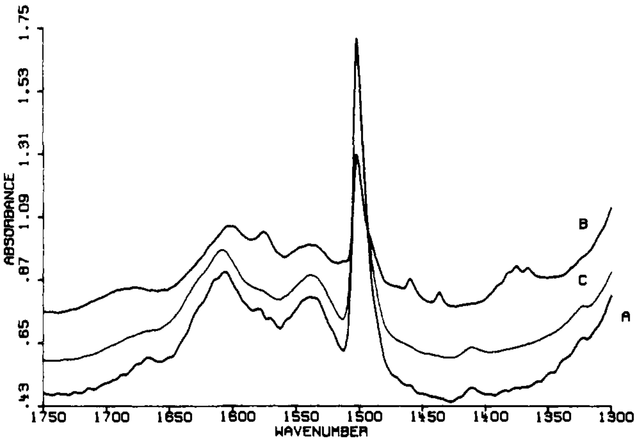


Figure 2. FT-IR spectra of HY-100 (trace A) and HYD-300 (trace B) used as host after exhaustive solid–liquid extraction. FT-IR spectra of commercial benzidine (10 mg) adsorbed on HY-100 (500 mg) (trace C).

In order to ascertain if the photochemical reaction was actually occurring inside the cavities of the faujasite structure and to obtain a quantitative indication of the possible contribution of the external surface, photolysis experiments were carried out in the presence of two acidic Y zeolites, with very similar physicochemical parameters, but different average crystallite size (HY-100, 0.8 μm; HY-P, 0.3 μm). A diminution of 2.6 times in the particle size must increase approximately 19 times the external-to-internal surface ratio of the HY-P compared to the HY-100 host. Therefore, if the reaction would mainly be occurring on adsorbed molecules at the external surface of the zeolite, a much higher activity should be expected for the HY-P zeolite.

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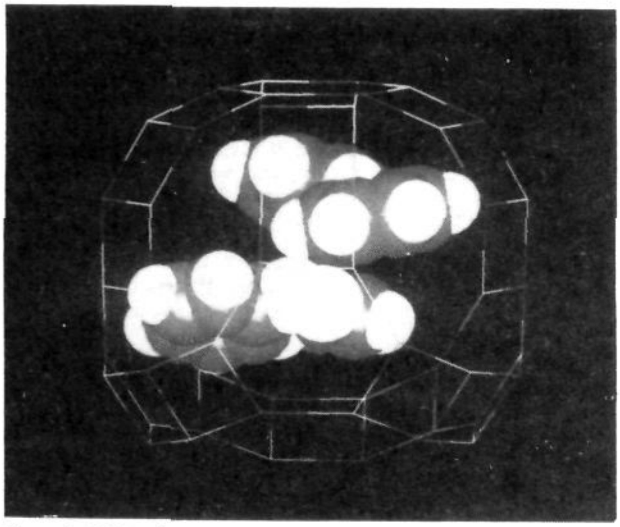

Figure 3. Molecular modeling visualization of AB inside the cavities of Y zeolite.

Results showed that this is not the case, but rather similar conversions are obtained with both zeolites samples. This constitutes strong evidence that the photochemical reaction is taking place inside the α-cavities of the Y zeolite. In addition, the total contribution of the internal sites must be much higher since H^+ are located overwhelmingly on the internal surface of the zeolites.

Moreover, as the process occurs in the internal voids, it becomes evident that if the photolysis is carried out in the presence of zeolite with a pore size which does not allow diffusion of AB, or the coupling of two molecules is restricted, then BC should not be formed. An experimental confirmation of this hypothesis was obtained by performing the AB irradiation in the presence of H-ZSM-5 (Si/Al = 20), a 10-membered ring zeolite with a pore diameter <6 Å. No formation of BC was observed under our reaction conditions and the starting material was completely recovered. Indeed, calculations using a graphic molecular modeling program[7] clearly show that in H-ZSM-5 the diffusion of AB is strongly impeded but the coupling of two molecules either in the channels or even in the wider spaces where two channels intersect is not geometrically feasible. This result is in agreement with the reported behavior of *trans*-stilbene which is a tight fit inside the voids of ZSM-5.[8,9]

Taking into account that the photochemical disproportionation is taking place in a confined space and that benzidine, when formed, remains strongly adsorbed in the zeolite Y α-cage, a molecular modeling simulation[7] was performed and it was determined that just two molecules of benzidine can be accommodated within the faujasite supercages. A visualization of this simulation is presented in Figure 3.

Moreover, as no more than two benzidine molecules can be formed per α-cage, it is predicted that not all the H^+ can participate in the photochemical cyclization. Therefore, the activity per site must increase as the number of H^+ per cage is decreasing for samples having more than the necessary H^+ per α-cage, up to a value corresponding to a sample where all H^+ present in the cavity are intervening in the reaction. At this point, the efficiency per H^+ of the zeolite must be maximum, and a further diminution of the H^+/cage ratio must not have any influence on the activity per site.

As the Brönsted acid sites in zeolites are associated to protons from bridged Al(OH)Si structures, the number of acid sites present in the faujasite supercages can be modified by changing the framework Si-to-Al ratio of the samples.

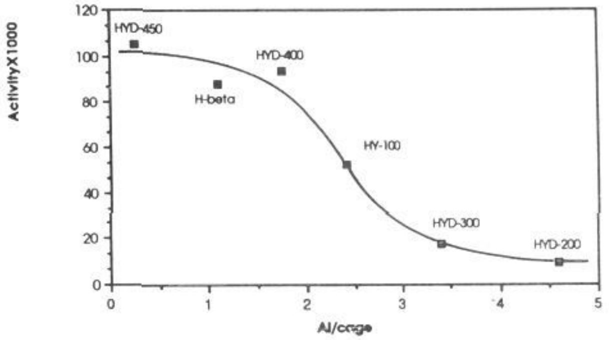

Figure 4. Plot of the molecules of BC per acid site formed at 2 h (activity) versus the number of Al per cage of the zeolite.

In order to check those expectatives, a series of dealuminated HYD zeolites with different framework Al content ranging from 4.6 to 0.25 Al/cage were prepared by treatment with $SiCl_4$. The results achieved using these HYD zeolites as hosts are presented in Figure 4. As can be seen there, the activity per acid site increases along with the dealumination of the zeolite framework up to samples near two H^+ per α-cage, in remarkable good agreement with the model predictions, and showing than only two protons per supercage can be active. Moreover, as dealumination of faujasite either by steam (HY-100) or by $SiCl_4$ treatment (HYD) always produces samples with inhomogeneties in the Al per cage distribution,[10] it is rather obvious that a sharp transition activity from a zeolite sample containing an average of 3 Al to another with 2 Al per cage cannot be expected.

Finally, another tridirectional large pore zeolite with β structure having one H^+ per cage was tested. According to the size of the voids of the β lattice, the molecular modeling program indicates that the behavior of the Y and β samples should be very similar. The activity per site found for the β host is also included in Figure 4 and fits well with the curve of the acidic dealuminated Y faujasite series, showing that the free spaces where two channels intersect in the β zeolite, although smaller than the Y supercavities, are still big enough to accommodate two benzidine molecules.

Conclusions

Photochemical disproportionation of azobenzene takes place within acid zeolites. Besides BC, benzidine is also formed equimolarly as revealed by FT-IR of the host. Influence of the zeolite particle size and crystalline structure evidenced that the reaction occurred mostly within the internal voids of the zeolite. Experimental results indicate that for Y and β zeolites only two protons per supercage can intervene in the photochemical reaction, as could be predicted from the relative sizes of the zeolite cavities and reactant molecules.

Experimental Section

Zeolites. HY-100 was prepared starting from a commercial NaY sample (Union-Carbide SK-40) by exhaustive NH_4AcO exchange and calcination following the protocol described in ref 11. Chemical analysis showed that the Na_2O content was less than 0.15 wt %, the average crystal size was 0.8 μm as measured by SEM, and X-ray diffraction showed that the crystallinity was 85%, with a unit cell size of 24.41 Å according to the ASTM D-3942-8 protocol. The HY-P sample was obtained following the same procedure as for HY-100 but starting with a NaY zeolite with an average crystal size of 0.30 μm.[12] The dealuminated zeolites (HYD-200, HYD-300, HY-400, and HYD-450, where the number indicates the temperature of the treatment) were prepared by dealumination with $SiCl_4$ at different temperatures for 3 h.[13] Their unit cell size was 24.56, 24.47, 24.36, and 24.25 Å, respectively. These solids were thoroughly washed with water and then submitted to H^+-

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(7) Docking using the Biosym graphic molecular modeling package Insight II.

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to-Na^+ exchange as for the HY-100 sample; their crystallinity was in all cases higher than 90%. H-β was synthesized starting from a Et_4N^+-β by calcination and NH_4^+-exchange as described in ref 14. The Si/Al ratio was 13 as determined by NMR MAS. HZSM-5 (Si/Al = 20) was obtained following the patent literature.[15]

Reaction Procedure. Activation of the zeolites was performed "in situ" just before their use by heating the solid (1.00 g) at 150 °C under 1 Torr for 2 h. After this time, a solution of AB (150 mg) in hexane (50 mL) was poured into the Pyrex vessel containing the activated zeolite. The resulting suspension was magnetically stirred at reflux temperature while being photolyzed with an array of 400-W high-pressure mercury lamps. At the end of the irradiation, the zeolite was filtered and washed with CH_2Cl_2, and the organic solutions were concentrated in vacuum and weighed. Analysis by GC (HP 5890 provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone) and GC-MS (HP 5988A spectrometer) showed that in all cases the residue consisted almost exclusively of AB. The zeolite was submitted to continuous solid–liquid extraction using micro-Soxhlet equipment and CH_2Cl_2 as solvent. After removal of the solvent, the residue was weighed and analyzed by GC, GC-MS, and GC-FTIR (HP 5890 GC coupled with a 5965A FT-IR detector). These extracts consist of variable mixtures of AB and BC.

IR spectra of the adsorbed organic compounds were carried out in a greaseless IR cell using a Perkin-Elmer 580B spectrophotometer equipped with a data station. Wafers of 10 mg cm^{-2} were pretreated at 200 °C and 10^{-3} Pa dynamic vacuum. The spectra in the 4000–1300-cm^{-1} region were recorded at room temperature.

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Supplementary Material Available: Photographs of Biosym molecular modeling program visualizations of azobenzene inside the cavities of β (E) and ZSM-5 (F) structures (1 page). Ordering information is given on any current masthead page.

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Photochemistry of Substituted 1-Naphthylmethyl Esters of Phenylacetic and 3-Phenylpropanoic Acid: Radical Pairs, Ion Pairs, and Marcus Electron Transfer

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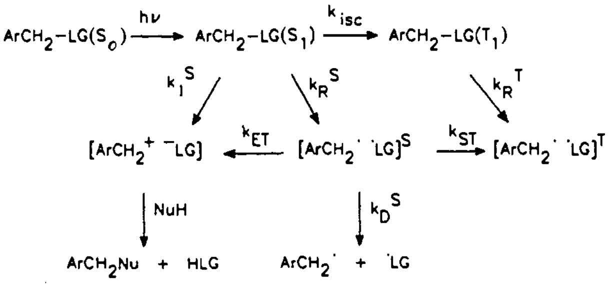
Abstract: The ring-substituted 1-naphthylmethyl esters of phenylacetic (**3a–k**) and 3-phenylpropanoic (**5a–c**) acid have been photolyzed in methanol solvent. The major products of these reactions are derived from two critical intermediates, the 1-naphthylmethyl radical/acyloxy radical pair and the 1-naphthylmethyl cation/carboxylate anion ion pair. The radical pair results in formation of the in-cage coupled products **8a–k** and **10a–c** after loss of carbon dioxide from the acyloxy radical. The ion pair leads to the methyl ethers **6a–k** and the carboxylic acids **7** and **9**. The competition between the radical and ionic pathways is very dependent upon the substituents on the naphthalene ring. Analysis of these substituent effects results in a proposed mechanism of initial homolytic cleavage of the carbon–oxygen bond of the ester from the excited singlet state. This radical pair then partitions between two pathways: decarboxylation of the acyloxy radical and electron transfer converting the radical pair to the ion pair. The rates of electron transfer are shown to fit Marcus theory in both the normal and the inverted region.

Introduction

The photochemistry of benzylic compounds with leaving groups ($ArCH_2$–LG) has been extensively studied in recent years. In most cases, products are obtained that result from an intermediate arylmethyl cation and the leaving group anion ($ArCH_2^+$ ^-LG) as well as from an arylmethyl radical and the leaving group radical ($ArCH_2^\bullet$ $^\bullet LG$). The ion pair, at least formally, results from heterolytic cleavage of the carbon-to-leaving-group bond. In analogy to ground-state solvolysis, the cation can be trapped by nucleophilic solvents (water, alcohols, etc.) and, therefore, this process is often called photosolvolysis. The radical pair results from homolytic cleavage of the same bond. Typical radical coupling and hydrogen atom abstraction products are obtained in this case. An excellent review that summarizes this material up to the early 1980s has been written.[1]

The competition between the pathways for formation of these two possible intermediates is dependent on many factors, including the leaving group, the aryl ring (i.e., benzene versus naphthalene or benzene versus substituted benzene), the solvent, and the multiplicity (singlet versus triplet) of the excited state involved.

Scheme I. General Mechanism for the Photolysis of Benzylic Substrates with Leaving Groups



As yet, these factors are not well enough understood to allow reliable predictions about product distribution for any given case. This is because there is more than one mechanistic pathway for the formation of the critical cation and radical intermediates after the initial absorption process gives the excited singlet state. These are outlined in Scheme I. For simplicity in this scheme, the

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[†] Current address: Department of Chemistry, University of Colombo, Colombo, Sri Lanka.

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