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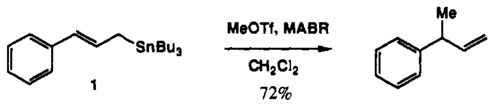
"kinetic" or "thermodynamic" enol silyl ethers,[9] regioselective primary α-alkylation can be easily realized (entries 5–8 and 10). (6) A salient feature of the MABR-promoted alkylation is that the alkylation of chiral enol silyl ethers shows opposite diastereomeric ratios compared to those with the corresponding metal enolates (entries 2–4 and 8–10).[10] In particular, the trimethylsilyl ethers of 2,6-disubstituted cyclohexanones exhibited high cis selectivity (entries 2–4) hitherto not observable in metal-enolate chemistry. (7) The selective alkylation of enol silyl ethers possessing base-sensitive functional groups appears feasible under the present reaction conditions (entry 11).[3] The mild reactivity of the oxygenophilic MABR is primarily responsible for the chemoselectivity of the reaction. For example, reaction of 5-(trimethylsiloxy)-4-nonene and methyl triflate with MABR proceeded smoothly at −40 °C in the presence of 2-undecanone to furnish 4-methyl-5-nonanone in 81% yield with 90% recovery of unreacted 2-undecanone.

The present alkylation has vast synthetic potential, as demonstrated by the regiocontrolled alkylation of allylic stannanes with alkyl triflates. For example, treatment of (*E*)-cinnamyltributylstannane (**1**) with methyl triflate in CH_2Cl_2 at −20 °C under the influence of MABR gave rise to the γ-methylation product, 3-phenyl-1-butene, exclusively in 72% yield. Since preparation of functionalized allylic stannanes has already been well-established,[11] the present method would be equally applicable to allylic systems possessing various base-sensitive functional groups.



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Photon-Promoted Chemiionization Reactions

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Received October 25, 1991
Revised Manuscript Received January 21, 1992

One of the "holy grails" of chemical physics has been the photon-promoted chemical reaction: a case where the course of a bimolecular chemical reaction is altered by the absorption of a photon *during* the reactive collision,[1] not where a reactant is excited before the collision. We have found a photon-promoted chemiionization reaction involving a large organic molecule. These reactions may be more common than previously thought, and the place to look for them may be in reactive systems with many degrees of freedom rather than the two- and three-atom cases studied to date.[1] We have been studying the dynamics of a series of organic chemiionization reactions, where the two reactants are neutral but the products are ions.[2] One example is the reaction of an acid and a base to produce a salt,[3,4] such as

$$HI + Qn \rightarrow I^- + HQn^+ \qquad (1)$$

where Qn is the bicyclic amine quinuclidine.

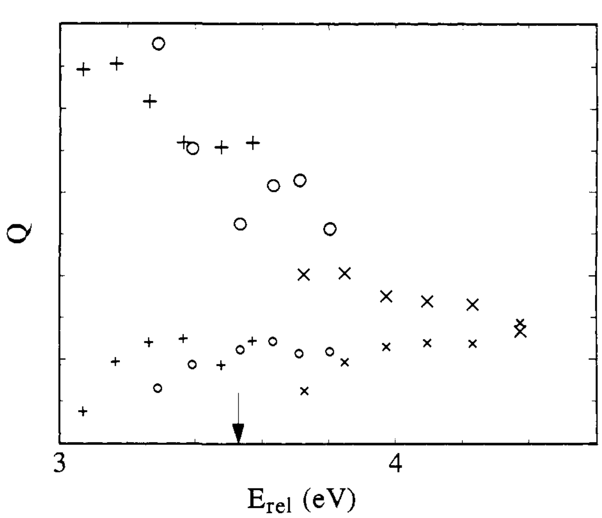

Figure 1. The large symbols show the cross section Q for the photochemical reaction of HI and quinuclidine (light on minus light off), and the small symbols show the cross section for the residual dark reaction. The HI beam is seeded in H_2, and the quinuclidine beam is seeded in He (+), a mixture of 40% H_2 and 60% He (○), and H_2 (×). The arrow gives the thermodynamic threshold for the dark reaction at 3.53 eV. Data are shown for the cation product.

The experimental setup is similar to the one used previously.[2-4] Each reactant is made into a seeded supersonic nozzle beam. The quinuclidine beam is made by passing inert carrier gas, e.g., H_2, He, or a mixture of 40% H_2 and 60% He, through crystals of the solid at 25 °C to produce a mixture of 0.16% quinuclidine in ~1 atm of carrier gas. The resulting mixture passes through a heated nozzle 40 μm in diameter. Two sources are used for HI. In one, the carrier gas is bubbled through *tert*-butyl iodide at −42 °C. The resulting mixture is then pyrolyzed at 260 °C to give HI and isobutene either in the heated nozzle or in a small chamber behind the nozzle. Because this source contains impurities, we also used a 5-L bulb containing 1% HI in H_2. Both sources give similar results. The relative energy is controlled by varying the nozzle temperature and the type of carrier gas for Qn. The light source is a 350-W high-pressure mercury arc lamp. The light is focused on the beam intersection region by a crown glass lens which cuts off all light below 300 nm. A beam flag turns the light off and on. Product ions are extracted with an electric field, focused with an ion lens, mass selected, and detected with an electron multiplier.

Figure 1 shows the data for the reaction of HI and Qn. There is only one cation at mass 112 (HQn^+), and there is only one anion at mass 127 (I^-). At each energy the cross section is measured with the light on and off several times in succession. Cross sections for the dark and the photochemical reactions are shown for reaction 1. The arrow gives the thermodynamic threshold for the dark reaction at 3.53 eV.[5] The small amount of the dark signal below this energy is due to the finite energy width in the beam and possibly to reactions of dimers in the beams. The signal for the dark reaction increases by over 1 order of magnitude[4] at energies above 4.0 eV. The photochemical signal is many times the background and requires both beams to be on. The photochemical cross section decreases with increasing energy as expected, since the lifetime of the reaction complex decreases with increasing energy.

We must make sure that the signal is due to reaction 1 and not to another process. Because we need to extract the product ions with a potential of ~75 V, the ions travel through the quadrupole mass filter at ~40 eV, and this degrades the resolution.

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It is therefore possible that the products of reaction 1 are HI$^-$ and Qn$^+$. This is unlikely, since the charge-transfer reaction is more endothermic than the proton-transfer reaction ($\Delta H = 7.2$ eV compared to 3.53 eV[5,6]). With the *tert*-butyl iodide source, we get no signal unless the pyrolysis cell is turned on, so that the signal cannot be due to unpyrolyzed *tert*-butyl iodide. The bulb source precludes this possibility as well. Quinuclidine does not start absorbing light until 256 nm,[7] well outside the window provided by the crown glass lens. The peak of the first absorption band of HI is at 208 nm, but the band extends up to 364 nm.[8] The absorption is entirely dissociative. I atoms can react by the charge-transfer reaction, $I + Qn \rightarrow I^- + Qn^+$, but this reaction is more endothermic than reaction 1 (4.3 eV as compared to 3.53 eV).[5] Although the photodissociation of HI produces translational energy in the products, almost all of this goes into the H. Thus, the photodissociation of HI produces a less reactive species than HI. I atoms do not absorb light in the region of interest. The first UV absorption is at 183 nm, and the spin-orbit transition at 1.3 μm gives too little energy to make a difference. We have added I$_2$ to the *tert*-butyl iodide, but this did not produce any extra signal. Dimers of HI or Qn have twice the energy of monomers and can react in the absence of light. Furthermore, the amount of dimers depends strongly on nozzle temperature, and we see no such temperature variation in our results. Complexes with carrier gases will react in much the same way as the uncomplexed species. There is a possibility that the ions are photodissociated from the surfaces in the reaction region. The only surface not at the extraction voltage is a fine cage made of nickel mesh coated with graphite (Aquadag). The surface would rapidly remove all the initial translational energy plus the energy of adsorption so that the photon would have to supply all of the 3.53 eV (351 nm) necessary for the reaction. It is highly unlikely that both positive and negative ions sitting on that surface would be photodissociated cleanly without reacting with the junk adsorbed on the surface.

Because of the unusual nature of the reaction, it is useful to give a plausible model for it. We believe that the reaction takes place on two potential-energy surfaces, one covalent, dissociating to the reactants, and one ionic, dissociating to the products. On the reactant side the covalent surface is lower in energy but becomes repulsive at small distances, since the neutral products I + HQn are not bound. The ionic surface is strongly attractive due to the Coulombic force and intersects the covalent surface. An electron then jumps from Qn to HI, and the reaction continues on the ionic surface. This is the "harpoon" mechanism used by Herschbach to explain the large cross sections in alkali reactions.[9] The products must then overcome their Coulombic attraction to form separated ions. The formation of separated product ions is endothermic by 3.53 eV,[5] but the formation of a bound ion pair is probably exothermic. Below the threshold for reaction, it is still possible to form the ion pair complex, but the complex does not have enough energy to dissociate. Because of the large number of vibrational modes in the system, the complex should have a long lifetime (microseconds) before dissociating to the reactants. Absorption of a photon promotes the complex to the repulsive covalent surface. Since the transition results in a large change in dipole moment, it should have a large oscillator strength. As it dissociates, it again crosses the ionic surface and can then form separated ions. The advantage of this type of system over those studied earlier is in the very long lifetime of the complex, comparable to the transit time in the reaction region.

There are roughly 5×10^{17} photons/s going into the reaction zone of 0.2 cm^3. With an extinction coefficient of 10^4 mol^{-1} dm^3 cm^{-1} we can then excite $\sim$0.02% of the complexes formed. Since the photoinduced signal is very roughly 1% of the dark signal at higher energies, the excited complex has about 50 times the reaction probability of the dark reaction.

We are now looking at the wavelength dependence of the effect as well as looking for other, similar reactions. Our reactions differ from previously studied photon-induced reactions[1] in the arrangement of surfaces and in the large number of vibrational modes.

Acknowledgment. This research was supported in part by the National Science Foundation under Grant CHE-8901577. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this work.

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Relaxed Triplet Energies of Phenylnorbornenes. The Role of Phenyl-Vinyl Torsions. On the Origin of Nonvertical Triplet Excitation Transfer

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Received June 20, 1991

In mechanistic organic photochemistry, the concept of "nonvertical" triplet excitation transfer (NVT)[3-9] refers to any process for which (a) triplet excitation transfer occurs from donors D with triplet energy $E_T(D)$ insufficient to provide isothermal or exothermic formation of the spectroscopically observed acceptor (A) triplet, and (b) the rate of the process is enhanced relative to the rate expected on the basis of making up the energy deficit $E_T(A) - E_T(D)$ by thermal activation. Such processes are encountered when the ground and excited triplet states have significantly different equilibrium geometries. The original evidence for NVT derived from experiments with *cis*-stilbene (**1**) as the acceptor,[3-7] and the origin of NVT to **1** was ascribed to torsion of the C=C double bond concomitant with NVT. However, Gorman et al.[9] showed that 2,3-diphenylnorbornene (**2**) as an acceptor exhibited rate enhancements nearly identical to those for **1**. The chromophores of **2** and **1** are identical but for the severe restriction of double-bond twisting in **2**. They concluded that the role of double-bond torsion in NVT to **1** was minimal and proposed that NVT to flexible and nonplanar acceptors (cf. **1** and **2**) was a consequence of single-bond torsion in the ground-state acceptor.

The relative importance of single-bond vs double-bond torsion in the relaxation of T$_1$ remained to be explored. We have now used time-resolved photoacoustic calorimetry (PAC)[10-13] to

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