products containing exocyclic methylene groups as well as groups derived from the methylene by diastereoface selective additions, e.g., hydrogenation, hydroboration, epoxidation. The procedure will be most effective when applied to ketones which will exhibit high diastereoface selectivity upon the addition of reagent **6**, as this will limit to two the diastereomeric β-hydroxysulfoximines to be separated.

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Base Catalysis in a Photochemical Smiles Rearrangement. A Case of General Base Catalysis of a Photoreaction

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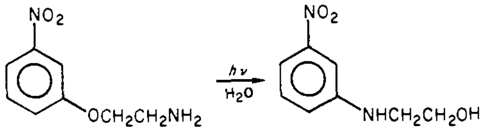
While phenomena identified as catalytic have been reported often for photochemical reactions,[2] fundamental criteria for the assessment of catalytic effects in photochemistry have not been defined. We wish to report the novel observation of base catalysis of a photochemical Smiles rearrangement[3] and to argue that our observations are best interpreted as a case of general base catalysis of an excited-state reaction.

The kinetic effect of sodium hydroxide on the photo-Smiles rearrangement of **1**, giving **2** in quantitative yield, was determined



1 **2**

by measuring quantum yields at 313 nm with a merry-go-round apparatus. The reactions were conducted in carbonate-free aqueous solutions containing 2.5×10^{-3} M **1** and varying amounts of sodium hydroxide (0.0001 to 0.02 M) at constant ionic strength (0.625 M KCl) and at 23 °C. The reactions were monitored by the absorbance at 405 nm (ϵ_{405} of **2** 1110); the actinometer was degassed 0.100 M valerophenone in benzene.[4] A double reciprocal plot of the data from these experiments is shown in Figure 1.

Inspection of the plot discloses two facts about the kinetic effect of hydroxide ion: (i) the linear region at high base concentrations indicates that the reaction is subject to base catalysis and (ii) the plateau at low base concentrations indicates that an uncatalyzed reaction, or one catalyzed weakly by water, also occurs.

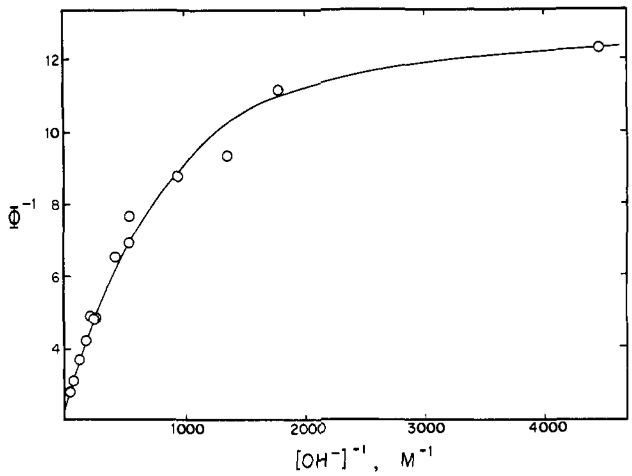


Figure 1. Dependence of quantum yields for photo-Smiles rearrangement of 1 on the concentration of NaOH.

Table I. Dependence of Quantum Yields on Bases[a]

base	conjugate acid pK_a	concn, M	Φ_{Smiles}
none			0.0880
NaOAc	4.76	0.100	0.103
$NaHCO_3$-Na_2CO_3	6.37 10.25	0.100[b]	0.200
Na_2HPO_4	7.21	0.100	0.206
morpholine	8.33	0.100	0.152[c]
$HOCH_2CH_2NH_2$	9.50	0.077	0.168[c]

[a] All reactions conducted at pH 10.04 ± 0.02. [b] Expresses total carbonate concentration. [c] Morpholine and ethanolamine may quench the excited state.

We next inquired whether the catalysis was general or specific. Solutions of **1** at pH 10.04 containing 0.1 M concentrations of a variety of weak bases were irradiated in parallel on the wheel, and quantum yields were determined. As shown in Table I, the added bases are effective catalysts at constant pH. Observations of this kind constitute a classical experimental test for general base catalysis in the ground state,[5] and we conclude accordingly that the photoreaction is subject to general base catalysis.

Before considering the kinetic description of the reaction, we wish to justify our use of the quantum yield as the experimental measure of catalysis. A ground-state catalyst may be defined as a substance which appears in the rate expression to a power higher than it appears in the stoichiometry.[6] The photochemist's measurement analogous to rate is quantum yield, which may be thought of as a ratio of rates—the rate of product formation divided by the rate of light absorption. We propose, analogous to the ground-state definition, that a photochemical catalyst be defined as a substance which appears in the quantum yield expression to a power higher than it appears in the stoichiometry.[7] We anticipate that, as is the case in the ground state,[6] explanations of photochemical catalysis will be couched in terms of rate constants for new and more efficient reaction pathways which the catalyst makes available.

The mechanism presented in Scheme I is consistent with all of our findings. The triplet state is implicated as the reactive excited state since the reaction sensitized by 0.043 M *p*-methoxyacetophenone in 50% CH_3CN-H_2O containing 0.01 M NaOH proceeds cleanly with a quantum yield 1.09 times greater than that of the comparable direct photoreaction. The quantum yield

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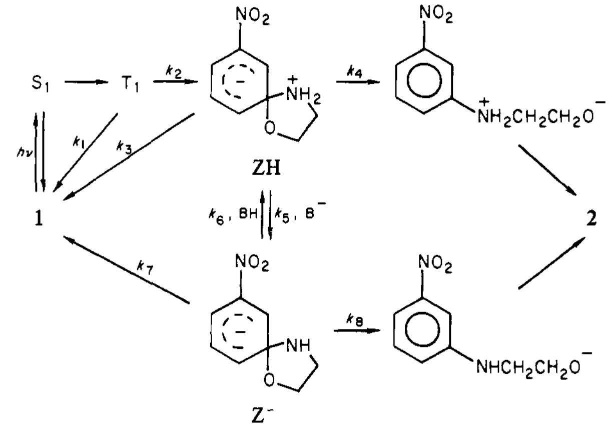
[7] The definition could be qualified by specifying a particular reactive state as the starting state, thereby excluding sensitizers and promoters of intersystem crossing from the category "catalyst". Medium effects will not qualify as catalysis since they will have no term in the rate expression. A paper exploring in more detail a definition of excited-state catalysis is in preparation, and we invite readers to draw our attention to novel examples of catalysis and related phenomena for excited-state reactions.

Scheme I



expressions below were derived by assuming a steady state for each intermediate. For the case of general base catalysis ($k_6 \ll k_7 + k_8$), eq 1 results, where $f = k_8/(k_7 + k_8)$ and $k_5[B]$ is the summation $\sum_i k_5^{B_i}[B_i]$. Inversion of this expression yields eq 2, for which two limiting conditions may be envisioned. At sufficiently low base concentration, $k_5[B]$ becomes small relative to k_4 in which case eq 2 is approximated by eq 3. At high base concentrations, $k_5[B]$ may become large relative to k_4 in which case eq 2 is approximated by eq 4. The behavior expected for eq 3 is shown in Figure 1 by the lack of dependence of quantum yield on hydroxide ion at low concentration. The behavior expected for eq 4 is shown by the linear region reached at high base concentration.

$$\Phi = \Phi_{ISC}\left(\frac{k_2}{k_1 + k_2}\right)\left(\frac{k_4 + fk_5[B]}{k_3 + k_4 + fk_5[B]}\right) \qquad (1)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{k_4 + fk_5[B]}\right) \qquad (2)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{k_4}\right) \qquad (3)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3}{fk_5[B]}\right) \qquad (4)$$

Were the reaction subject to specific base catalysis, the zwitterionic intermediate, ZH, would achieve prototropic equilibrium, and the general expression for the quantum yield in eq 5 would result, where f_{ZH} indicates the fraction of the intermediate in the protonated form. This fraction may also be represented by $K_b/(K_b + [OH^-])$ where K_b is the basicity constant of Z^-. Under the limiting condition of low hydroxide ion concentration, the relationship (inverted) is approximated by eq 3. At high hydroxide ion concentration, eq 6 becomes appropriate. These results show that kinetic expressions for general and specific base catalysis may both be derived for this photochemical system and that either description could satisfy the observed results for hydroxide ion catalysis. The observation of buffer enhancement of the quantum yield at constant pH forces the conclusion that the catalysis is general base catalysis.

$$\Phi = \Phi_{ISC}\left(\frac{k_2}{k_1 + k_2}\right)\left[f_{ZH}\left(\frac{k_4}{k_3 + k_4}\right) + (1 - f_{ZH})\left(\frac{k_8}{k_7 + k_8}\right)\right] \qquad (5)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{ISC}}\left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{K_b}{[OH^-]}\right)\left(1 + \frac{k_7}{k_8}\right) \qquad (6)$$

By making use of eq 3 and 4, the intercept of Figure 1 ($1/\Phi = 2.36$), the slope to intercept ratio at high hydroxide ion concentration (0.00445), and the value of the asymptote ($1/\Phi = 11.37$),[8] several rate constants and rate constant ratios may be evaluated. We assume that k_5 for hydroxide ion is diffusion controlled ($k_5^{OH} = 2.0 \times 10^{10}$ M^{-1} s^{-1}),[9] and that the partitioning factor, f, in eq 2 and 4 is unity.[10,11] We calculate that $k_4 = 2.3 \times 10^7$ s^{-1} and $k_3 = 8.9 \times 10^7$ s^{-1}. The rate constants in step k_5 for HPO_4^{2-} and acetate ion, calculated according to eq 2, are 5.9×10^8 and 3.2×10^7 M^{-1} s^{-1}, respectively.[12]

These experiments establish the first case known to us of a photoreaction subject to general base catalysis. In addition, they provide compelling evidence that nucleophilic aromatic photosubstitution reactions on nitrophenyl ethers proceed through intermediate σ complexes.[13] The photo-Smiles rearrangement of 2-(4′-nitrophenoxy)-1-anilinoethane studied by Mutai et al.[2i] involves electron transfer prior to σ-complex formation, and their reaction also shows catalysis by a base. The strikingly different regiospecificities of their systems[14] and ours[3] may be attributed to the absence of electron transfer preceding the σ complex in our reactions. Electron transfer is favored in their system by the lower ionization potential of the RNHPh moiety compared with that of a primary amine.

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(8) This is the value of the asymptote corrected for the small portion of **1** (7.9%) which is protonated at pH 10.35. The pK_a of **1** is 9.25 ± 0.20.

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(10) We cannot evaluate f directly, but since the leaving group abilities of RNH$^-$ and RO$^-$ differ greatly in a system sensitive to such differences,[11] we expect that f would be close to unity.

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(12) An alternative treatment of the kinetics is possible if k_4 were negligible and the "uncatalyzed" reaction were actually due to base catalysis by water in k_5. This seems unlikely for two reasons: **1** appears to photorearrange in acetonitrile with modest efficiency, and the rapid falloff of k_5 with decreasing base strength suggests that 55 M water acting as a base could not account for the residual quantum yield.

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Identification and Structure of the Benzene-Hydrogen Chloride Complex from Microwave Spectroscopy

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We wish to report the identification and structural characterization of a 1:1 gas phase complex formed between benzene and hydrogen chloride. The experimental technique used here is pulsed Fourier-transform microwave spectroscopy carried out in a Fabry-Perot cavity with a pulsed supersonic expansion of gas used to generate the molecular complexes.[1,2] A gas mixture of 2% benzene and 3% hydrogen chloride in argon at 2 atm of pressure was pulsed into the evacuated region between the Fabry-Perot mirrors. A $\pi/2$ microwave pulse is used to polarize the gas. After the polarizing radiation has dissipated the coherent emission from all the polarized rotational transitions within the bandwidth of the cavity is observed as a beat with the local

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† Deceased.

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