the flask 10 mL of THF, 5.0 mmol of an alcohol, and 5.0 mmol of a suitable alkene, say 1-decene, were introduced. The reaction flask was surrounded by a bath at 25 °C. After the system reached equilibrium, 2.5 mmol of $(9\text{-BBN})_2$ in THF was added and the amount of H_2 gas evolved was measured. After the reaction was complete, the number of mmol of H_2 evolved was calculated, after correcting for the temperature and pressure, which corresponds to the amount of alcohol reacted. From this, the amount of alkene reacted was computed. From the initial and final amounts of alcohol and alkene, the relative rate was calculated by using the Ingold–Shaw expression:[6]

$$\frac{k_{\text{alcohol}}}{k_{\text{alkene}}} = \frac{\ln\,[\text{alcohol}]_{\text{initial}} - \ln\,[\text{alcohol}]_{\text{final}}}{\ln\,[\text{alkene}]_{\text{initial}} - \ln[\text{alkene}]_{\text{final}}}$$

In the case of less reactive alcohols and phenols, *cis*-2-nonene was used for the competition experiment.

Acknowledgment. We thank the National Science Foundation for Grants CHE 76-20846 and CHE 79-18881.

Registry No. $(9\text{-BBN})_2$, 70658-61-6; CH_3OH, 67-56-1; PhOH, 108-95-2; $(CH_3)_3COH$, 75-65-0; $(C_2H_5)_3COH$, 597-49-9; *p*-nitrobenzyl alcohol, 619-73-8; *p*-chlorobenzyl alcohol, 873-76-7; benzyl alcohol, 100-51-6; 1-decene, 872-05-9; *p*-methoxybenzyl alcohol, 105-13-5; ethanol, 64-17-5; isopropyl alcohol, 67-63-0; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; cycloheptanol, 502-41-0; 2,3-dimethyl-2-butanol, 594-60-5; *p*-methoxyphenol, 150-76-5; *o*-cresol, 95-48-7; 2,6-dimethylphenol, 576-26-1; *p*-nitrophenol, 100-02-7; *o*-*tert*-butylphenol, 88-18-6; 2,6-diisopropylphenol, 2078-54-8; 2,6-di-*tert*-butylphenol, 128-39-2; tri-*n*-octylcarbinol, 17687-72-8; 2,2,4-trimethyl-3-pentanol, 5162-48-1.

Nucleophilic Attacks on Activated 9-Methylenefluorenes. Application of the Ritchie Equation to Low-Lying LUMO Substrates

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Rate constants (k_{nuc}) for nucleophilic attacks on 9-(dinitromethylene)-, 9-(dicyanomethylene)-, and 9-(nitromethylene)fluorene (FDN, FDCN, and FN, respectively) have been determined. The slope of the plots of log k_{nuc} vs. N_+ values are 1.23 ($r = 0.998$) for FDN and 1.29 ($r = 0.983$) for FDCN. These results indicate the need for incorporating a selectivity parameter in the Ritchie equation. FN displays an ambidentic behavior. In aqueous medium, CN^- reacts with FN at position 9 of the fluorene ring, whereas in Me_2SO and DMF, position α becomes more reactive. The final product of the reaction of CN^- at C-α is the corresponding vinyl cyanide. MeO^- in MeOH reacts with both sites with a ca. fivefold preference for position 9. The reactivity order of the three substrates is FDN > FDCN > FN. This order does not correlate with the pK_a of the activating groups, i.e., dinitromethane, malononitrile, and nitromethane. However, it does correlate with their deprotonation rate constants, indicating that the anomalous behavior of nitro-activated carbon acids in deprotonation reactions is not necessarily associated with a pyramidal nature in the transition state. It is suggested that the difference between substrates which obey the Ritchie equation and those which follow the Swain–Scott equation stems from the dissimilarity in the energies of their LUMOs. The first class of compounds is characterized by low LUMOs (LL) whereas high-energy LUMOs (HL) are typical of the second class. This results in a difference in the nature of the transition state of these reactions. On the basis of current theories it is suggested that the transition state of nucleophilic reactions with LL substrates is characterized by a relatively large extent of nucleophile–electrophile electron transfer as compared to reactions with HL substrates. This hypothesis is supported by the observed correlation between the thermodynamic ability to transfer electrons in solution and the nucleophilicity order $N_3^- > OH^- > CN^-$ which characterizes the N_+ scale. It is noteworthy that this order is the reverse of that typical for reactions with HL substrates where the Swain–Scott n scale is operative.

In spite of numerous theoretical studies and the wealth of experimental data gathered, nucleophilic reactions do not cease to attract the attention of organic chemists. Several years ago Ritchie established a new empirical nucleophilicity scale based on the reactions of nucleophiles with malachite green.[1] The reactivity was correlated by a single parameter equation ($\log k/k_0 = N_+$) which was found later to be applicable to other substrates such as diazonium ions,[1] carbonyl compounds,[2] electron-deficient aromatics,[3] and with some modification also activated olefins.[4] Ritchie noted that reactions which obey his equation display a different behavior pattern from that observed with reactions correlating with the Swain–Scott equation[5] ($\log k/k_0 = \text{sn}$). He suggested[1] that this difference could originate from the fact that in the first class of reactions, the nucleophile–electrophile bond formation is not coupled with the departure of the nucleophuge as is the case for substrates obeying the Swain–Scott equation.

We point out that there is an additional feature which is not common to these two reaction classes and that is the energy of the LUMO of the electrophiles. While the first class of substrates is highly electrophilic and posses low-lying LUMOs (LL), the LUMOs of the second class are generally σ^* orbitals and therefore of relatively much higher energy (HL for high LUMO). Since it is generally accepted that frontier orbital interaction, namely, HOMO(nucleophile)–LUMO(electrophile), determines the energetics and the course of the reaction,[6] it is highly likely

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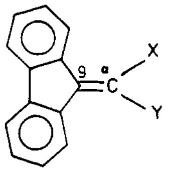
(1) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348.
(2) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.
(3) Ritchie, C. D.; Sawada, M. *J. Am. Chem. Soc.* **1977**, *99*, 3754.
(4) Hoz, S.; Speizman, D. *Tetrahedron Lett.* **1978**, 1775.
(5) Swain, C. G.; Soctt, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.
(6) Fujimoto, H.; Fukui, K. In "Chemical Reactivity and Reaction Paths"; Klopman, G., Ed.; Wiley: New York, 1974; Chapter 3.

that this dichotomy in the nature of the substrate (LL vs. HL substrates) is responsible for the different pattern of behavior displayed by the two reaction classes. In this study we report additional examples of the applicability of the Ritchie equation to LL substrates, as well as some deviation from this equation. The substrates chosen for this study are 9-methylenefluorene derivatives (1) where the methylene group was substituted by two nitro groups (FDN), by two cyano groups (FDCN) or by a single nitro group (FN).



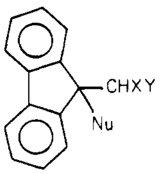
X = Y = NO_2 (FDN)
X = Y = CN (FDCN)
X = H; Y = NO_2 (FN)

1

Results

The kinetics of the reactions of various nucleophilic systems [defined as nucleophile (solvent)[1]] with the olefinic substrates were measured under pseudo-first-order conditions (excess of nucleophile). Substrate concentrations ranged from 10^{-4} to 10^{-5} M. Reactions rates were followed spectroscopically usually at the λ_{max} of the substrate. In some cases, such as the reactions of FDN with CN^- (Me_2SO) and CN^- (DMF), where the absorption of the formed anion largely overlapped with that of the starting material, the reactions were followed at a wavelength in which there was the largest difference between the extinction coefficients of products and starting materials. For fast reactions, the stopped-flow technique was employed. These reactions were carried out in an air-conditioned room (24.5 ± 0.5 °C). Slower reactions were thermostated at 25 ± 0.1 °C.

The products obtained in the kinetic experiments were identified by comparing their TLC and UV spectrum with that of the authentic compounds. In general, the reactions go to completion. (In water, less than 2% fluorenone was obtained.) In most cases the "normal adduct" 2 or its anion 3 were obtained. Exceptions are the reactions of FDN with N_3^- (Me_2SO) and FN with CN^- (Me_2SO, DMF) and with MeO^- (MeOH). In the reaction of FDN with N_3^- in Me_2SO the nucleophilic attack at C-9 is followed by consecutive reactions which yield *N*-cyano-9-iminofluorene as the final product.[7] The reactions of FN with CN^- in DMF and Me_2SO gave vinyl cyanide (4, Nu = CN). The reaction of FN with MeO^- in MeOH gave both the normal adduct and the vinyl ether (4, Nu = MeO). Repetitive scanning spectroscopy in the range 220–390 nm reveals the following features for the reaction of FN with MeO^- in MeOH: A relatively fast decrease of the absorption is observed around 350 nm (λ_{max} for FN), indicating that most of the starting material vanished during this step. A slower decrease is observed around 327 nm (λ_{max} for the vinyl ether). In the second step, the absorption around 327 nm slowly increases, giving in the end the spectrum of the vinyl ether.



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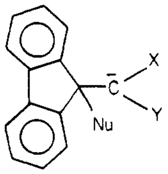
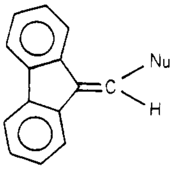


3



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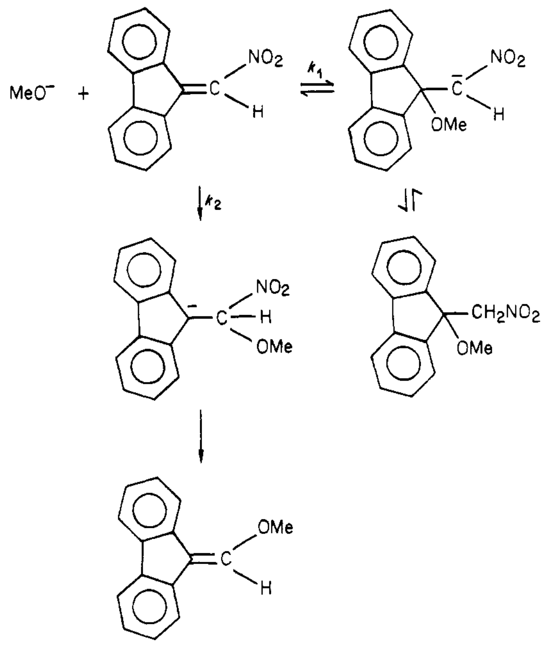
Scheme I



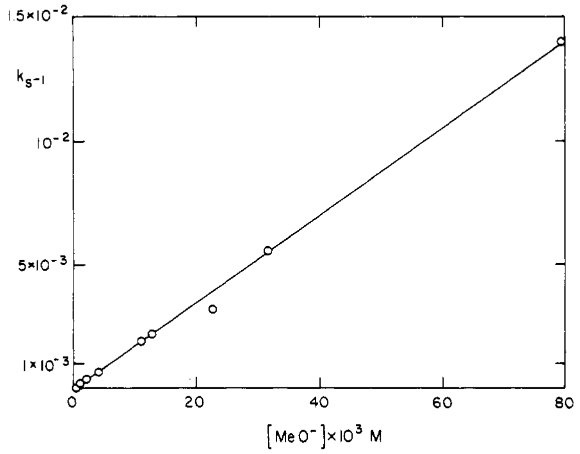


Figure 1. First-order rate constants vs. MeO^- concentration in the reactions of FN with MeO^- (MeOH).

These observations are consistent with competitive nucleophilic attacks at C-9 and C-α. The former yields reversibly the "normal" adduct, whereas attack at the latter leads to the irreversible formation of the vinyl ether as shown in Scheme I.

If, during the first step, the rate by which the adduct reverts to FN is significantly slower than the rate by which FN is converted to the vinyl ether, FN will disappear in a pseudo-first-order reaction according to eq 1.

$$k_{obsd} = (k_1 + k_2)[MeO^-] \quad (1)$$

Indeed, the first step displays first-order kinetics for all concentrations of methoxide (5×10^{-4}–1×10^{-2} M). A plot of the pseudo-first-order reaction rate constant k_{obsd} vs. $[MeO^-]$ gave a straight line with a slope 0.177 $M^{-1}\ s^{-1}$ (r = 0.9985) as shown in Figure 1. Monitoring the reaction

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(7) Hoz, S.; Speizman, D. *Tetrahedron Lett.* **1979**, 4855.

Table I. Second-Order Rate Constants for the Reactions of Nucleophiles with FDN, FDCN, and FN

		k_{nuc}, M^{-1} s^{-1}			
nucleophilic system	N_+	FDN	FDCN	FN(**9**)[a]	FN(α)[b]
CH_3OH	1.18	$1.8 \pm 0.2 \times 10^{-4}$ [c]			
CN^- (H_2O)	3.67	0.27 ± 0.03			
CN^- (25% sulfolane-H_2O)	5.65[d]	71 ± 2.6	3.64 ± 0.13	$1.6 \pm 0.03 \times 10^{-2}$	
CN^- (CH_3OH)	5.94	318 ± 46	1.2 ± 0.01		
CH_3O^- (CH_3OH)	6.27[d]	426 ± 43		0.145	0.032
CN^- (Me_2SO)	8.6	$3.78 \pm 0.45 \times 10^5$	$2.51 \pm 0.07 \times 10^4$		13 ± 1.6
CN^- (DMF)	9.33	$4.25 \pm 0.26 \times 10^6$	$4.5 \pm 0.7 \times 10^4$		62 ± 20
N_3^- (Me_2SO)	10.07	$1.06 \pm 0.03 \times 10^7$			

[a] Reaction at C-9 of FN. [b] Reaction at C-α of FN. [c] Units of s^{-1}. [d] Calibrated according to reactions with FDN.

at 325 and 354 nm simultaneously enabled a quantitative determination of each of the constituents of the reaction mixtures at any reaction time. (The adduct does not absorb in this region and at the end of the reaction, the OD_∞^{325} is directly proportional to the vinyl ether concentration which is equal to the initial concentration of the substrate). The product distribution ratio (eq 2) was found to be 4.53 ± 0.37. This, in combination with the values

$$[\text{adduct}]/[\text{vinyl ether}] = k_1/k_2 \qquad (2)$$

for the sum of the rate constants ($k_1 + k_2 = 0.177$ M^{-1} s^{-1}), gives $k_1 = 0.145$ M^{-1} s^{-1} and $k_2 = 0.032$ M^{-1} s^{-1}.

In order to assess the validity of the assumed reaction scheme, we performed a preparative reaction in which the reactants concentrations were kept similar to those in the kinetic experiments in a large volume of solution. When according to the UV spectrum the first step was completed, the reaction was quenched. In the subsequent workup of the solution, adduct **2** (Nu = MeO) and vinyl ether **4** (Nu = MeO) were isolated in a molar ratio 2.3:1, respectively (after recrystallization). When the reaction mixture was allowed to stand for 2 days, the vinyl ether was obtained in almost quantitative yield. Interestingly there was no indication spectrally, kinetically, or by product analysis for any significant formation of the vinyl anion of FN.

Unlike the reaction of MeO^- (MeOH), the formation of the vinylic product **4** (Nu = CN) in the reaction of CN^- (Me_2SO, DMF) with FN results from a direct attack at C-α without any prior interaction with position 9. Such an interaction would lead to the formation of the "normal" adduct, which has been shown to be stable under the reaction conditions and does not decompose to give the vinylic compound **4** (Nu = CN) or the starting olefin.

Another product that was found to be able to revert to starting material was the product of FDCN with cyanide. However, under the reaction conditions in all solvents, the absorption of FDCN vanished completely, indicating that the reverse reaction can be essentially neglected.

The solubility of all three substrates in pure water is very low and give rise to zero-order kinetics (probably due to aggregation phenomenon).[8] Interestingly, FDN, whose solubility somewhat exceeds that of the other compounds, presents normal first-order kinetics in the presence of Dabco buffer. A somewhat similar behavior was reported by Jencks et al. for the reaction of acetate esters in water in the presence of nicotinamide.[9] In order to overcome this solubility difficulty, a mixture of 25% sulfolane–75% water was used for the reactions of CN^- in aqueous medium. Since a change in the solvent entails a change in the nucleophilicity, the data for FDN which gives good correlation with N_+ was used to determine the N_+ value of CN^- in this solvent. The concentration of CN^- was evaluated from the pH of the solution by using a calibration curve of the pH meter reading vs. NaOH concentration. The pK_a of HCN in 25% sulfolane–water was found to be 9.63.

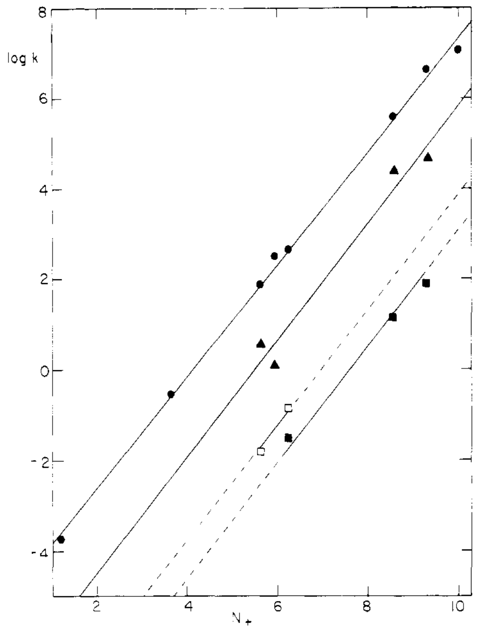

Figure 2. Plot of log k_{nuc} vs. N_+. All lines were drawn with a slope of 1.2. Actual slopes are as follows: 1.23 (r = 0.998) for FDN (●); 1.29 (r = 0.983) for FDCN (▲); 1.5 for FN(**9**) (□); 1.1 (r = 0.999) for FN(α) (■).

Although the reaction of FDN with CN^- (MeOH) was buffered according to Ritchie's procedure,[10] it was found to be unnecessary since the methoxide formed upon introduction of the cyanide salt does not compete effectively with the CN^- present in the solution. Once again the correlation between log k and N_+ for FDN was used for assigning a new value for the N_+ of MeO^- (MeOH).

Second-order rate constants for the reactions of the nucleophile systems with the three substrates are presented in Table I. The correlation of these rate constants with N_+ values are shown in Figure 2.

Discussion

Of the three olefins, FDN, is the most reactive. Table I indicates that, in its reactions with MeOH (MeOH) on the one hand and N_3^- (Me_2SO) on the other, FDN spans 10 units of the N_+ scale and nearly 11 orders of magnitude in rate constants. MeO^- in MeOH is the only nucleophile which deviates largely (−1.75 log units) from the regression line.[11] Methoxide does not give a stable adduct with the

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(8) Hoz, S.; Speizman, D.; Gross, Z., to be submitted for publication.

(9) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622.

(10) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 1589.

(11) This deviation can be associated with the absence or presence of a general base catalysis mechanism in the various cases.

second substrate FDCN. Either the absence of a forward reaction or the presence of a very efficient reverse reaction would explain this phenomenon. Interestingly, FDCN does not react with azide either. Ritchie has also observed an unusual reactivity pattern for azide, the reasons of which are not entirely clear.[12] Of our three substrates, FN is the least reactive and displays a most unusual behavior. Thus, as one ascends the N_+ scale, the reactive electrophilic site changes from position 9 of the fluorene system to the α-position. The vinylic compounds (4) are apparently obtained by the common nucleophilic vinylic substitution mechanism. The rate-limiting step is likely to be the nucleophilic attack[13] as is usually the case in most other nucleophilic vinylic substitution reactions.[14] According to the Ritchie equation, it is only the reactivity of the nucleophile which is affected by the nature of the solvent. The electrophilicity of the substrate, on the other hand, is either solvent independent or affected equally by the various media regardless of the nature of the substrate.[1] The ambidentical behavior of FN is, to the best of our knowledge, the first marked exception to this rule. In the case of FN, not only does the selectivity parameter change along the N_+ scale but, more importantly, the electrophilicity of the reactive sites of the substrate is also inverted.

In an attempt to understand the anomalous behavior of FN and its dependence on the various zones of the N_+ scale, let us first consider the factors which control the direction of a nucleophilic attack on a double bond. Nucleophilic attacks on double bonds are known to depend primarily on the electron-withdrawing ability of the activating group.[14] As a rough measure for this ability, one can use the thermodynamic acidity of the pertinent conjugated acid. This means that to the first approximation the competition of the two electrophilic sites, the 9- and α-positions, for a given nucleophile will be determined by the relative acidities of fluorene and nitromethane. In order to shift the nucleophilic attack from one position to the other, one needs to alter the relative acidities of the two sites on which the incipient carbanion is located. The pK_a of fluorene is relatively insensitive to solvent changes and remains probably within the range of 21–22[15,16] for water and Me_2SO. The pK_a of nitromethane, on the other hand, is increased by 7 pK_a units as one goes from water (10.2) to Me_2SO (17.2).[15,16] Furthermore, the presence of the nitro group at the α-position may compensate for the remaining pK_a gap between the fluorenyl and nitromethyl ends of FN since it is well-known that electronegative substitution at the α-position markedly enhances nucleophile vinylic reactions rates.[14] However, as tempting as this explanation may be, we believe that structure–reactivity considerations (see following discussion) largely rule out the justification for using it as an explanation for the ambidentic behavior of FN. At this stage we are unable to offer any explanation to this phenomenon.[17]

Structure–Reactivity Relationships. Rate–equilibrium and rate–rate correlations are two of the most powerful probes commonly employed in mechanistic studies.[18] General considerations[14] point to the ability of the activating group to withdraw electrons as the major factor governing the reactivity of the electrophiles used in this study. The activating group has an influence on the reactivity by exerting two different effects. The first one is the stabilization of the incipient negative charge at the transition state; thus, the electron-withdrawing power of activating group will directly affect the transition-state energy. The second effect is the ground-state destabilization of the substrate due to a partial antiaromatization of the fluorene ring. (One of the resonance structures places a positive charge on the cyclopentadienic ring). This is also expected to correlate with the extent of electron withdrawal by the activating groups. An attempt to reveal a correlation between log k of nucleophilic attacks (log k_{nuc} for a given nucleophilic system) and the thermodynamic acidity (as a measure of the electron-withdrawing ability) of dinitromethane, malononitrile, and nitromethane (pK_a of 3.6, 11.2, and 10.2, respectively[19]) in aqueous media shows that such a correlation does not exist. Nitromethane is more acidic than malononitrile by ca. 1 pK_a unit whereas FN is less reactive than FDCN by ca. 2 log units. On the other hand, a correlation does exist between log k_{nuc} and the logarithm of the ionization rate constants for dinitromethane, malononitrile, and nitromethane in water (0.83, 1.5×10^{-2} and 4.3×10^{-8} s^{-1}, respectively;[19] figure not shown, slope 0.47, $r = 0.972$[20]). Thus, the anomaly observed in the unexpected slowness of proton removal from nitroalkanes is also displayed in nucleophilic reactions on activated double bonds. It should be noted that in the latter reactions, the hybridization of the α-carbon is essentially sp^2 in the products as well as in the starting material. This rules out the assumption that the origin of the anomaly in deprotonation of nitro compounds results from the intermediacy of a pyramidal anion or a phase lag between the processes of C–H bond braking and planarization around the carbon bearing the nitro group.[21] The same conclusion is also derived from another study recently reported by Bernasconi in which the reactions of benzylidenemalononitrile, β-nitrostyrene, and p-(dimethylamino)benzylidene (Meldrum's acid) with piperidine and morpholine were thoroughly investigated.[22]

One can estimate an effective or intrinsic value for the thermodynamic acidity of nitromethane by using the rate constant for its deprotonation and the regression line [log k(ionization) vs. pK_a] reported by Pearson and Dillon.[19] The pK_a value obtained in this way is 17.3. The pK_a of CH_3NO_2 in Me_2SO was found to be 17.2[16] which is very close to its effective value in water. This behavior is typical of carbon acids which display a "normal" behavior and for

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[12] Ritchie, C. D.; Sawada, M. *J. Am. Chem. Soc.* **1977**, *99*, 3754.

[13] The identity of the rate-limiting step can be infered from the relative nucleofugicity of NO_2^- vs. MeO^- and NO_2^- vs. CN^-. In nucleophilic aromatic substitution the nucleofugicity order found for NO_2^- and MeO^- is $NO_2^- \gg MeO^-$ (Miller, J. "Aromatic Nucleophilic Substitution"; Elsevier: New York, 1968; Chapter 5). The order $MeO^- \gg CN^-$ was found in ElcB reactions (Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1898). Thus, for the pair NO_2 CN, the order is likely to be $NO_2 \gg CN$.

[14] Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1; *Acc. Chem. Res.* **1981**, *14*, 7.

[15] Coetzee, J. F.; Ritchie, C. D. "Solute-Solvent Interactions"; Marcell Dekker: New York, 1969; Chapter 4.

[16] Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Comforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. I.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

[17] The role of the solvent in this reaction is under further investigation.

[18] Fuchs, R.; Lewis, E. S. In "Techniques in Chemistry", 3rd ed., Lewis, E. S., Ed., Wiley: New York, 1973; Vol. VI, Chapter 14.

[19] Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

[20] Three-point correlation graphs are not shown here and in the following discussion. Correlation coefficients albeit only for three points are reported as a rough measure for the quality of the correlation.

[21] Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3107 and references cited therein. Kresge, A. J. "Proton-Transfer Reactions"; Caldin, E. F., Gold, V., Eds., Chapman and Hall: London, 1975; Chapter 7. Albery, W. J.; Campbell, A. N.; Curran, J. S. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 2206.

[22] (a) Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810. (b) A referee has suggested that if FN is not planar in its ground state, then at the transition state of the addition reaction Cα will aquire a pyramidal geometry which is the origin of the anomaly. However, since in a dipolar aprotic solvent the anomalous behavior of FN is absent, we believe that solvent effects are responsible for this anomaly.

which no "unusual" reorganizations have been invoked.[15] Thus, the effective pK_a value for CH_3NO_2 can be interpreted as the pK_a of CH_3NO_2 in which the carbanion formed does not undergo internal or external (solvent) reorganization at later stages of the deprotonation process.

The similarity between the effective acidity of CH_3NO_2 in water and its pK_a in Me_2SO also supports the suggestion[22,23] that the origin of the anomalous behavior of nitro-activated carbon acids stems mainly from solvent effects.

Obviously, a plot of log k_{nuc} vs. the pK_a of the carbon acids activated by the same group(s) for which a pK_a of 17.3 was used for nitromethane gives a linear correlation (slope $\approx$ 0.3, $r \approx 0.996$).[24] These results, together with those obtained by Bernasconi et al.,[22] clearly indicate that a correlation between log k_{nuc} and the electron-withdrawing power of the activating groups expressed in terms of pK_a of the corresponding methane derivative does exist.

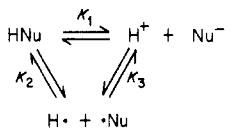
Rate–equilibrium correlations are frequently employed as probes for retrieving information regarding transition-state structure. In this respect we would like to comment on three points which, in our opinion, deserve some attention. First, the value of the slope of the plot of log k_{nuc} vs. pK_a (which in a fashion analogous to β_{nuc} should be designated α_{nuc}) can span a range larger than 0–1.[25] Thus an $\alpha_{nuc} \approx 0.3$ does not necessarily mean that the activating moiety bears a one-third negative charge at the transition state.

Secondly, whenever a series of reactions can be correlated by a linear free energy relationship with a known parameter, the structure of the transition state is assumed to remain constant within this series.[18] As can be seen from primary kinetic H/D isotope effects, the transition state for deprotonation reactions of nitro compounds ($k_H/k_D > 3$)[26] differs significantly from that of cyano compounds ($k_H/k_D \approx 1$).[27] The previously mentioned rate–rate correlation suggests analogous differences in the transition-state structure of the nucleophilic addition reactions in spite of the existence of a LFER.

Finally, the existence of a rate–equilibrium correlation demands that the stability of the products be partly reflected in the transition state of the reaction. This rate–equilibrium correlation exists between log k_{nuc} and the pK_a of the corresponding methane derivatives. It should be noted, however, that the adduct of FDCN with CN^- is much more acidic (pK_a = 5.65 in aqueous sulfolane)[28] than malononitrile itself. Unless α_{nuc} of ~0.3 is interpreted as an indication of a very early transition state, one should expect a significant positive deviation of FDCN in the plot of log k_{nuc} vs. pK_a; nevertheless, such a deviation was not found.

It can be concluded that the present study provides an additional example which demonstrates that one need be wary of overextending empirical relationships.

Scheme II



Nature of the Transition State. Current theories suggest that a partial electron transfer is a characteristic feature of the transition state in bond-cleavage and bond-formation reactions.[29] Thus, in addition to partial charges (δ±), a transition state should be characterized by its partial radical character (δ·) as well. For a given nucleophile, the pivotal question is how the nature of the substrate will affect the importance of the contribution of the diradicaloid structure. A straightforward answer can be easily obtained from the theoretical model developed by Shaik[29a] and Pross.[29b] According to this model, the transition state is defined by a linear combination of reactant configurations (eq 3), where D and A refer to the nucleophile and the substrate, respectively. DA is the ground state of the reactants, D^+A^- is an excited state in which an electron is transferred from the nucleophile to the substrate to form diradicaloid pair, and DA* is a monoexcited state of the electrophile with no electron transfer. The other three states are diexcited and do not contribute significantly to the transition-state structure. The extent to which these configurations are mixed into the transition state is governed by the energy gap between each of the individual configurations and the ground state (DA). Thus it is immediately apparent that for a given nucleophile (D), the amount by which the diradicaloid structure D^+A^- will contribute to the transition state depends on the stability of A^-, i.e., on the electron affinity of A and therefore on the energy of its LUMO. Hence, for a given nucleophile the amount of the electron transfer at the transition state will be larger for LL substrates than for HL substrates. In the introductory section of this paper we pointed out that the common denominator for the array of substrates which obey the Ritchie equation is the existence of low-lying LUMOs, whereas high LUMOs are typical of substrates which obey the Swain–Scott equation. If this hypothesis is correct, then there should be a larger amount of nucleophile to substrate electron transfer in the transition state of the reactions of the first group than of the second one.

$$\psi = C_1(DA) + C_2(D^+A^-) + C_3(D^+A^{-*}) + C_4(DA^*) + C_5(DA^{**}) + C_6(D^{2+}A^{2-}) \quad (3)$$

A criterion for the validity of this hypothesis can be found in the nucleophilicity order $N_3^- > OH^- > CN^-$ which is quoted by Ritchie[1] as a characteristic feature of the N_+ scale, whereas it reverse is typical of the n scale. This order correlates very well with the thermodynamic ability of the nucleophile to transfer an electron in the reaction K_3 of Scheme II. In employing the thermodynamic cycle of Scheme II for evaluation of the ΔGs associated with K_3 (ΔG_3), it is assumed that solvent effects on ΔG_2 (bond strength energies are obtained from gas phase data)[30] are either small or constant throughout the series. This is likely to be a valid assumption since all species involved in K_2 are uncharged. The values obtained for ΔG_3 are 78.5, 97.3, and 107 kcal/mol for N_3^-, OH^-, and CN^-, respectively.

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[23] Keefe, J. R.; Morey, J.; Palmer, C. A.; Lee, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1295.

[24] Using the value of 3.6 for the pK_a of dinitromethane gives a slope of 0.26 (r = 0.993). However, dinitromethane is very sensitive to steric effects, and its pK_a rises above 6.0 in heavily substituted systems (Jones, J. R. "The Ionization of Carbon Acids"; Academic Press: New York, 1973; Chapter 5). Employing a pK_a of 6.3, which was measured for alkoxy adducts of FDN (Hoz, S.; Perach, S. S. *J. Org. Chem.* **1982**, *47*, 4056). In the correlation yields, one obtains a slope of 0.33 (r = 0.999).

[25] This is an analogy to a value of 1.7 suggested for β_{nuc}, (Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622).

[26] Leffek, K. T. In "Isotopes in Organic Chemistry"; Buncel, E.; Lee, C. C.,Eds., Elsevier: New York, 1975; Vol. 2, Chapter 3.

[27] Hoz, S.; Aurbach, D. *J. Am. Chem. Soc.* **1980**, *102*, 2340. Hibbert, F.; Long, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 2836.

[28] Hoz, S.; Gross, Z., unpublished results.

[29] (a) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. (b) Pross, A. *Ibid.* **1981**, *103*, 3702. (c) Walling, C. *Ibid.* **1980**, *102*, 6854. (d) Salem, L. *Ibid.* **1974**, *96*, 3486.

[30] H–Nu bond strength values of 85, 119 and 120 kcal/mol and pK_a's of 4.68, 15.75, and 9.3 for HN_3, HOH and HCN, respectively where employed. ("CRC Handbook of Chemistry and Physics", 52nd ed., CRC Press: Cleveland, OH, 1971–1972).

The correlation of the order of reactivity and ΔG_3 provides strong support to our aforementioned assumption.[31]

A reactivity order of $N_3^- > CN^-$ was also observed in the nucleophilic reactions with another substrate, *N*-(methoxymethyl)-*N*,*N*-dimethylanilinium ions.[32] This is highly consistent with our assumption since there is convincing evidence[32] for the high electrophilicity of this substrate in their encounter with the nucleophiles.[33]

Significance of the S_+ Parameter. The Ritchie equation is unique in its ability to correlate a vast range of nucleophilic reactions by using a single parameter.

Thus, all the reaction studies by Ritchie's group demonstrate a constant (unity) selectivity. This is one of the major features by which the Ritchie equation differs from that of Swain–Scott. On the basis of our results with FDN (slope = 1.23, r = 0.998) we have previously suggested that this equation should be modified by a selectivity parameter, S_+.[4] This was also suggested by Scott on the bases of his results with TAM.[34] The data shown in Figure 2, which includes, in addition to the FDN line, three other lines [with the following statistics: FDCN, 4 points, slope = 1.29, r = 0.983; FN (9) 2 points, slope = 1.5; FN(α) 3 points, slope = 1.1, r = 0.99], strongly supports the previous conclusion necessitating the incorporation of a selectivity parameter into the Ritchie equation. However, since the significance of experimental data is by and large a subjective matter and in order to minimize as much as possible this element of subjectivity, the data of FDN (6 points, slope = 1.23, r = 0.998, over 11 orders of magnitude in rate constants) was further analyzed by employing a statistical probe called the T test.[35] Using the stringent demand of a 95% confidence level, it was found that the actual slope can range from 1.13 to 1.33. Thus not only is the value 1 clearly out of the range of the slope but also so is 1.1. It is therefore concluded, on the basis of all the data gathered, that in order for Ritchie equation be able to accommodate all the reactions whose rate constants (in the logarithmic form) are linearly correlated with the N_+ values, *a selectivity parameter must be incorporated into the equation.*

Experimental Section

Starting Materials. 9-(Dinitromethylene)fluorene (FDN) was prepared from 9-diazofluorene and iodonitroform; mp 187 °C (lit.[36] mp 189 °C) (**Caution**: iodonitroform is prepared from $C(NO_2)_4$; all stages are highly explosive).

9-(Nitromethylene)fluorene was prepared from 9-iminofluorene and nitromethane; mp 134 °C (lit.[37] mp 134 °C).

9-(Dicyanomethylene)fluorene was prepared by condensation of fluorenon with malononitrile.[38,39]

Reaction Products. 9-Cyano-9-(dinitromethyl)fluorene. A mixture of 220 mg (0.82 mmol) of FDN and 2.5 g (38 mmol) of KCN in 30 mL of EtOH and 10 mL of H_2O was gently heated until all the solid dissolved. A yellowish solid precipitated after addition of crushed ice followed by acidification with AcOH to pH ~5. Recrystallization from petroleum ether gave a white solid: mp 151 °C; NMR ($CDCl_3$) δ 6.08 (1 H, s), 7.4–7.9 (8 H, m).

9-Methoxy-9-(dinitromethyl)fluorene. A mixture of 200 mg (0.75 mmol) of FDN with 1 g (25 mmol) of MeONa in 10 mL of MeOH was heated gently until all the solid dissolved. Crushed ice was added, and the solution was mildly acidified with dilute HCl. (The product is unstable under acidic conditions.) The product was extracted with cold ether, dried over Na_2SO_4, and evaporated. The product was recrystallized from petroleum ether (bp 60–80 °C): mp 92 °C; NMR ($CDCl_3$) δ 2.48 (3 H, s), 6.82 (1 H, s), 7.2–7.7 (8 H, m).

The pertinent data for the reaction of FDN with N_3^- to give *N*-cyano-9-iminofluorene was reported elsewhere.[7]

9-Cyano-9-(dicyanomethyl)fluorene was prepared according to published procedure.[39]

9-Cyano-9-(nitromethyl)fluorene was prepared by slow addition of a solution of a sample (223 mg, 1 mmol) in 80 mL of dioxane to a solution of 1 g of KCN (15 mmol) in 80 mL of H_2O. After 12 h at room temperature, the reaction mixture was acidified with 3 mL of concentrated HCl and evaporated (caution HCN). The residue was extracted with CH_2Cl_2, washed with H_2O, and dried over $MgSO_4$. The CH_2Cl_2 was evaporated, and the red residue was separated via thick-layer chromatography. When eluted with toluene, the adduct appeared immediately after the fluorenone: mp 153–154 °C (from petroleum ether); NMR ($CDCl_3$) δ 4.7 (2 H, s), 7.4 (8 H, m).

9-Methoxy-9-(nitromethyl)fluorene was prepared by dissolving 125 mg (0.56 mmol) of FN in a 600-mL solution of dry MeOH which was 0.07 M in MeO^-. After the first step was practically completed (according to the UV spectrum, 365 nm), the reaction mixture was cooled with ice and was acidified with AcOH. The solvent was evaporated, and the residue was extracted with ether. Thick-layer chromatography separation (toluene) gave 70 mg of the adduct [mp 140 °C (petroleum ether); NMR ($CDCl_3$) δ 2.8 (3 H, s), 4.7 (2 H, s), 7.4 (8 H, m)] 25 mg of 9-(methoxymethylene)fluorene.[40] If the reaction mixture was allowed to react for more than 1 day, the vinyl ether was the only product. For synthetic purposes much higher reactant concentrations could be employed with the same procedure. The TLC separation of the adduct could be replaced by repetitive recrystallizations from petroleum ether until a constant melting point was achieved.

All new compounds gave satisfactory C, H, and N analyses. The NMR spectra were recorded on a Varian HA-100 spectrometer.

Kinetic Measurements. The reactions of the three substrates with nucleophiles were followed spectroscopically. After each of the reactions was first monitored by repetitive scanning in the UV–vis region (Perkin-Elmer 402 spectrophotometer), the actual kinetic measurements were performed either on a Gilford 2400 or a Durrum D-110 stopped-flow spectrophotometer, both attached to a PDP 11/40 minicomputer for data handling. The wavelength selected for the monitoring was chosen from the repetitive scanning experiments. The Gilford 2400 was equipped with a circulating bath. Temperature within the cell compartment was 25 ± 0.1 °C. The reactions on the stopped-flow apparatus were performed in an air-conditioned room (24.5 ± 0.5 °C). Reactions in aqueous media performed on the Gilford spectrophotometer were carried out by injecting ca. 20 μL of substrate

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[31] Ionization potentials in the gas phase retain the order CN^- (3.82 eV) > N_3^- (2.7 eV). However, OH^- deviates largely (1.82 eV) probably due to special solvation effects. (Reference for N_3^-: Jackson, R. L.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1981**, *103*, 1802. For CN^-: Berkowitz, J.; Chupka, W. A.; Walter, T. A. *J. Chem. Phys.* **1969**, *50*, 1497. For OH^-: Hotop, H.; Lineberger, W. C. *Ibid.* **1974**, *60*, 1806.

[32] Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.

[33] (a) The stabilization of the transition state in the nucleophilic reactions with α-effect nucleophiles is also highly consistent with this theory. Since the α effect is manifested almost solely in reactions with LL substrates, the nucleophile will acquire a large $\delta\cdot$ at the transition state. The interaction of the $\delta\cdot$ with the neighboring lone pair provides a stabilization mechanism which is unavailable to any "normal" nucleophile, thus giving rise to the α-effect phenomenon. (Hoz, S. *J. Org. Chem.* **1982**, *47*, 3545.) (b) In reactions where a complete electron transfer was proposed such as in the nitrations of aromatics (Perrin, C. L. *J. Am. Chem. Soc.* **1977**, *99*, 5516), the general reactivity and hence the intermolecular selectivity was assumed to be governed by the first step whereas the positional (intramolecular) selectivity is determined in the second one. One should note that the relative reactivity of FN with respect to the two other substrates remains roughly the same independently of the position of the attack (C-9 or C-α). It can be speculated here, as well, that the reactivity of FN is determined by some general factor such as the LUMO energy of the FN whereas the positional selectivity might be governed by secondary interactions.

[34] Miller, K.; Scott, J. M. W.; Barnes, D. J.; Steel, F. J. P. *Can. J. Chem.* **1976**, *54*, 3312.

[35] Hays, W. L. "Statistics", 2nd ed., Holt, Pinehart and Winston, Inc.: New York, 1973; Chapter 10.

[36] Gabitov, F. A.; Fridman, A. L.; Nikolaeva, A. D. *Zh. Org. Khim.* **1969**, *5*, 2245.

[37] Charles. G. *Bull. Soc. Chim. Fr.* **1963**, 1573.

[38] von Schenk, R.; Finken, H. F. *Justus Liebigs Ann. Chem.* **1928**, *462*, 272.

[39] Hartzler, H. D. *J. Org. Chem.* **1966**, *31*, 2654.

[40] Wittig, G.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 1373.

solution in sulfolane into the preincubated reaction mixture. Buffering of the solution when needed was made according to the procedure developed by Ritchie.[41] The concentrations of CN^- were determined by pH reading and a calibration curve of OH^- concentration in the same media.

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Registry No. 1 ($X = Y = NO_2$), 25945-85-1; 1 ($X = Y = CN$), 1989-32-8; 1 ($X = H$; $Y = NO_2$), 74373-02-7; 2 ($Nu = CN$; $X = Y = NO_2$), 86120-10-7; 2 ($Nu = OMe$; $X = Y = NO_2$), 82615-43-8; 2 ($Nu = CN$; $X = H$; $Y = NO_2$), 86120-11-8; 2 ($Nu = OMe$, $X = H$; $Y = NO_2$), 86120-12-9.

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[41] Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966.

Photochemistry of Phenyl Alkyl Ketones in the Presence of Triphenylphosphine

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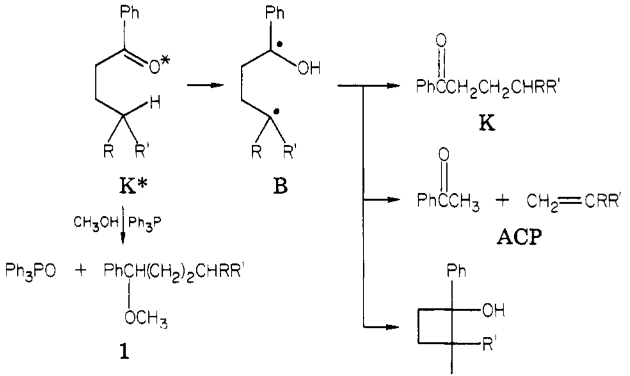
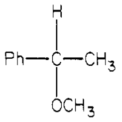
Photolysis of butyrophenone, valerophenone, γ-methylvalerophenone, and acetophenone in methanol in the presence of triphenylphosphine gave triphenylphosphine oxide and 1-phenyl-1-methoxyalkanes in addition to the expected Norrish type II products. Kinetic studies of these photoreactions by steady-state measurements show that triplet-state ketones are quenched by Ph_3P but that the corresponding biradicals do not interact with Ph_3P.

Studies of the Norrish type II reaction of phenylalkanones[1,2] have made significant contributions to our understanding of ketone photochemistry in recent years.[3-9] As shown in Scheme I, the key step of Norrish type II reactions is the generation of a biradical B, which can fragment to acetophenone (ACP) and an olefin or cyclize to a cyclobutanol (CB). Direct proofs of the intermediacy of biradicals have been gained from trapping experiments[3] and from direct observations in laser flash photolysis.[4] In connection with kinetic studies, interactions of a variety of quenchers with the triplet and biradical states of phenylalkanones have been studied.[6-12] The biradicals have been shown to undergo H abstraction,[3,7] electron transfer,[4] addition to double bonds and oxygen,[11] and paramagnetic interaction.[8] For example, while organic phosphines and phosphites[14] are quenchers of carbonyl triplet states,[13-17] organic phosphates interact with the biradicals to promote the Norrish type II reaction.[10] Photolysis of aryl ketones in the presence of triphenylphosphine has been shown to give the phosphine oxide and various products that can be derived from phosphoranes and/or carbenes.[18] In the

Scheme I



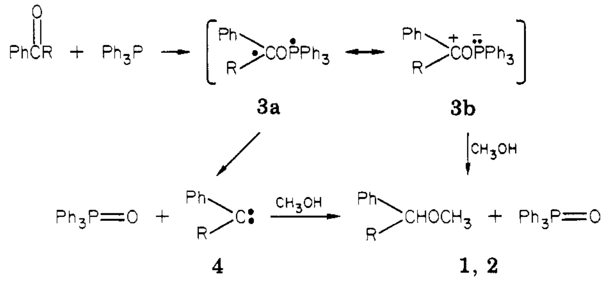
a, $R = R' = H$
b, $R = CH_3$; $R' = H$
c, $R = R' = CH_3$



$PhCH(OCH_3)CH_3$

2

Scheme II



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[1] J. C. Scaiano, E. A. Lissi, and M. V. Encina, *Rev. Chem. Intermed.*, **2**, 139 (1978).

[2] P. J. Wagner, *Acc. Chem. Res.* **4**, 168 (1970).

[3] P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7480 (1972); P. J. Wagner and R. G. Zepp, *ibid.*, **94**, 287 (1972).

[4] R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977); *J. Phys. Chem.*, **81**, 828 (1977).

[5] P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7506 (1972).

[6] J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977).

[7] M. V. Encinas, P. J. Wagner, and J. C. Scaiano, *J. Am. Chem. Soc.*, **102**, 1357 (1980).

[8] J. C. Scaiano, G. W. B. Lee, Y. L. Chow, and B. Marciniak, *J. Phys. Chem.*, **86**, 2452 (1982).

[9] R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 2126 (1977).

[10] J. C. Scaiano, *J. Org. Chem.*, **43**, 568 (1978).

[11] R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 4512 (1978).

[12] M. V. Encinas and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 7108 (1978).

[13] J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973/74).

[14] R. S. Davidson and P. F. Lamberth, *J. Chem. Soc. D.*, 1098 (1969).

[15] J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972).

[16] J. C. Scaiano, *J. Photochem.*, **2**, 471 (1973/74).

[17] R. H. Lema and J. C. Scaiano, *Tetrahedron Lett.*, 4361 (1975).

0022-3263/83/1948-2910$01.50/0