π Nucleophilicity: The Effect of Charge Delocalization on the Efficiency of Internal Displacements in E1cB Reactions[1]

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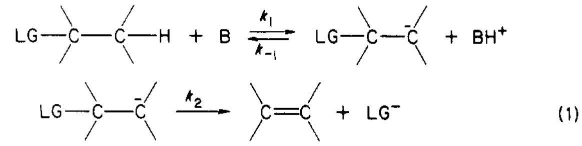
The effect of negative charge (de)localization by the activating group on the efficiency of the second step of an E1cB reaction was investigated. Rate constants for the reactions of carbanions **1**(LG)$^-$ and **2**(LG)$^-$ with LG = CN, MeO were determined in 25% sulfolane–75% water at 25 °C. The results show that the relatively localized dicyano-stabilized carbanion **2**(CN)$^-$ is much more reactive than the delocalized nitro-stabilized carbanion **1**(CN)$^-$. The proximity of the β-cyano group does not greatly affect the pK_a of the nitromethyl moiety in **1**(HCN) whereas a decrease of ca. 6 pK_a units was observed for the malononitrile moiety in **2**(HCN). The pK_as obtained are 9.6 and 5.6, respectively. This increased acidity was not observed for the methyl analogue **3** of **2**(HCN) (pK_a = 10.4), providing additional support for the assumption that cyano-stabilized carbanions are more localized than the nitro ones. A short ab initio calculation at the 4-31G level was performed on $CH_2NO_2^-$ and CH_2CN^- in order to determine whether (de)localization occurs at the HOMO level or is an overall effect. The results indicate that unlike the case of the enolate ion (de)localization in the two carbanions occurs at both the HOMO and inner levels as well.

For many years E1cB (eq 1) was considered to be a rare mechanism.[2] Numerous studies of the mechanism appearing during the last decade have rendered it a rather common reaction. In spite of this, much of the basic understanding of the E1cB mechanism is still lacking.



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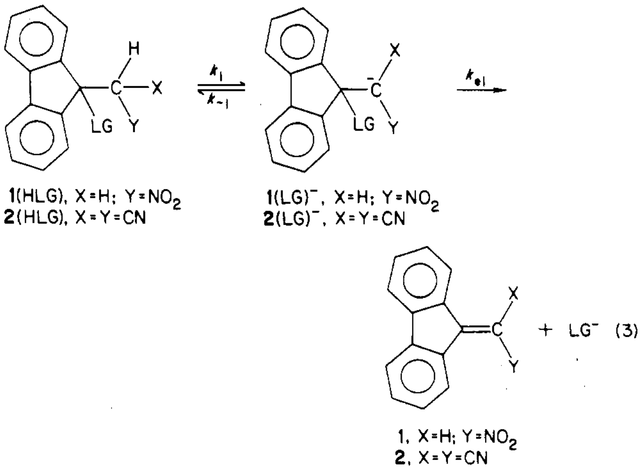
While information relevant to the first step can be relatively easily retrieved from the extensively studied chemistry of deprotonations of carbon acids, the second step is still by and large a terra incognita. The major reason for this probably lies in the instability of the intermediate carbanion whose existence is often indirectly inferred. Nevertheless, information available in the literature reveals a most intriguing feature in this second step of the E1cB mechanism. The data indicates that π nucleophilic displacements (internal displacement reactions which result in the formation of double bonds) are much more effective than σ nucleophilic reactions (in which a σ bond is formed as in S_N2 reactions, i.e., eq 2).

$$Nu^- + CH_3LG \rightarrow NuCH_3 + LG^- \qquad (2)$$

This has been demonstrated in previous studies[3,4] where it was found that groups such as CN, OR, SPh, P(O)(OEt)$_2$, etc., which do not partake in S_N2 reactions, do serve as leaving groups in π nucleophilic displacements. These observations are quite surprising[5] since it is clear that the driving force in the π nucleophilic reactions is smaller than that in the σ nucleophilic reactions due to the substantial difference in the energies of the bonds formed (π vs. σ). While there is no doubt that the difference between π and σ nucleophilicity stems in part from the entropy factor associated with the bimolecularity of the reaction,[6] it seems likely that other factors may also be involved.[7] At this point, however, there are not enough experimental grounds to substantiate any hypothesis as to the origin of this phenomenon.

In this study we have chosen to concentrate on the effect of charge (de)localization by the activating group on its efficiency as a π nucleophile. The nitro and the cyano groups were chosen as models for delocalizing and localizing groups, respectively. In order to enable a fair comparison, the two derived carbanions should be of similar stability. Since two cyano groups are similar to a single nitro group in acidification of methane (pK_as are 11.2 and 10.2, respectively),[8] the comparison was made between nitromethide and malonitrile carbanions as π nucleophiles. These two moieties were incorporated into a molecular system to give **1**(HLG) and **2**(HLG) (see eq 3). These



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[1] Presented in part at the 50th Anniversary Meeting of the Israel Chemical Society, Jerusalem, April 1984.

[2] Gould, E. "Mechanism and Structure in Organic Chemistry"; Holt-Dryden: New York, 1959; p 480. Banthorpe, D. V. "Elimination Reactions"; Elsevier: Amsterdam, 1963; p 80.

[3] (a) Farrel, P. G.; Newton, J. *J. Chem. Soc. B* **1970**, 1630. (b) Lord, E.; Naan, M. P.; Hall, C. D. *Ibid.* **1971**, 220. (c) Rappoport, Z.; Shohamy, E. *Ibid.* **1971**, 2060. (d) Albeck, M.; Hoz, S.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1248. (e) Fouad, M. F.; Farrell, P. G. *Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1496.

[4] Stirling, C. J. M. *Acc. Chem. Res.* **1979**, *12*, 198.

[5] This exceptional efficiency of π nucleophilicity can be observed in other systems as well. An example is the fast unimolecular decomposition of methoxymethyl chloride (Ballinger, P.; de la Mare, P. D. B.; Kohnstam, G.; Prest, B. M. *J. Chem. Soc.* **1955**, 3641. Modena, G.; Scorrano, G.; Venturello, P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1). However, the electron pair on the oxygen atom functions only rarely as a nucleophile in S_N2 reactions.

[6] Jencks, W. P. *Adv. Enzymol.* **1975**, *43*, 219.

[7] For example, it is pososible that interelectronic repulsion between the electron clouds of the nucleophiles and the substrate contributes significantly to the transition-state energy in S_N2 reactions. On the other hand, in the case of π nucleophiles, the nucleophile is already located within a σ bond distance from the electrophilic carbon and the electronic repulsion is not drastically changed upon going from reactants to the transition state leading to reactions that have a lower activation energy.

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

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Table I. Rate Constants for the Elimination of MeOH from 1(HOMe) in 25% Aqueous Sulfolane at 25 °C as a Function of pH

pH	9.43	9.81	9.99	10.57	10.63	11.11	11.86	13.16
$10^5 k_{\text{obsd}}$, s^{-1}	1.2	1.5	1.75	5.5	7.87	13.4	19.0	19.0

systems were chosen since data regarding the same reactions in the reverse direction were available from our previous studies.[9] CN and MeO were used as leaving groups (LG). In order to clarify the term (de)localization some ab initio studies on the two carbanions were also performed.

Results

The reactions were carried out in a buffered aqueous sulfolane solution (25% sulfolane in water, v/v) at 25 °C. Repetitive scanning spectroscopy in the UV range was performed before the kinetics of the reaction was studied at a single wavelength. The products of the kinetic experiments were identified by their UV spectra and their R_f in thin layer chromatography which were compared with those of authentic samples. The pH measurements were performed in the following way: A standard combined glass electrode calibrated in buffered aqueous solution was used to read the pH of the various 25% sulfolane–water solutions. The actual H^+ concentration was evaluated from a calibration curve (not shown) in which the actual log H^+ was plotted against the pH meter reading of the sulfolane solution. $HClO_4$ and NaOH were employed in the preparation of the data for this curve. The actual concentration of H^+ in the basic region was calculated by using pK_w = 14.34 as determined by Wooley et al.[10] for the 25% aqueous sulfolane solution at 25 °C.

Reactions of 1(HOMe). The reactions were carried out in the pH range 9.43–13.16. Usually, the kinetics of the reactions were followed at λ 365 nm, which is the $\lambda_{\max}$ of the product 1. However, under basic conditions 1 is hydrolyzed to give fluorenone. Up to pH 12 this reaction is slow enough and does not interfere with the following of the reaction kinetics by monitoring the rate of product formation. At higher pH, the reaction was followed at λ 258 nm ($\lambda_{\max}$ of fluorenone) since the decomposition of 1 to fluorenone was very fast under these conditions and no accumulation of 1 could be detected in the repetitive scanning experiments.

The observed first-order rate constants are given in Table I. The change in these rate constants as a function of pH is described by a sigmoid curve (Figure 1). This behavior is typical of the mechanism depicted in eq 1, in which the concentration of the intermediate conjugated base is pH dependent. The overall rate equation for the process is given in eq 4, where K_a is the acidity constant

$$k_{\text{obsd}} = k_{\text{el}} \frac{K_a}{K_a + [H^+]} \tag{4}$$

of the substrate (k_1/k_{-1}). Under highly basic conditions ($[H^+] \ll K_a$), practically all the starting material is converted to its conjugated base and k_{el} can be directly measured as it equals k_{obsd} at the plateau in Figure 1. The acidity constant of 1(HOMe) can also be estimated from this sigmoid plot since it equals the pH where $k_{\text{obsd}} = k_{\text{el}}/2$. In order to obtain more accurate values for k_{el} and K_a, we have treated the estimated values of these constants in a nonlinear regression program using eq 4. The k_{el} and K_a values obtained in this way (Table III) were used to draw the theoretical line in Figure 1 (points are experimental data).

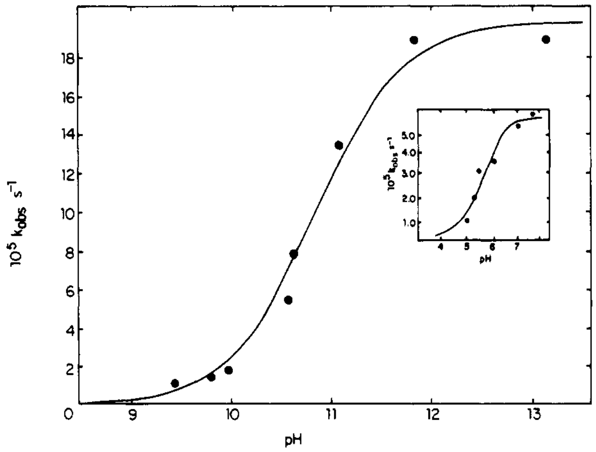

Figure 1. First-order rate constants for the reactions of 1(HOMe) and 2(HCN) (inner frame) in 25% sulfolane in H_2O (v/v) at 25 °C as a function of the pH.

Reactions of 1(HCN). This compound was found to be inert under basic conditions. Even after a 12-h incubation at pH 13.16, its UV spectrum remained unchanged with no indication of formation of either 1 or fluorenone. In order to show that the failure of 1(HCN) to eliminate HCN does not result from too low an acidity of its α-proton, the pK_a of 1(HCN) was spectroscopically determined. The $\lambda_{\max}$ of 1(HCN) is 262 nm. In its ionized form $1(CN)^-$) it shows a distinct absorption at 258.5 nm. Changes in the spectrum due to addition of acid or base were found to be completely reversible. Using eq 5 where

$$pK_a = pH - \log \frac{A - A_a}{A_b - A} \tag{5}$$

A is the observed OD at a given pH (A_a and A_b are the OD's measured in highly acidic and basic solutions (HCl and NaOH), respectively) the pK_a of 1(HCN) was determined. The results obtained from analysis at the three pHs, 9.25, 9.43, and 9.99 (Borax buffer), are 9.56, 9.53, and 9.69, respectively. Thus the pK_a value of 1(HCN) (9.6 ± 0.07) clearly indicates that the pH 13.16 it is completely ionized. Therefore its inability to undergo the HCN elimination is not due to an unexpectedly low acidity of 1(HCN) but rather to a relatively low value of k_{el}. On the basis of the assumed experimental error, the upper limit for k_{el} was estimated to be 10^{-7} s^{-1}.

Reactions of 2(HOMe). We were unable to prepare this compound. The method used to synthesize the substrates for the elimination reactions was nucleophilic addition of the leaving group to the olefins 1 or 2, followed by a mild acidification. Yet, 2 is not affected by a 1 M solution of NaOMe in MeOH at 25 °C. After 24 h no change was detected in its UV spectrum. Reflux of 2 in neutral or acidic methanol gave 100% recovered starting material. Nevertheless, a lower limit for k_{el} can be estimated as will be shown later.

Reactions of 2(HCN). The elimination of HCN from this compound was followed at 350 nm ($\lambda_{\max}$ of 2) over the pH range 5.06–7.44. Under these conditions the product (2) does not hydrolyze to fluorenone to any detectable extent. First-order rate constants are given in Table II. The change in the rate constant as a function of the pH also follows a sigmoid curve (Figure 1). Using the same nonlinear regression technique as was previously described

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(9) Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904.

(10) Wooley, E. M.; George, R. E. *J. Solution Chem.* **1974**, *3*, 119.

Table II. Rate Constants for the Elimination of HCN from 2(HCN) in 25% Aqueous Sulfolane at 25 °C as a Function of pH

pH	5.06	5.29	5.57	5.93	7.0	7.44
10^5k_{obsd}, s^{-1}	1.07	1.86	2.82	3.53	5.21	5.68

Table III. k_{el} and pK_a Values in 25% Aqueous Sulfolane at 25 °C

substrate	10^5k_{el}, s^{-1}	pK_a
1(HOMe)	20 ± 0.7	10.86 ± 0.05
1(HCN)	≤0.01	9.6 ± 0.07
2(HOMe)	$\geq 10^3$ (10^6)[a]	
2(HCN)	5.6 ± 0.15	5.62 ± 0.04
3		10.38 ± 0.04[b]

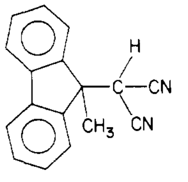
[a] See text. [b] 30% sulfolane–70% H_2O.

for eq 2, k_{el} and K_a were evaluated (Table III).

In light of the low pK_a (5.62) measured for 2(HCN), we have determined the pK_a of its methyl analogue **3**. This was performed by measuring the pH of partially neutralized solutions of **3**. Due to its low solubility in 25% sulfolane–water, the pK_a of **3** was determined in a solution of 30% sulfolane in water. (A calibration curve for this sulfolane concentration was used). Knowing the initial concentrations of OH^- and **3** and the resulting final concentration of OH^-, the pK_a of **3** was calculated by using eq 6; pK_a values of 10.38, 10.43, 10.38, and 10.33 were

$$pK_a = pH + \log \frac{[OH^-]_0 - [OH^-]}{[3]_0 - ([OH^-]_0 - [OH^-])} \tag{6}$$

obtained for experiments in which the initial pH of the solutions were in the range 11.1–11.4.



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Discussion

Although we were unable to prepare 2(HOMe), which was one of our four target molecules, the lower limit for its k_{el} value can be estimated in the following way: As previously mentioned we were unable to detect any addition of MeO^- to **2** in a 1 M solution of MeO^- in MeOH. This is most likely due to the fact that the addition equilibrium (eq 7) lies largely to the left. Since this compound as well as other malononitrile derivatives undergo relatively easily alkaline hydrolysis,[11] there is no reason to assume that **2** does not undergo nucleophilic attack by oxygen nucleophiles such as MeO^-. In order to obtain k_{el}, the equilibrium constant k_{add}/k_{el} of eq 7 and k_{add} must be evaluated first. Since no change in the UV spectrum of the equilibration mixture was observed, the upper limit for the conversion is at most 1% (estimated from the line width of the recorded spectrum). This leads to an equilibrium constant $<10^{-2}$ M^{-1}. k_{add} can be evaluated from the modified[9,12,13] Richie equation (eq 8), which as we have

$$2 + MeO^- \underset{k_{el}}{\overset{k_{add}}{\rightleftharpoons}} 2(OMe)^- \tag{7}$$

$$\log k/k_0 = S_+N_+ \tag{8}$$

shown[9,13] is capable of accommodating nucleophilic attack on activated double bonds including **2** itself. The value of N_+ for MeO^- (MeOH) is 6.27, S_+ for **2** is 1.29, and log $k_0 = -7.09$. Thus using these data in combination with eq 8 gives k_{add} (in MeOH) of 9.8 M^{-1} s^{-1}. Assuming that k_{add} and k_{el} are of similar magnitude in MeOH as well as in 25% sulfolane–water, the lower limit for k_{el} is calculated to be 10^3 s^{-1}.

Another procedure for approximating k_{el} for $2(OMe)^-$ is based on the nucleofugality scale developed by Stirling.[14] This scale is based on elimination reactions from β-substituted nitriles, sulfones, etc. (which are also considered as nondelocalizing groups). Stirling[14] reports that k_{el} of alkoxides is larger than that of CN^- by at least 11 orders of magnitude. Since k_{el} for $2(CN)^-$ was determined as 5.6 × 10^{-5} s^{-1}, k_{el} for $2(OMe)^-$ will therefore be about 5.6 × 10^6 s^{-1}. The conclusion from these two independent estimation procedures is that k_{el} for $2(OMe)^-$ is indeed very large and is at least 7 orders of magnitude larger than k_{el} for $1(OMe)^-$. Since $1(CN)^-$ essentially does not expel CN^- whereas $2(CN)^-$ does so relatively fast, it is clear that in these systems the expulsion of the leaving group is more efficient from the cyano-stabilized carbanions (localized) than from the nitro-stabilized carbanion (delocalized). It should be pointed out that k_{el} is not likely to be significantly affected by the stability of the formed double bond since, as we have previously reported,[9] **2** is more reactive toward nucleophiles than **1** is by ca. 2 orders of magnitude.

In outlining the strategy for this work, it was mentioned in the introductory section that, in order to enable a "fair" comparison, the two families of substrates used were derivatives of CH_3NO_2 and $CH_2(CN)_2$ which have similar pK_as in aqueous solutions. The fact that the carbanions derived from 2(HLG) are more reactive (having larger k_{el}) than those derived from 1(HLG), in spite of being more stable as well (as can be judged from their acidities, see Table III), further strengthens our aforementioned conclusion.

Charge Delocalization by the Activating Groups. It is generally believed that while the nitro group is capable of delocalizing the negative charge onto the oxygen atoms, in the case of the cyano group a relatively large amount of the negative charge resides on the α-carbon.[15] The pK_as of 1(HCN) and 2(HCN) also provide some support for this assumption. Thus, in the case of the nitro group where the charge is highly delocalized from the α-carbon onto the oxygen atoms, a β electron withdrawing substituent is not expected to significantly affects its stability and therefore the pK_a of its conjugated acid. Indeed, the pK_a of 1(HCN) is close to that of nitromethane ($\Delta pK_a = 0.6$). On the other hand, in cases where the charge is largely localized on the α-carbon (cyano-activated acids), a neighboring β substituent is more likely to affect the carbanion stability. Again this was manifested by 2(HCN) whose pK_a is much smaller than that of malonitrile ($\Delta pK_a = 5.6$). This increased acidity exhibited by tricyanoethanes was also observed by other groups.[3a] In order to exclude the possibility that the unexpected high acidity of 2(HCN) originates from steric effects, the pK_a of **3** was determined and was found to be close to that of malononitrile ($\Delta pK_a = 0.8$).

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(11) (a) Patai, S.; Rappoport, Z. *J. Chem. Soc.* **1962**, 383; *Ibid.* **1962**, 392. (b) Rappoport, Z. in "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley: London, 1964; Chapter 8. (c) Bernasconi, C. F. B.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

(12) Miller, K.; Scott, J. M. W.; Barnes, D. J.; Steel, F. J. P. *Can. J. Chem.* **1976**, *54*, 3312.

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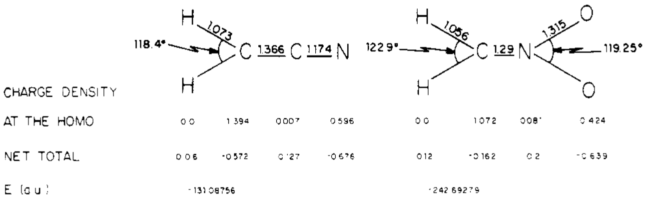

Figure 2. Geometrical parameters, energies, and charge densities at the HOMO level and net total for CH_2CN^- and $CH_2NO_2^-$. Charge densities when listed below two atoms (e.g., O,O or H,H) related to a single atom only.

Thus it is highly likely that the β-cyano group affects the acidity by interacting with the neighboring negative charge largely concentrated on the α-carbon.

The term delocalization, however, is not completely unambiguous since the negative charge can be delocalized by two different channels. The first of which is at the HOMO level (classic resonance), while the other operates via the rest of the available inner MOs. The enolate anion provides the classic example for the nonidentity of these two delocalization mechanisms.[16] In this case the overall negative charge density resides as expected mainly on the oxygen. On the other hand, the largest coefficient at the HOMO level is found on the α-carbon.[16] One of the first and major pieces of evidence in favor of the "localization theory" is the "normal" behavior (in the Eigen sense) displayed by cyano-activated carbon acids.[15,17] However, there is no clear indication as to whether the invoked localization relates to the HOMO or to the other electronic levels. It is worth noting that even the decrease in the pK_a observed in going from malononitrile (11.2)[8] to **2**(HCN), although indicating that charge is localized on the α-carbon, is not indicative as to electronic level in which the localization occurs. Both modes of localization can in principle lead to the same effect. Localization at the HOMO level will lead to stabilization of the anion by negative hyperconjugation[18] whereas localization at the other electronic levels will be largely affected by the polar inductive effect of the β-cyano group.

In order to shed some light on this problem we have performed some ab initio calculations on both cyano- and nitro-stabilized carbanions. Although the limitations of the "Mulliken population" are well recognized,[19] in the absence of a more straightforward and easy method of estimating charge densities we have employed the Mulliken population as the criterion in this comparative study. Using the same logic that guided us in the elimination reactions, namely, that the two substrates should be of the same acidity, we have chosen to compare $^-CH_2CN$ and $-CH_2NO_2$. This is because in the gas phase the free energy of the ionization (eq 9) of nitromethane ($R = NO_2$) is closer

$$RCH_3 \rightarrow RCH_2^- + H^+ \tag{9}$$

to that of acetonitrile ($R = CN$, $\delta\Delta G = 12$ kcal/mol) than to that of malonitrile ($\delta\Delta G = 22$ kcal/mol).[20] The calculations were performed by using a GAUSSIAN 80 program[21a] with a 4-31G basis set and full optimization procedures.[21a] Both anions were found to be planar with geometries (Figure 2) similar to those reported earlier in the literature.[22] The charge densities at the HOMO and the overall charge densities are given in Figure 2. The data clearly indicate that the charge is much more localized on the α-carbon both overall and at the HOMO level in $^-CH_2CN$ than in $^-CH_2NO_2$. The enolate anion[16] is therefore an intermediate case between these two anions as its HOMO is largely localized on the α-carbon as in $^-CH_2CN$, and the overall charge density resides largely on the oxygen atom as in $^-CH_2NO_2$.

It should be pointed out that the quantity "charge density" cannot be directly translated into energy terms. Estimates of the relative importance of inductive and resonance effects based on comparison of σ_I and σ_R for example are based on the energetics involved in the model reactions. Therefore and unfortunately, no straightforward correlation can be drawn between these two approaches.

Possible Origin of the Effect. The elimination rate constant (k_{el}) was found to be dependent on the nature of the activating group. It is orders of magnitude smaller in the case of nitro (**1**(HLG)) group than in the case of the cyano groups (**2**(HLG)). This study was limited to nitro and cyano as activating groups since other groups such as carbonyls, sulfones, etc., were not suitable for this study as they failed to meet the basic condition, namely, having similar acidity of the respective methano acids without inflicting large steric crowding.[23] Since this study involves only one example of each type, a general conclusion cannot be safely drawn. Nevertheless, one should try to provide an explanation regarding the different behavior displayed by these two groups. One explanation can be based on Klopman theory[24] regarding chemical reactivity. According to this theory the elimination step should be classified as an orbital-controlled reaction. Since at the HOMO the coefficients are larger on the α-carbon in the cyano derivatives and smaller in the nitro derivatives, the former should react faster as was indeed observed. Another parameter which will induce an effect in the same direction is the HOMO–LUMO energy gap between the reacting groups. Using electron affinity as a measure for the HOMO energy it is found that the latter decreases in the order $^-CH_2CN > ^-CH(CN)_2 > ^-CH_2NO_2$ (E_a values are 35, 45, and 54 kcal/mol, respectively.[20,25] Assuming that the σ^* of the C leaving group bond is similar in all systems, one can predict that the cyano derivatives will be more reactive than the nitro derivatives.

An alternative point of view could be the association of the sluggishness of the nitro derivatives in these reactions

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[23] Molecular models show a slight steric interaction between the NO_2 oxygen in **1** and the hydrogen on C-1 of the ring. However, the steric compression for the disulfone analogue which is of suitiable acidity, is considerably larger.

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with the general notion that in many reactions higher barriers are observed for annihilation as well as formation of highly delocalized carbanions.[26] However, this is more a classification approach rather than an explanation. It may well be that delocalization induces other phenomena such as enhanced solvation, which could be a major contributor to the observed effect.[9,11c,27]

Experimental Section

Syntheses. The following compounds were prepared according to published procedures. 9-(Nitromethylene)fluorene[28] (1), 9-(dicyanomethylene)fluorene[29] (2), 9-methoxy-9-(nitromethyl)fluorene[9] (1(HOMe)), 9-cyano-9-(nitromethyl)fluorene[9] (1(HCN)), 9-cyano-9-(dicyanomethyl)fluorene[29b] (2(HCN)), and 9-methyl-9-(dicyanomethyl)fluorene[30] (3). Attempts to prepare 9-methoxy-9-(dicyanomethyl)fluorene (2(HOMe)) were performed under neutral, acidic, and basic conditions. The results were analysed by TLC and UV spectroscopy; 0.1 g of 2 was dissolved in 25 mL of MeOH and refluxed for 2 h. Examination of the reaction mixture after cooling to room temperature showed no reaction of the starting material; 1 g of *p*-toluenesulfonic acid was added to the reaction vessel and the solution was refluxed for two additional hours. Again, only starting material was detected. The reaction under basic condition was performed in a UV cell at ambient temperature. The concentration of MeONa was 1 M. No reaction was observed.

Determination of the $\mathrm{p}K_a$ of 1(HCN). The $\mathrm{p}K_a$ was determined spectroscopically. Under acidic or neutral condition 1(HCN) showed λ_{max} at 262 nm. In basic solutions the extinction coefficient approximately doubled and the λ_{max} moved to a shorter wavelength, 258.5 nm. These changes are pH dependent and are completely reversible. The spectra were measured in buffered solutions (borax) which were then acidified with minute amounts of concentrated HCl followed by addition of concentrated NaOH. The absorbances at each stage (corrected for dilution) were used in eq 5 to calculate the $\mathrm{p}K_a$ of 1(HCN) where A, A_a, and A_b are the observed ODs in the buffered, acidic, and basic solutions, respectively.

Determination of the $\mathrm{p}K_a$ of 3. The $\mathrm{p}K_a$ was determined by a potentiometric method using a regular combined glass electrode in a 30% sulfolane-70% water solutions (due to the low solubility of 3 in 25% aqueous sulfolane). Four solutions each of ca. 5×10^{-3} M in 3 were partially neutralized with NaOH solutions. From the pH meter reading and a calibration curve, the H^+ concentrations were evaluated and were used to determine the $\mathrm{p}K_a$ of 3.

Kinetics. According to the pH ranges, the buffers used were phthalate, NaH_2PO_4, borax Na_2HPO_4, and KOH. The pHs were determined by using a combined glass electrode. The actual H^+ concentration in the reaction medium was calculated from a calibration curve (not shown). Before performing a kinetic run the reactions were followed by repetitive scanning (Perkin-Elmer Model 402 spectrometer) in the 250–510-nm range. The actual kinetics were studied at a single wavelength. (λ_{max} of the olefin, 355 nm for 1 and 350 nm for 2. At pH >13 the reaction of 1(HOMe) was followed at 258 nm, which is λ_{max} of the final product fluorenone.) The reactions were initiated by injection of the substrate in sulfolane solution with a micro syringe to the preincubated UV cell. The data were analyzed on-line via a PDP 11/40 minicomputer.

Registry No. 1 (HOMe), 86120-12-9; 1 (HCN), 86120-11-8; 2 (HOMe), 94620-62-9; 2 (HCN), 7009-36-1; 3, 6235-08-1; $CH_2NO_2^-$, 18137-96-7; CH_2CN^-, 21438-99-3.

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Cationic Cyclocodimerization. 3.[1] Syntheses of [3.3]Paracyclo(1,4)naphthalenophane and [3.3](1,4)Naphthalenophane Derivatives. Stereoselectivity Governed by the Structures of α-Naphthylmethylcarbenium Ion and 1-Vinylnaphthyl Moiety

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The cationic cyclocodimerization of 1-(4-vinylnaphthyl)-3-(*p*-vinylphenyl)propane and 1,3-bis(4-vinylnaphthyl)propane with 2-phenylpropene, indene, 1,1-diphenylethylene, and styrene gave [3.3]paracyclo(1,4)naphthalenophanes and [3.3](1,4)naphthalenophanes, respectively, in 11.5–53.6% yields. From the structures of carbophanes produced, it is concluded that the stereoselectivity shown in the cationic cyclocodimerization can be attributed to the structures of major conformers of α-naphthylmethylcarbenium ion and its parent 1-vinylnaphthyl moiety. The variable-temperature NMR spectroscopic analysis of some [3.3]paracyclo(1,4)naphthalenophanes and a [3.3](1,4)naphthalenophane showed that the activation energy for the flipping of the substituted methylene chain is not so affected by the steric hindrance of the peri hydrogens of the naphthalene rings.

Compared with reported methods for [3.3]paracyclo(1,4)naphthalenophanes[2] and [3.3](1,4)naphthalenophanes,[3,4] the usefulness of the cationic cyclocodimerization[5] was briefly communicated.[1] Further study on the construction of these carbophanes revealed several new aspects, so we would like to report the synthesis, the stereoselectivity of the reaction and its origin,

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