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Reactions of 9-Substituted Fluorenide Carbanions with Allyl Chlorides by S_N2 and S_N2' Mechanisms

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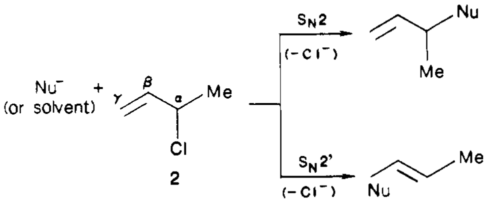
Abstract: The average ratio of S_N2 rate constants for benzyl chloride vs. allyl chloride reacting with 9-substituted fluorenide carbanions, 9-G-Fl$^-$ (G = Me, PhS, Ph, *o*-tol, or *t*-Bu), in Me_2SO solution is 2.3, which is close to the ratio previously observed for reactions of smaller nucleophiles with more localized charges, such as iodide ion, in various solvents. Brønsted plots of log *k* vs. pK_{HA} (both in Me_2SO) are used to calculate reactivity values (*r*) for 9-G-Fl$^-$ ions of the same basicity reacting with allyl chloride. The *r* values reveal the same order of steric effects for G in these S_N2 reactions as was found previously for benzyl chloride, i.e., Me < Ph < *o*-tol < *t*-Bu, but the effects are slightly smaller for allyl chloride. The second-order rate constants for reactions with four families of 9-G-Fl$^-$ ions were found to increase progressively and appreciably with γ-methyl substitution, i.e., $CH_2{=}CHCH_2Cl$ (**1**) < $MeCH{=}CHCH_2Cl$ (**4**) < $Me_2C{=}CHCH_2Cl$ (**5**), whereas the Brønsted β values decreased progressively. The second-order rate constants for reactions with families of 9-G-Fl$^-$ ions were found to follow a somewhat different pattern for α-methyl substitution, i.e., $CH_2{=}CHCH_2Cl$ (**1**) > $CH_2{=}CHCH(Me)Cl$ (**2**) $\approx$ $CH_2{=}CHC(Me)_2Cl$ (**3**); the rate differences were small, but the β values again decreased progressively. Product studies indicated that **1** reacts with 9-G-Fl$^-$ ions by an S_N2 mechanism but that **2** gives S_N2' products in amounts increasing along the series G = Me, Ph, *o*-tol, *t*-Bu; **3** appears to give only S_N2' products. The rates of reactions of 9-CN-Fl$^-$ and 9-CO_2MeFl$^-$ ions with **3** to form S_N2' and S_N2 products are independent of the carbanion concentration. The first-order reaction of 9-CN-Fl$^-$ ion with *t*-BuCl in MeOH gives 17% yield of 9-CN-9-*t*-BuFl. Enthalpies of activation for S_N2 reactions of 9-G-Fl$^-$ ions reacting with **5** are 7–9 kcal/mol lower, and entropies of activation are 18, or more, eu units less positive than for S_N2' reactions of 9-G-Fl$^-$ ions with **3**. Mechanisms for S_N2' reactions are discussed in light of these findings.

In the 1950's detailed investigations of the reactions of allyl chloride (**1**) and its α- and γ-substituted derivatives were made by Young and his students[1] and by de la Mare and Vernon,[2] in hydroxylic, dipolar nonhydroxylic, and nonpolar solvents, both in the presence and absence of nucleophiles. Allylic chlorides were shown to react by a wealth of mechanistic pathways, including: (a) ionization by hydroxylic solvents in the absence of a nucleophile (S_N1), (b) bimolecular substitution by a nucleophile initiated by attack at either the α-position (S_N2) or the γ-position (S_N2'; giving a rearranged product), (c) elimination of HCl (E1 or E2), and (d) an intramolecular arrangement (S_Ni). The S_N2 and S_N2' mechanisms are illustrated in Scheme I for α-methylallyl chloride (**2**).

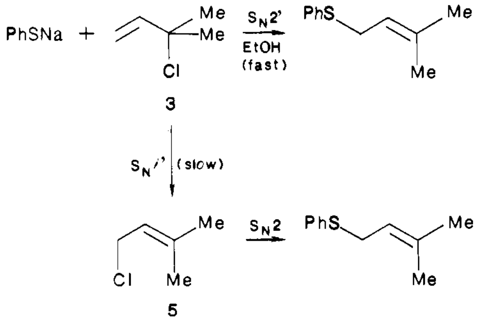
The S_N2 pathway was found to be preferred for reactions of **2** with most nucleophiles in most media. Restricting ourselves to examples where second-order kinetics were demonstrated and prior or subsequent rearrangements were ruled out, formation of S_N2' products appeared to be limited to just three types of nucleophiles: (a) $NaCH(CO_2Et)_2$ in EtOH (10% of S_N2' product),[1a] (b) R_2NH in various solvents of low dielectric constant, e.g., excess neat Et_2NH (>82% S_N2' product),[1b] and (c) Me_3N in acetone[1c] or benzene[1d] (ca. 70% S_N2' product and 30% S_N2 product in each instance). Sodium ethoxide[1e] or PhSNa[2c] in EtOH gave only S_N2 products with **2**.

The extent of S_N2' reaction was found to be increased, to at least some degree, by replacing the α-Me group in **2** by an α-*t*-Bu group[2a] or an α-chlorine atom,[2b] apparently because these groups retard the S_N2 pathway. Also, the corresponding tertiary chloride, $CH_2{=}CHC(Me_2)Cl$ (**3**) gave the S_N2' product with PhSNa in EtOH.[2c] The rate of the latter S_N2' reaction was about twice as fast as that of the S_N2 reaction of PhSNa with **2** in EtOH, suggesting that α-Me substitution accelerated the S_N2' process. It was conceivable that the S_N2' product from **3** and PhSNa could have been formed by an S_Ni' rearrangement followed by an S_N2 reaction since the S_Ni' rearrangement has been shown to occur by an intramolecular mechanism, probably involving a bridged chloronium ion intermediate,[3] during acetolysis of **3**[1b] and during solvolysis of **3** in 75% aqueous EtOH.[2c] Rearrangement of **3** is slow in EtOH, however, and does not occur under the conditions where S_N2' products were formed from **3**.[2d] These results are summarized in Scheme II.

Scheme I



Scheme II



In 1956 Stork and White showed that reaction of neat excess piperidine with the 2,6-dichlorobenzoate of *trans*-6-isopropyl-2-cyclohexen-1-ol at 130 °C gave an S_N2' product by a syn displacement.[4a] This result was later confirmed and extended to

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(1) (a) Kepner, R. E.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 115–119. (b) Young, W. G.; Webb, I. D.; Goering, H. L. *Ibid.* **1951**, *73*, 1076–1084. (c) Young, W. G.; Clement, R. A.; Shih, C.-H. *Ibid.* **1955**, *77*, 3061–3066. (d) Young, W. G.; Wilk, I. J. *Ibid.* **1957**, *79*, 4793–4795. (e) DeWolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753–901.

(2) (a) de la Mare, P. B. D.; Hughes, E. D.; Merriman, P. C.; Pichat, L.; Vernon, C. A. *J. Chem. Soc.* **1958**, 2563–2566. (b) de la Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc.* **1952**, *3325*–3334, 3628–3631. (c) de la Mare, P. B. D.; Vernon, C. A. *Ibid.* **1953**, 3555–3559; **1954**, 2504–2510. (d) de la Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc. B* **1971**, 1699–1700.

(3) Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571–752. Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962.

(4) (a) Stork, G.; White, W. N. *J. Am. Chem. Soc.* **1956**, *78*, 4609–4619. (b) Stork, G.; Kreft, A. F. III. *J. Am. Chem. Soc.* **1977**, *99*, 3850–3851. (c) Dobbie, A. A.; Overton, K. H. *J. Chem. Soc., Chem. Commun.* **1977**, 722–723.

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Table I. Rate Constants for Reactions of Benzyl and Primary Allylic Chlorides with 9-Substituted Fluorenide Carbanions (9-G-Fl$^-$) in Me$_2$SO at 25 °C

	pK_a^{a}	105^b (M^{-1} s^{-1})			
		CH$_2$=CHCH$_2$Cl	MeCH=CHCH$_2$Cl	Me$_2$C=CHCH$_2$Cl	PhCH$_2$Cl
9-MeFl$^-$	22.3	180			490
2-Cl-9-MeFl$^-$	20.0	30			89
2,7-Br$_2$-9-MeFl$^-$	17.7	4.2			16.5
		(β = 0.35)			(β = 0.31)
9-*t*-BuFl$^-$	24.3	4.25	17	109	4.71
2-Br-9-*t*-BuFl$^-$	21.7	0.51	3.5	29.9	0.78
2,7-Br$_2$-9-*t*-BuFl$^-$	19.4	0.088	0.71	7.93	0.17
		(β = 0.34)	(β = 0.28)	(β = 0.23)	(β = 0.29)
9-*o*-tol-Fl$^-$	18.8	0.17	1.45		0.201
9-*p*-MeSO$_2$-*o*-tol-Fl$^-$	16.9	0.0245	0.26		0.0452
		(β = 0.45)^c	(β = 0.40)^c		(β = 0.35)^c
9-*p*-tol-Fl$^-$	18.3	4.35	28	230	9.0
9-Ph-Fl$^-$	17.9	2.8	19	165	6.1
9-*m*-ClC$_6$H$_4$Fl$^-$	16.8	0.94	6.6	59.6	2.6
9-*p*-MeSO$_2$C$_6$H$_4$Fl$^-$	15.1	0.20			0.64
		(β = 0.43)	(β = 0.41)	(β = 0.39)	(β = 0.36)
9-PhS-Fl$^-$	15.4	1.05	6.1	61.7	2.5
9-*p*-BrC$_6$H$_4$S-Fl$^-$	14.8	0.68	4.2	43.4	1.7
2-Br-9-PhS-Fl$^-$	13.2	0.17	1.3	15.0	0.56
2,7-Br$_2$-9-PhS-Fl$^-$	11.15		0.27	4.6	0.19
		(β = 0.36)^d	(β = 0.32)^d	(β = 0.27)^d	(β = 0.31)
9-CO$_2$Me-Fl$^-$	10.35		0.66	6.9	0.27
9-CN-Fl$^-$	8.3			2.1	0.057

^{a}pK_a of 9-G-FlH; see ref 9. ^{b}The result of two or more runs reproducible to ±10% or better. ^{c}Two-point β value. ^{d}Two- or three-point β excluding the 9-*p*-BrC$_6$H$_4$S-Fl$^-$ point. The β_{NU} values including this point are, however, only 0.01 unit higher.

the corresponding *trans*-2,4,6-trimethylbenzoate, which gave 92% of syn S$_N$2′ product; the cis isomer also gave syn S$_N$2′ product (80%) accompanied by 20% S$_N$2 product. Somewhat different results were obtained with *n*-PrSNa nucleophile in refluxing *n*-butyl alcohol where major amounts of S$_N$2 product were formed.[4b] The (minor) S$_N$2′ product from the trans ester was again formed predominantly by syn displacement (~9:1), but the cis isomer gave an excess of anti displacement (anti:syn = 65:35).[5] The successful realization of the S$_N$2′ pathway in these examples apparently depends on (a) the use of R$_2$NH and RSNa type nucleophiles, (b) use of a poor leaving group, which retards (but does not exclude) the S$_N$*i*′ pathway, and (c) the presence of the 6-isopropyl group which retards the S$_N$2 reaction. For anionic nucleophiles it is possible that the stereochemistry is affected by the nature of the counterion since these experiments were carried out in solvents of low dielectric constant.

It was clear from these results that the S$_N$2′ pathway could be realized only by use of certain types of nucleophiles with substrates where the S$_N$2 pathway was inhibited. Later work confirmed these conclusions. A study of reactions of chloride ion with a cyclic analogue of **2**, optically active 5-methyl-2-cyclohexenyl chloride in acetonitrile, where cis–trans isomerization, isotopic exchange of chloride ion, and racemization can occur simultaneously, led to the conclusion that neither syn- nor anti-S$_N$2′ mechanisms are important.[7] A similar study of isotopically labeled chloride ion reacting with **1** in acetonitrile showed that the rate of attack of Cl$^-$ ion at saturated carbon in allyl chloride is 3000–8000 times faster than attack at the π-bonded γ-carbon atom. Also, the latter attack is 200–600 times slower than that on *n*-propyl chloride.[8]

Recent measurements in our laboratory of rate constants in Me$_2$SO for S$_N$2 reactions of 9-substituted fluorenide carbanions, 9-G-Fl$^-$, with PhCH$_2$Cl have shown that the rates decrease progressively for changes in G in the order Me > PhS > Ph > *o*-tol > *t*-Bu, when comparisons were made at equal carbanion basicities.[9] Since these rate changes, which cover a 2.6 log unit span, are believed to be caused by increased steric hindrance in the nucleophile, it was of interest to see whether S$_N$2 reactions with **2** and some of these carbanions could be inhibited to the point where S$_N$2′ reactions could be brought to the fore. Studies with these carbanions in Me$_2$SO offer several advantages in differentiating S$_N$2, S$_N$2′, and S$_N$*i*′ pathways: (a) carbanions with a wide range of basicities and steric effects are available;[10] (b) the Me$_2$SO solvent greatly enhances the nucleophilicity of the carbanion, relative to hydroxylic solvents; (c) reactions with fluorenide carbanions are free of counterion effects with K$^+$; (d) ionization of the C–Cl bond is inhibited, relative to hydroxylic solvents, preventing interference from the S$_N$*i*′ mechanism; and (e) carbanions exhibit an unusually strong tendency to effect substitution rather than elimination in reactions with alkyl halides.[11] In the present paper we will first examine the effect of increasing steric hindrance in the 9-G-Fl$^-$ ion on rates of reactions with allyl chloride and compare these results with those on benzyl chloride. Next we will examine the effect of γ-methyl substitutions on the rates of reactions with 9-G-Fl$^-$ ions. Finally we will show that for reactions of 9-G-Fl$^-$ ions with the allylic chlorides **2** and **3**, S$_N$2′ substitutions often compete successfully with S$_N$2 and E2 pathways and present information relative to the mechanisms of these reactions.

Results and Discussion

Steric Effects in Reactions of Nine-Substituted Fluorenide Carbanions (9-G-Fl$^-$) with Allyl and Benzyl Chlorides. The second-order rate constants for reactions of CH$_2$=CHCH$_2$Cl and PhCH$_2$Cl with six families of 9-G-Fl$^-$ ions are summarized in Table I.

A comparison of the rate constants for the reactions of members of the 9-Me-Fl$^-$ ion family with benzyl chloride (Bz) vs. allyl chloride (Al) shows that the k^{Bz}/k^{Al} rate constant ratio decreases progressively as the family members become more basic (k^{Bz}/k^{Al} = 3.9 for 2,7-Br$_2$-9-MeFl$^-$, 3.0 for 2-Cl-9-MeFl$^-$, and 2.7 for 9-MeFl$^-$). The decrease is caused by a greater sensitivity of the

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(5) A difference in stereochemistry with a change in nucleophile donor atom has also been observed for intramolecular S$_N$2′ processes where anti displacement has been observed for a thianion nucleophile with an ester leaving group,[6a] whereas syn displacement has been observed with a carbanion nucleophile and an epoxide leaving group.[6b]

(6) (a) Stork, G.; Kreft, A. J. III. *J. Am. Chem. Soc.* **1977**, *99*, 3851–3853. (b) Martel, J.; Toromanoff, E.; Mathieu, J.; Nominé, G. *Tetrahedron Lett.* **1972**, 1491–1496.

(7) Lesnini, D. G.; Buckley, P. D.; Noyes, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 668–678.

(8) Hemmingson, J. A.; England, B. D. *J. Chem. Soc. B* **1971**, 1347–1352.

(9) (a) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2206–2215. (b) Bordwell, F. G.; Hughes, D. L. *Ibid.* **1983**, *48*, 2216–2222. Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 7300–7309.

(10) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3114–3320, 3320–3325.

(11) Bordwell, F. G.; Mrozack, S. R. *J. Org. Chem.* **1982**, *47*, 3803–3805.

rate constants for allyl chloride to changes in the basicities of the carbanions than is true for benzyl chloride. (The Brønsted β values are 0.35 and 0.31, respectively.) Similar decreases in k^{Bz}/k^{Al} ratios are observed for the reactions of allyl and benzyl chlorides within other 9-G-Fl$^-$ ion families in Table I. The *average* k^{Bz}/k^{Al} ratios are as follows: 9-MeFl$^-$ ions, 3.2; 9-*t*-BuFl$^-$ ions, 1.5; 9-*o*-tol-Fl$^-$, 1.5; 9-PhFl$^-$ ions, 2.6; 9-PhS-Fl$^-$ ions, 2.7.[12] The overall average ratio of 2.3 differs but little from the average ratio of 3.0 for other types of nucleophiles in different types of media compiled by Streitwieser.[3] This result may seem surprising when one considers the large difference in size and degree of charge delocalization between fluorenide carbanions and the nucleophiles used by Streitwieser in determining the average (I$^-$ in Me$_2$CO; I$^-$ in EtOH; pyridine in EtOH; (H$_2$N)$_2$C=S in MeOH). It is consistent, however, with the observation that changes in relative rate constants with structural changes along the series *n*-BuBr, *i*-BuBr, *i*-PrBr, *c*-C$_6$H$_{11}$Br for reactions with the 9-MeFl$^-$ ion family are remarkably similar to those for I$^-$ ion or N$_3^-$ ion,[11] and this, together with other evidence, indicates that flat, delocalized carbanions of different sizes have comparable reactivities when measured at the same basicity.[9b]

Brønsted plots of log *k* vs. pK_{HA} for 9-MeFl$^-$, 9-PhS-Fl$^-$, 9-PhFl$^-$, 9-*o*-tol-Fl$^-$, and 9-*t*-BuFl$^-$ ion families reacting with CH$_2$=CHCH$_2$Cl give a series of nearly parallel lines displaced to varying degrees from one another. A similar pattern was observed previously for Brønsted plots of data for S$_N$2 reactions of PhCH$_2$Cl with these and other 9-G-Fl$^-$ ion families. The displacements of the lines are caused by changes in steric and electronic effects of G relative to Me in the 9-MeFl$^-$ ion family, which has been adopted as a reference standard wherein G exerts minimal steric and electronic demands.[9b] Brønsted plots for PhCH$_2$Cl and for CH$_2$=CHCH$_2$Cl reacting with several 9-G-Fl$^-$ ion families are compared in Figure 1.

Examination of Figure 1 shows that the line for the 9-PhS-Fl$^-$ ion family reacting with PhCH$_2$Cl is essentially an extension of the 9-MeFl$^-$ ion family reference line. The displacements of the 9-Ph-Fl$^-$ and 9-*t*-BuFl$^-$ ion family lines to the right of these lines are caused by steric effects brought about by protrusion of parts of the 9-Ph and 9-*t*-Bu substituents from *both* sides of the flat fluorenide ion ring.[9] The lines for 9-MeFl$^-$, 9-PhFl$^-$, and 9-*t*-BuFl$^-$ ion families reacting with CH$_2$=CHCH$_2$Cl show a similar relationship, but the displacements of the 9-PhFl$^-$ and *t*-BuFl$^-$ ion family lines from the 9-MeFl$^-$ ion line are not as large (solid lines in Figure 1). These lines also have consistently larger slopes.

The displacement of the lines in Figure 1 for reactions of 9-G-Fl$^-$ ions of equal basicity with PhCH$_2$Cl or CH$_2$=CHCH$_2$Cl can be expressed as reactivity (*r*) values by means of eq 1, where ΔpK_a

$$r = \beta(\Delta pK_a) - \log (k^{Me}/k^{G}) \qquad (1)$$

= pK_a (9-MeFlH) − pK_a (9-G-FlH).[9b] For PhCH$_2$Cl the *r* values, calculated with $\beta = 0.31$, are as follows: (0.0), −0.15, −0.58, −2.2, and −2.6 for G = Me, PhS, Ph, *o*-tol, and *t*-Bu, respectively.[9b] The progressively more negative values for Ph, *o*-tol, and *t*-Bu, relative to Me, provide quantitative estimates of the size of the steric effects in the carbanion on the rates of the S$_N$2 reactions. For CH$_2$=CHCH$_2$Cl, the *r* values, calculated with $\beta = 0.39$ (an average value) are as follows: (0.0), 0.46, −0.09, −1.7, and −2.4, for Me, PhS, Ph, *o*-tol, and *t*-Bu, respectively. The less negative *r* values for CH$_2$=CHCH$_2$Cl than PhCH$_2$Cl for reactions with 9-PhFl$^-$, 9-*o*-tol-Fl$^-$, and 9-*t*-Bu-Fl$^-$ indicate less steric hindrance in the S$_N$2 reactions of 9-G-Fl$^-$ ions with allyl chloride. The change in sign of *r* for the PhS substituent corresponds to a reversal in the relative positions of the 9-MeFl$^-$ and 9-PhS-Fl$^-$ lines in the reactions with CH$_2$=CHCH$_2$Cl and PhCH$_2$Cl (Figure 1). The effect of the PhS group is believed to be a composite of a rate accelerating electronic (polarization) effect and a rate retarding steric effect.[9b] The steric effect dominates in reactions with PhCH$_2$Cl, leading to a retarding effect relative to 9-Me-Fl$^-$ ions of the same basicity, but in reactions with CH$_2$=CHCH$_2$Cl the electronic effect is dominant, leading to an accelerating effect. A positive *r* value has also been observed for the reaction of the 9-PhS-xanthenide ion with PhCH$_2$Cl.[9b]

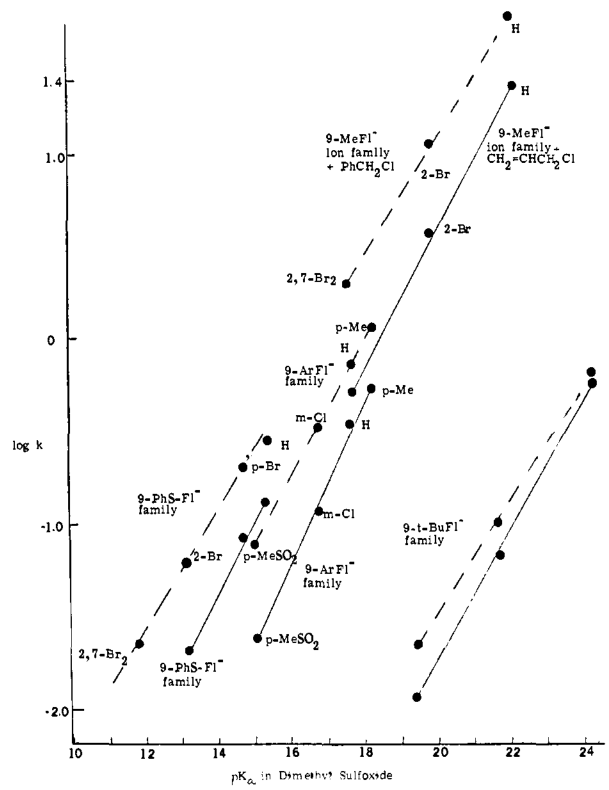
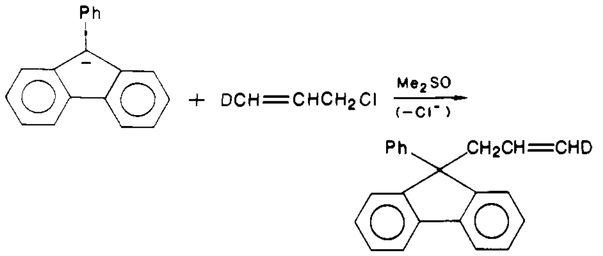


Figure 1. Plots of rate constants (log *k*) for reactions of 9-substituted fluorenide carbanions, 9-G-Fl$^-$, with benzyl chloride (---) and allyl chloride (—).

An NMR analysis of the product formed from the reaction of γ-*d*-allyl chloride with 9-Ph-Fl$^-$ showed that the reaction followed an S$_N$2 rather than an S$_N$2′ pathway (eq 2).[12]



(2)

γ-Methyl Effects on the Rates of Reactions of 9-G-Fl$^-$ Ions with Primary Allylic Chlorides. The rate data summarized in Table II show that for the reactions of 9-PhS-Fl$^-$, 9-Ph-Fl$^-$, and 9-*t*-BuFl$^-$ ion families with MeCH=CHCH$_2$Cl vs. CH$_2$=CHCH$_2$Cl the γ-Me substituent causes average rate accelerations of six-, seven-, and sixfold, respectively.[13] The presence of a second γ-Me substituent (Me$_2$C=CHCH$_2$Cl) causes a further rate acceleration in each instance, bringing the total effect to 70-, 58-, and 55-fold, respectively. These γ-methyl accelerating effects are similar to, but somewhat larger than, the effects of γ-methyl substitution observed for S$_N$2 reactions of MeCH=CHCH$_2$Cl vs. CH$_2$=CHCH$_2$Cl with NaOEt in EtOH or KI in acetone, as is brought out by the comparisons in Table II. Once again we see that these large delocalized carbanions respond to substituent effects in a manner very much like small localized ions.

The progressive rate accelerations observed along the series CH$_2$=CHCH$_2$Cl (**1**), MeCH=CHCH$_2$Cl (**4**), Me$_2$C=CHCH$_2$Cl (**5**) are accompanied by a progressive decrease in

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[12] The small k^{Bz}/k^{Al} ratios observed for the reactions of 9-*o*-tol-Fl$^-$ and 9-*t*-BuFl$^-$ ions suggest that some S$_N$2′ reaction may be occurring when these ions react with allyl chloride.

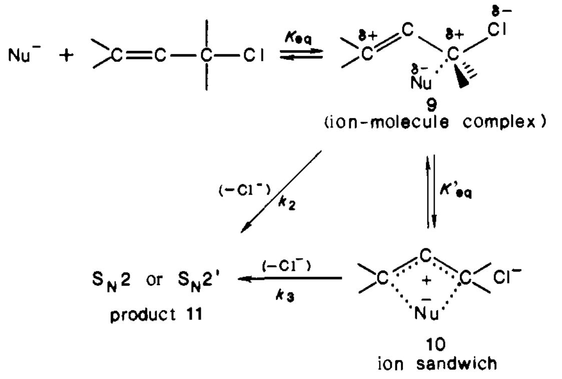
[13] Since the β values for various 9-G-Fl$^-$ ions reacting with CH$_2$=CHCH$_2$Cl and MeCH=CHCH$_2$Cl differ somewhat (Table I), the rate acceleration varies somewhat depending on the basicity chosen for comparison. For example, the rate ratios for the 9-PhS-Fl$^-$ ion family calculated from the data in Table I are the following: 5.8, 6.2, and 7.6 (average = 6.5).

Table II. γ-Methyl Effects on Rate of S_N2 Reactions of Primary Allylic Chlorides with Various Anionic Nucleophiles (Nu^-)

	relative rates		
Nu^- (solvent)	$CH_2{=}CHCH_2Cl$	$MeCH{=}CHCH_2Cl$	$Me_2C{=}CHCH_2Cl$
EtO^- (EtOH)[a]	(1.0)	4.4	17
I^- (Me_2CO)[a]	(1.0)	1.6	28
9-PhS-Fl$^-$ (Me_2SO)[b]	(1.0)	6.5[c]	70[c]
9-Ph-Fl$^-$ (Me_2SO)	(1.0)	6.7[c]	58[c]
9-*o*-tol-Fl$^-$ (Me_2SO)	(1.0)	9.5[c]	
9-*t*-Bu-Fl$^-$ (Me_2SO)	(1.0)	6.3[c]	58[c]

[a] Reference 3. [b] The rate for allyl chloride reacting with 9-PhS-Fl$^-$ in Me_2SO is about 10^3 times that for KI in Me_2CO or NaOEt in EtOH obtained from ref 3. [c] These are average values for the family.

Scheme III. Ion-Molecule Dipole and Ion Sandwich Mechanisms

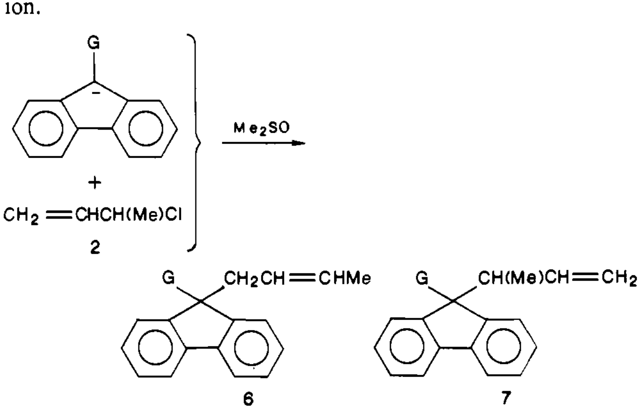


Brønsted β for each family (9-*t*-BuFl$^-$ ions: 0.34, 0.28, 0.23; 9-*o*-tol-Fl$^-$ ions: 0.45, 0.40; 9-PhFl$^-$ ions: 0.43, 0.41, 0.39; 9-PhS-Fl$^-$ ions: 0.36, 0.32, 0.27). These β values are not highly accurate since they are derived from three-point plots (two points for the *o*-tol-Fl$^-$ ion family). The trend is consistent, however. There is also a consistent trend in β values for these 9-G-Fl$^-$ ion families reacting with $CH_2{=}CHCH_2Cl$ vs. $PhCH_2Cl$ (higher for allyl chloride by an average of 0.07 unit; Table I). The higher β for allyl chloride shows that the rates for allyl chloride (log k) are more sensitive to changes in the basicities of 9-G-Fl$^-$ ions than are the rates for benzyl chloride. Substitution of a γ-methyl group causes a decrease in β by an average of 0.04 units and the presence of a second γ-methyl results in a further decrease in β. Product analyses of the reactions of 9-Ph-Fl$^-$ with $CH_3CH{=}CHCH_2Cl$ and $(CH_3)_2C{=}CHCH_2Cl$ showed that only S_N2 products were formed.

The rate accelerations observed for γ-methyl substitution in allyl chloride are similar to those observed for *o*-, *m*-, and *p*-methyl substitution in $PhCH_2Cl$ but larger in size. For example, *o*-, *m*-, and *p*-methyl substituents in $PhCH_2Cl$ cause rate accelerations in reactions with 9-PhFl$^-$ ion of 2.5-,[14] 1.7-,[10] and 1.1-fold,[10] respectively, compared to 6.8-fold for a γ-Me substituent in allyl chloride. The latter effect is twice that of the (more strongly electron donating) *p*-MeO substituent in benzyl chloride.[10] The alkene π system is clearly better at transmitting these electron donor effects than is the benzene π system. The decrease in β caused by γ-Me substituents in allyl chloride is also similar to that brought about by the presence of donor substituents in benzyl chloride. For example, for reactions of the 9-PhFl$^-$ ion family β decreases from 0.365 for $C_6H_5CH_2Cl$ to 0.30 for *p*-$MeOC_6H_4CH_2Cl$.

Reactions of 9-G-Fl$^-$ Carbanions with $CH_2{=}CHCH(Me)Cl$ (2) and $CH_2{=}CHC(Me)_2Cl$ (3). Reaction of 9-PhFl$^-$ ion with 3-chloro-1-butene (**2**) gave a mixture of two products (in a ratio of 65:35, according to NMR analysis) which were separated by column chromatography. The major product **6** was found to be identical with that obtained from the reaction of 9-PhFl$^-$ ion with $MeCH{=}CHCH_2Cl$, which means that it was formed by an S_N2' pathway. The NMR spectrum of the isomeric minor product showed it to be 9-(1-methyl-2-propenyl)-9-phenylfluorene (**7**, G = Ph), an S_N2 product.

A mixture of products was also obtained by the reaction of 9-MeFl$^-$ ion with **2**. This mixture could not be separated by column chromatography, however. NMR analysis indicated that it consisted of about 30% S_N2' and 70% S_N2 product. Reaction of 9-*o*-Tol-Fl$^-$ ion or 9-*t*-BuFl$^-$ ion with $CH_2{=}CHCH(Me)Cl$ (**2**) gave only S_N2' products. (Some E2 reaction occurs, however, as indicated by recovery of about 10% of 9-*o*-tol-FlH and 9-*t*-BuFlH.) The S_N2' product, 9-*tert*-butyl-9-(2-butenyl)fluorene (**6**, G = *t*-Bu), formed in the reaction of *t*-BuFl$^-$ ion with **2** was shown by mp and NMR spectrum to be the same as (the S_N2 product) formed from the reaction of $MeCH{=}CHCH_2Cl$ with 9-*t*-BuFl$^-$ ion.



G	%S_N2'	+	G	%S_N2
Me	30		Me	70
Ph	65		Ph	35
o-tol	100		*o*-tol	0
t-Bu	100		*t*-Bu	0

Reaction of 9-PhFl$^-$ ion with **3** gave an S_N2' product **8** identical with the S_N2 product formed from a comparable reaction with **5**. No rearrangement of **3** to **5** occurred under these conditions, however, ruling out the possibility that **8** is formed from **3** via **5**.

The Effect of α-Branching on S_N2 and S_N2' Rates for Reactions of Allyl Halides. Comparisons of S_N2 rates for $CH_2{=}CHCH_2Cl$ (**1**) vs. $CH_2{=}CHCH(CH_3)Cl$ (**2**) reacting with NaOEt in EtOH and with LiCl in acetone show 20- and 37-fold retarding effects, respectively, presumably due to steric effects.[3] On the other hand, examination of Table III shows that the rate ratios, k^1/k^2, average only about 2 for five 9-G-Fl$^-$ ion families reacting with these allylic substrates. The shift from an S_N2 to an S_N2' mechanism for **2** is no doubt one of the principal causes of this smaller ratio. This conclusion is supported by the observation that the highly hindered 9-*o*-tol-Fl$^-$ and 9-*t*-BuFl$^-$ ions (r = −1.7 and −2.4, respectively toward allyl chloride), which react with **2** entirely by an S_N2' mechanism have slightly *smaller* k^1/k^2 ratios than the less hindered 9-PhS-Fl$^-$, 9-MeFl$^-$, and 9-PhFl$^-$ ions (r = 0.46, 0.0, and −0.09, respectively). This trend is continued for rates of reactions of **2** vs. the tertiary chloride, $CH_2{=}CHC(Me)_2Cl$ (**3**), which reacts only slightly slower by S_N2' mechanisms with 9-G-Fl$^-$ carbanions than does **2** by mixed S_N2 and S_N2' mechanisms (k^3/k^2 for 9-*t*-BuFl$^-$, 9-PhFl$^-$, and 9-PhS-Fl$^-$ ions are 0.9, 0.8, and 0.8, respectively). The S_N2' k^3/k^2 ratios are 0.9 for *t*-BuFl$^-$ ion and 1.1 for 9-PhFl$^-$ ion, indicating that the switch from S_N2 for **2** to S_N2' for **3** is caused primarily by retardation of the S_N2 reaction. Comparison of rates for S_N2' reactions of 9-*t*-BuFl$^-$, 9-PhFl$^-$, and

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(14) Hughes, D. L. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1981.

Table III. Rate Constants for Reactions of 3-Chloro-1-butene and 3-Chloro-3-methyl-1-butene with Substituted Fluorenide Carbanions (9-G-Fl$^-$) in Me_2SO at 25 °C

		$10k^b$ (M^{-1} s^{-1})			
9-G-Fl$^-$	pK_a^{a}	$CH_2{=}CHCH(Cl)CH_3$	$CH_2{=}CHC(Cl)(CH_3)_2$	$(k^{1°}/k^{2°})^{c,e}$	$(k^{3°}/k^{2°})^{c,f}$
9-MeFl$^-$	22.3	44			
2-Cl-9-MeFl$^-$	20.0	9.7		3.2	
2,7-Br_2-9-MeFl$^-$	17.7	1.7			
		(β = 0.31)			
9-*t*-BuFl$^-$	24.3	2.0	1.9	1.7	0.9
2-Br-9-*t*-BuFl$^-$	21.7	0.335			
2,7-Br_2-9-*t*-BuFl$^-$	19.4	0.064			
		(β = 0.30)			
9-*o*-tol-Fl$^-$	18.8	0.13		1.2	
9-*p*-$MeSO_2$-*o*-tol-Fl$^-$	16.9	0.024			
		(β = 0.39)			
9-*p*-tol-Fl$^-$	18.3	2.1	1.6		
9-Ph-Fl$^-$	17.9	1.4	0.94	1.9	0.8^d
9-*m*-ClC_6H_4Fl$^-$	16.8	0.47	0.46		
9-*p*-$MeSO_2C_6H_4$Fl$^-$	15.1	0.12			
		(β = 0.39)	(β = 0.34)		
9-PhS-Fl$^-$	15.4	0.37	0.20		
9-*p*-BrC_6H_4S-Fl$^-$	14.8	0.25	0.17	2.6	0.8
2-Br-9-PhS-Fl$^-$	13.2	0.071	0.088		
		(β = 0.33)	(β = 0.17)		

[a] pK_a of 9-G-FlH; see ref 9. [b] The result of two or more runs reproducible to ±5%. [c] Average ratios; $k^{1°}$ is the rate constant for allyl chloride. [d] $k^{3°}/k^{2°}$ = 1.1 when only the rates of formation of S_N2' products are considered. [e] For $CH_2{=}CHCH(Cl)CH_3$. [f] For $CH_2{=}CHC(Cl)(CH_3)_2$.

9-PhS-Fl$^-$ ions with **3** shows that they are 2.2, 3.0, and 5.2 times slower, respectively, than the S_N2 reactions with **1**, and 57, 175, and 308 times slower, respectively, than with **5**, which gives the same product by an S_N2 reaction. Since 9-PhFl$^-$ ion gave only an S_N2 product with $DCH{=}CHCH_2Cl$, it would appear that the S_N2' reaction has been accelerated at least by 35-fold for one α-Me substitution and by 1.1-fold for the second.

Mechanisms of S_N2' Reactions. Fifteen years ago we concluded from a survey of the literature that attack by the nucleophile on an ion pair intermediate appeared to be the mechanism of choice for S_N2' reactions.[15,16] The results of de la Mare and Vernon, which show that α-methyl substitution (as in the change from **2** to **3**) favors C–Cl bond dissociation and also the S_N2' mechanisms with PhS$^-$ ion, are consistent with this view.[2] The present investigation of reactions of 9-G-Fl$^-$ carbanions with **2** and **3** provides further support. In Scheme III we present a general mechanism of this type for reactions of allylic chlorides with nucleophilic anions wherein an ion–molecule dipole complex **9** is formed reversibly in an initial state, followed by dissociation of the C–Cl bond to form an ion sandwich **10**, which collapses to the S_N2' product **11**. Alternatively, **9** can yield S_N2' or S_N2 products by synchronous formation of a Nu–C bond and breaking of the C–Cl bond. The partitioning of S_N2 and S_N2' products depends on the number and kind of substituents at the α- and γ-carbon atoms and on the nature of the nucleophile.

The size of β_{Nu}, which measures the sensitivity of the reaction to changes in Nu$^-$ ion basicity, is believed to be determined primarily by electrostatic interactions in the ion–molecule complex **9**.[9c] We have seen that progressive methyl substitution at either the α- or γ-carbon atom leads to a progressive decrease in β_{Nu}. (These effects are similar to, but larger than, the effects on β_{Nu} of introducing donor substituents into benzyl electrophiles.[9c]) γ-Methyl substitutions are accompanied by progressive rate increases, but α-methyl substitution are not. This is consistent with our observations of the effects of structural changes on β_{Nu} in S_N2 reactions, which indicate that there is no direct correlation between changes in β_{Nu} values and changes in rates.[9c] The rates are believed to be determined primarily by the second stage in the reaction where bonds are formed and broken. The difference in rate responses to α- and γ-methyl substitution points to a difference in mechanism at the second reaction stage, e.g., concerted S_N2 for $Me_2C{=}CHCH_2Cl$ (**5**) and ion sandwich formation, leading to S_N2' products, for $CH_2{=}CHC(Me)_2Cl$ (**3**). An increase in steric demands in the 9-G-Fl$^-$ ions reacting with $CH_2{=}CHCH(Me)Cl$ (**2**) evidently dictates a change from the concerted mechanism leading to S_N2 products to the ion sandwich mechanism leading to S_N2' products. For the concerted process, according to Scheme III, the overall rate depends on the product of K_{eq}, the equilibrium constant for ion–molecule complex formation, and k_2, whereas for the dissociation process the overall rate depends on the product of K_{eq}, K'_{eq}, and k_3. The question of the stereochemistry of S_N2' reactions needs additional study. The syn stereochemistry observed for R_2NH nucleophiles in weakly polar solvents may be dictated by intramolecular hydrogen bonding. For anionic nucleophiles the nature of the counterion may be important. The way is now open for a study of the stereochemistry with "free" carbanion nucleophiles, e.g., the reaction of 9-*t*-BuFl$^-$ ion with optically active *E*- and *Z*-$DCH{=}CHCH(Me)Cl$ in dilute Me_2SO solution with K^+ counterion needs to be examined. If the S_N2' reaction occurs by either of the mechanisms shown in Scheme III anti stereochemistry would be expected.

Solvolysis of $CH_2{=}CHCMe_2Cl$ (3) and $Me_2C{=}CHCH_2Cl$ (5). The relative ease of dissociation of the C–Cl bond in allylic chlorides increases with either α- or γ-methyl substitution, as indicated by the following relative solvolysis rates in 50% aqueous ethanol:[19] **1** (1.00), **2** (81), **3** (5.5×10^5), **4** (90), **5** (1.3×10^5). Solvolysis rates in Me_2SO were measured to obtain information concerning C–Cl bond dissociation in this solvent. The rates were followed by monitoring the disappearance of the absorbance for a number of weakly basic indicator ions, including 4-NO_2-2,6-di-*t*-$BuC_6H_2O^-$, 2,6-di-*t*-$BuC_6H_3O^-$, 9-CO_2MeFl$^-$, and 9-CN-Fl$^-$ or by monitoring the disappearance of the chloride and/or the appearance of products by NMR (Table IV). Measurements made with *t*-BuCl in MeOH by using these methods gave good agreement with the literature value. The methanolysis rates for **3** and **5** were each over 10^2 faster than that with *t*-BuCl, which can be attributed to the ability of the allylic system to delocalize the positive charge in the cationic species formed as intermediates. The solvolysis rates for **3** and **5** in Me_2SO were also found to be nearly 10^2 times faster than that with *t*-BuCl, which again points to the formation of a delocalized cationic species. The allylic

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(15) Bordwell, F. G. *Acc. Chem. Res.* **1970**, *3*, 281–290.

(16) In this review[15] and in a later one,[17] we discounted the importance of concerted mechanisms, including the S_N2' mechanism, purported to involve the simultaneous making and breaking of four or more bonds. Recently, Dewar has come to the same conclusion, independently, on the basis of hypothetical reaction profiles.[18]

(17) Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 374–381.

(18) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209–219.

(19) Vernon, C. A. *J. Chem. Soc.* **1954**, 423–428, 4462–4470.

Table IV. Rate Constants for Solvolysis of Halides at 25 °C

halide	solvent	k_{solv} (s^{-1})	method
t-BuCl	MeOH	7.9×10^{-7}	*a*
t-BuCl	MeOH	8.2×10^{-7}	*f*
$CH_2{=}CHCMe_2Cl$ (**3**)	MeOH	1.4×10^{-4}	*a*
$CH_2{=}CHCMe_2Cl$ (**3**)	MeOH-d_4	3.5×10^{-4}	(at 35 °C)[c]
$Me_2C{=}CHCH_2Cl$ (**5**)	MeOH-d_4	1.0×10^{-4}	(at 35 °C)[c]
t-BuCl	Me_2SO	4.7×10^{-8}	*d*
$CH_2{=}CHCMe_2Cl$ (**3**)	Me_2SO	3.6×10^{-6}	*a*
$CH_2{=}CHCMe_2Cl$ (**3**)	Me_2SO	4.1×10^{-6}	*b*
$CH_2{=}CHCMe_2Cl$ (**3**)	Me_2SO-d_6	1.8×10^{-6}	*c*
$CH_2{=}CHCMe_2Cl$ (**3**)	Me_2SO	3.9×10^{-6}	*d*
$CH_2{=}CHCMe_2Cl$ (**3**)	Me_2SO	4.5×10^{-6}	*e*
$CH_2{=}CHCH(Me)Cl$ (**2**)	Me_2SO	7.0×10^{-8}	*a*
$MeCH{=}CHCH_2Cl$ (**4**)	Me_2SO	4.5×10^{-7}	*a*
$Me_2C{=}CHCH_2Cl$ (**5**)	Me_2SO	3.1×10^{-6}	*a*
t-BuCl	Me_2SO	3.8×10^{-8}	*a*

[a] Trapping with 4-NO_2-2,6-di-*t*-$BuC_6H_2O^-$ ion. [b] Trapping with 2,6-di-*t*-$BuC_6H_3O^-$ ion. [c] Monitoring the appearance of products by NMR. [d] Trapping with 9-CN-Fl^- ion. [e] Trapping with 9-CO_2MeFl^- ion. [f] Literature value (titrimetric rate). Grunwald, E., Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

Table V. Rate Constants for Reactions of 9-CO_2MeFl^- and 9-CN-Fl^- with $CH_2{=}CHCMe_2Cl$ (**3**) and $Me_2C{=}CHCH_2Cl$ (**5**) at 25 °C[a]

anion	pK_{HA}	solvent	k^3 (s^{-1})	k^5 ($M^{-1}\ s^{-1}$)
9-CO_2MeFl^-	10.3_5	Me_2SO	$(4.5 \pm 0.2 \times 10^{-6})$[c]	(0.693 ± 0.030)[e]
9-CN-Fl^-	8.3	Me_2SO	$(3.9_5 \pm 0.1 \times 10^{-6})$[c]	(0.208 ± 0.05)[e]
9-CN-Fl^-	14.2[b]	MeOH	$(1.3 \pm 0.2 \times 10^{-3})$[d]	(3.71 ± 0.032)[e]

[a] Yields of S_N2 and S_N2' products are ca. 90%. [b] In MeOH. [c] Product type: 20% S_N2; 80% S_N2'. [d] Product type: 35% S_N2; 65% S_N2'. [e] Product distribution: 100% S_N2.

chlorides containing one methyl group (**2** and **4**) solvolyze at rates only moderately faster than that found for *t*-BuCl.

The rate of formation of the rearrangement product, $Me_2C{=}CHCH_2Cl$ (**5**) and isoprene by solvolysis of $CH_2{=}CHC(Me)_2Cl$ (**3**) in Me_2SO-d_6 is shown in Figure 2.

Trapping of Cationic Species Derived from 3 and 5 with 9-CO_2MeFl^- and 9-CN-Fl^- Carbanions. We have seen in an earlier section that 9-G-Fl^- ion in Me_2SO reacts with **3** by second-order kinetics to give S_N2' products when G = *t*-Bu, *o*-tol, Ph, or PhS. On the other hand, reactions with the much more weakly basic carbanions, 9-CO_2MeFl^- and 9-CN-Fl^- ions, proceed at rates that are *independent of the concentration of the carbanion* (Table V). In other words, first-order solvolysis rates are observed (compare Table IV). (This behavior was not unexpected since other halides prone to dissociation, such as *t*-BuBr, Ph_2CHCl, and Ph_2CHBr, have been observed to undergo first-order solvolyses in Me_2SO in the presence of these weakly basic carbanions.[20]) The products from these reactions are formed principally by attack at the γ-carbon atom; i.e., they are S_N2'-type products formed by a first-order pathway. In contrast, the isomeric primary chloride **5** reacted with 9-CO_2MeFl^- and 9-CN-Fl^- ions by second-order kinetics to give S_N2 products. Similar results were obtained in MeOH, but the solvolysis rate for **3** was accelerated by over 200-fold, and the S_N2 rate for **5** was accelerated by 18-fold. (The S_N2 rate for 9-CN-Fl^- ion with $PhCH_2Cl$ was also accelerated by a shift from Me_2SO to MeOH.[10]) It is clear from the results that 9-CO_2MeFl^- and 9-CN-Fl^- are reacting with **3** and **5** by different mechanisms. For **5** the concerted mechanism in Scheme III seems most likely. For **3**, C–Cl bond dissociation must occur *prior* to attack by the carbanion, e.g., Scheme IV.

The 9-CO_2MeFl^- and 9-CN-Fl^- carbanions are excellent trapping agents for the intermediate cationic species formed by solvolysis in Me_2SO. In their absence the cation slowly rearranges to **5** or is deprotonated to give isoprene (Figure 2). Evidently the Me_2SO solvent can play the role of the nucleophile in Scheme III, which will lead to a solvated ion pair, but the barriers for conversion of this ion pair to **5**, or deprotonation to form isoprene, are much higher than that for attack by these carbanions, which are more basic than Me_2SO by many powers of ten.

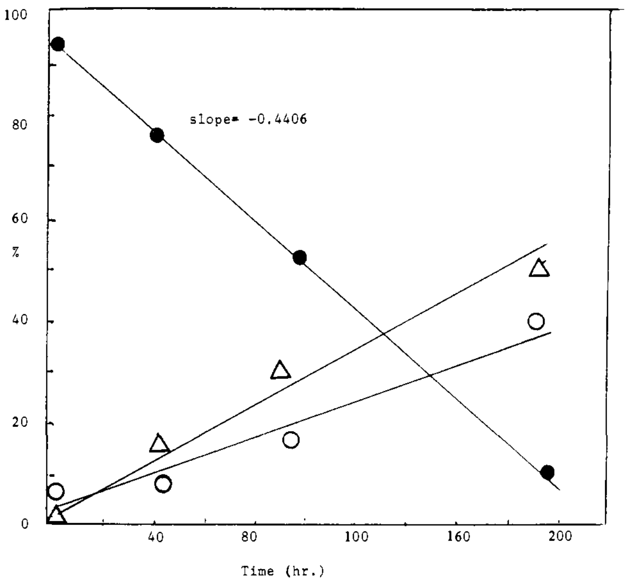
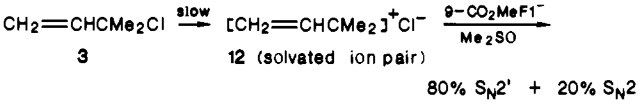


Figure 2. Plot of the rate of disappearance of $CH_2{=}CHC(Me)_2Cl$ (●) for solvolysis in Me_2SO-d_6 and the rate of formation of $Me_2C{=}CHCH_2Cl$ (○) and $CH_2{=}CHC(Me){=}CH_2$ (△).

Scheme IV



If this mechanistic view is correct, there must be a borderline where reaction via the ion sandwich in Scheme III and the solvated ion pair **12** in Scheme IV become nearly equal. This behavior was observed within the 9-PhS-Fl^- ion family reacting with **3**, where the kinetics show progressively more first-order behavior as the basicities decrease, as judged by the R^2 values for the kinetics plots for 1.5 half-lives: 0.9994 for 9-(*p*-MeC_6H_4S)-Fl^- (pK_{HA} = 15.7); 0.9985 for 9-PhS-Fl^- (pK_{HA} = 15.4); 0.997 for 9-(*p*-BrC_6H_4S)-Fl^- (pK_{HA} = 14.8); 0.996 for 2-Br-9-PhS-Fl^- (pK_{HA} = 13.2). Inspection of the kinetic plots for 2-Br-9-PhS-Fl^- shows that in the later part of the reaction the rate becomes nearly linear, i.e., independent of the anion concentration. The rate constant estimated from this part of the plot was ca. $5 \times 10^{-6}\ s^{-1}$, which is close to the solvolysis rate.

One would expect the ion-pair mechanism shown in Scheme IV to be applicable to other tertiary chlorides, such as *t*-BuCl. Solvolysis of *t*-BuCl in Me_2SO occurs about 100 times slower than for **3** (Table IV). In the presence of 9-CN-Fl^- ion only elimination occurs. However, in MeOH, where the solvolysis rate is only about 5 times slower than that of **3**, 17% of 9-CN-9-*t*-BuFl is formed when 9-CN-Fl^- is present; it is presumably formed by Scheme IV.

Activation Parameters for Reactions of 9-G-Fl^- Ions with $CH_2{=}CHCMe_2Cl$ (3) and $Me_2C{=}CHCH_2Cl$ (5). Measurements of rate constants for reactions of **3** and **5** in Me_2SO at several different temperatures were carried out to obtain activation parameters (Table VI). Examination of Table VI shows that $\Delta H^{\ddagger}$ values for the reactions of 9-G-Fl^- ions with **5** are relatively low, ~9 kcal/mol, and the $\Delta S^{\ddagger}$ values are highly negative, a pattern similar to that observed for S_N2 reactions with $PhCH_2Cl$.[14] The $\Delta S^{\ddagger}$ value for 9-*t*-$BuFl^-$ reacting with **5** is 14 eu more positive than that for the reaction of 9-Ph-Fl^- with **5** or the reaction of 9-*t*-BuFl with $PhCH_2Cl$. The more positive $\Delta S^{\ddagger}$ and higher $\Delta H^{\ddagger}$ value is suggestive of a looser structure for the ion–molecule complex **9** when Nu^- is 9-*t*-Bu and in a looser transition state leading to products.

The reactions of **3** show marked increases in activation enthalpies accompanied by similar marked increases in activation

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[20] Mrozack, S. R. Ph.D. Dissertation, Northwestern University, 1981.

Table VI. Second-Order Rate Constants (M^{-1} s^{-1}) and Activation Parameters for Reactions of 9-G-Fl^- Ions with CH_2=$CHCMe_2Cl$ (**3**), Me_2C=$CHCH_2Cl$ (**5**), and $PhCH_2Cl$

9-G-Fl^-	RCl	temperature °C 20	25	35	45	47	$R^{2\,b}$	$\Delta H^{\ddagger\,c}$ (kcal)	$\Delta S^{\ddagger\,c}$ (eu)
9-Ph-Fl^-	**3**		0.094	0.258				18	−3.7
9-*t*-Bu-Fl^-	**3**		0.188	0.599				$20._5$	+6.8
3-Me-9-PhFl^-	**5**	19.9				79.5		9.0	−22
9-PhFl^-	**5**	12.7	16.5	25.8		46.3	0.999	8.2	$-25._5$
2-Br-9-PhFl^-	**5**	2.94				12.7		9.5	−24
2-$PhSO_2$-9-PhFl^-	**5**	0.849 (β = 0.28)				3.21 (β = 0.28)		8.6	−30
9-*t*-BuFl^-	**5**		10.9	22.7				13	−11
9-CN-Fl^-	**5**		0.208	0.361	0.618		0.9999	9	−29
9-PhFl^-	$PhCH_2Cl^a$		0.630					10	−25
9-CN-Fl^-	$PhCH_2Cl^a$		0.0_2619					14	−22
9-*t*-BuFl^-	$PhCH_2Cl^a$		0.47					10	−25

[a] Reference 14. [b] Square of the correlation coefficient for a plot of $\ln(k/T)$ vs. $1/T$. [c] Evaluated from the equations $\ln(k/T) = -\Delta H^{\ddagger}/RT + C$ and $\Delta S^{\ddagger} = \Delta H^{\ddagger}/T + 4.58 \ln(k/T) - 47.4$ by using linear regression analysis.

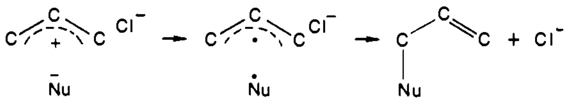
entropies for these S_N2' reactions, compared to the S_N2 reactions with **5**. These differences in activation parameters are a clear indication of a change in mechanism, and the more positive entropies accompanied by higher activation energies are consistent with a dissociative mechanism (ion-sandwich in Scheme III).[21]

The present results appear to establish reaction via a preformed solvated ion pair **12** for the formation of S_N2' products from reactions of 9-CN-Fl^- and 9-CO_2MeFl^- ions with **3** in Me_2SO solution, where the kinetics are independent of the carbanion concentration (Scheme IV). For more basic carbanions such as 9-PhS-Fl^- and 9-*t*-BuFl^- ions the anion–molecule dipole complex **9** will be formed rapidly in high concentration and the kinetics for the S_N2' reaction will be first-order in carbanion concentration and follow an overall second-order rate law with the ion sandwich **10** as an intermediate (Scheme III). If ionization is made less favorable, for example, by replacing an α-Me by hydrogen atom in **3** to form **2**, the concerted pathway (Scheme III) may intervene.

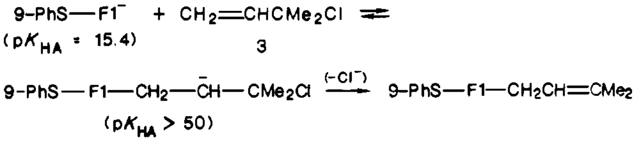
Schemes III and IV are versatile enough to accommodate almost any combination of nucleophile and electrophile reacting to form S_N2 and/or S_N2' products. For example, the demonstration by Georgoulis and Ville that S_N2' products are formed from optically active **2** by attack on either the neutral substrate or on a polarized species less ionized than an intimate ion pair can be accounted for by either the concerted pathway (**9** → **11**) or by formation of an optically active ion pair (analogous to **10**) that proceeds to products with no internal return.[22a] Also, the formation of S_N2' products from reactions of nucleophiles with 4-bromo-3,5,5-trimethylcyclohex-2-enone in various solvents by what appear to be concerted mechanisms[22b] can be looked on as being analogous to the reactions of **2**. Recent examples of syn S_N2' displacements include the following: (a) LiOAc in HMPA reacting with a bicyclic allylic mesylate[23] and (b) $NaOCH_3$ reacting with *cis*-3,4-dichlorocyclobutene,[24] and secondary amines reacting with optically active isotopically labeled **2**.[25] The participation of oxanions in S_N2' reactions is unusual, however, as will be brought out in a later paper.

Is a Radical Pair Mechanism a Reasonable Alternative? A recent analysis based on oxidation potentials of 9-G-Fl^- ions indicates that these carbanions are comparable single electron donors to ArS^- ions of equal basicity and much better than oxanions and nitranions.[26] Nevertheless, the reduction potentials of simple alkyl halides RCl, RBr, and RI are nowhere near positive enough to elicit electron transfer from even the best 9-G-Fl^- ion donors. On the other hand, stable carbocations, such as (p-$MeOC_6H_4)_3C^+$, have reduction potentials that are positive enough to make e_T^- appear feasible. The CH_2=$CHCMe_2^+$ cation should have an even more positive reduction potential, but the presence of a Cl^- counterion in the ion sandwich in Scheme III will reduce the potential. It is conceivable, then, that reaction by an electron-transfer mechanism could occur from the ion sandwich by Scheme V.

Scheme V



Scheme VI. Addition–Elimination Mechanism



This mechanism appears to be inconsistent, however, with the low β_{Nu} values obtained for reactions of the 9-PhFl^- and 9-PhS-Fl^- ion families with **3** (β_{Nu} = 0.34 and 0.17; Table III). Reactions of the 2-substituted 9-PhFl^- ion family with the electron acceptors $PhSO_2CH_2Br$, $PhSO_2CH_2I$, 1,1-$(NO_2)_2$-c-C_6H_{10}, c-C_6H_{10}-(NO_2)Ts, c-$C_6H_{10}(NO_2)$CN, and $Me_2C(NO_2)$Ts have all given β_{Nu} values near unity, and this is believed to be characteristic of an electron-transfer mechanism.

Is an Addition–Elimination Mechanism Feasible? In a recent paper Dewar remarks that "it has been generally assumed that the S_N2' reaction is synchronous, partly because there seemed to be no reasonable alternative." (Apparently he considers attack of the nucleophile on an ion pair as unreasonable.) He goes on to say that MNDO calculations by Dewar and Pierina for the gas-phase reaction of Cl^- ion with allyl chloride were found to contradict the previously accepted conclusion that addition of the nucleophile to the C=C bond cannot precede major weakening of the bond to the leaving group.[18] Dewar's addition–elimination mechanism for an S_N2' reaction in the gas phase is reasonable by analogy with Brauman's studies on the S_N2 reactions, which have shown that, when an alkyl halide and anion approach one another in the gas phase, ion–dipole interactions cause the reactants to combine and drop into a potential well, and that the barrier for completion of the reaction is lower than the original ground-state energies of the reactants.[27] But the reader is left with the impression that this mechanism is also reasonable in solution. It is not. Jorgensen and his students have shown that when their calculations of the gas-phase S_N2 reactions of Cl^- ion with CH_3Cl were altered so as to take into account the presence

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(21) Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1–33.

(22) (a) Georgoulis, C.; Ville, G. *J. Chem. Res., Synop.* **1978**, 248–249 and *J. Chem. Res., Miniprint* **1978**, 33444. (b) Meislich, H.; Jasne, S. J. *J. Org. Chem.* **1975**, *40*, 2216–2222, **1982**, *47*, 2517–2520.

(23) Ikota, N.; Ganem, B. *J. Am. Chem. Soc.* **1978**, *100*, 351–352.

(24) Kirmse, W.; Scheidt, F.; Vater, H.-J. *J. Am. Chem. Soc.* **1978**, *100*, 3945–3946.

(25) Magid, R. M.; Fruhey, O. S. *J. Am. Chem. Soc.* **1979**, *101*, 2107–2112.

(26) Bordwell, F. G.; Cheng, J.-P., unpublished results.

(27) Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219–4228. Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993–5999.

of 50 or more H_2O or DMF molecules, an ion–molecule dipole complex, similar to that in the gas phase, was formed, but at the same time a steep barrier arose, caused by the inability of dipole attraction to compensate for desolvation.[28] A similar situation would be expected to obtain in S_N2' reactions.

The requirement that the nucleophile attack the nonactivated double bond has long been considered to be an unattractive feature of the concerted S_N2' mechanism in solution.[29] For example, we estimate that the addition of 9-PhS-Fl^- to **3** to form a carbanion (Scheme VI) would be uphill by at least 55 kcal/mol.[30] This estimate indicates that the concentration of the carbanion intermediate would be too low to make Dewar's addition–elimination S_N2' mechanism viable in solution.

Summary and Conclusions

Previous studies have indicated that the S_N2' pathway for allylic substrates can be realized only by use of certain types of nucleophiles and/or with substrates where the S_N2 pathway is inhibited. The present studies have shown that the presence of the α-methyl substituents in $CH_2{=}CHCH(CH_3)Cl$ (**2**) and $CH_2{=}CHC(CH_3)_2Cl$ (**3**) are sufficient to inhibit the S_N2 pathway and allow the S_N2' pathway to emerge when 9-substituted fluorenide carbanions, 9-G-Fl^-, are used as nucleophiles in Me_2SO solution. When G = *t*-Bu, Ph, or PhS the rates of S_N2' reactions are first-order in substrate and first-order in carbanion. With more weakly basic carbanions (G = CO_2Me or CN) the rates with **3** become independent of the carbanion concentration and are comparable in size to the rates of solvolysis of **3**. These results show that C–Cl bond dissociation is occurring without participation by the carbanions. The carbanions do participate in the product-determining step, however, since high yields of substitution products (80% S_N2' and 20% S_N2) were obtained. Mechanistic Schemes III and IV can be used to accommodate these results. Scheme III can also be used to account for the accelerations in S_N2 reactions with weak as well as strong carbanion nucleophiles when one or two γ-methyl groups are substituted into allyl chloride. The marked differences in enthalpies and entropies of activation for S_N2 reactions of 9-G-Fl^- ions with $(CH_3)_2C{=}CHCH_2Cl$ (**5**) and $PhCH_2Cl$ as compared to the S_N2' reactions of 9-G-Fl^- ions with **3** (Table VI) indicate that C–Cl bond dissociation is occurring to a greater extent with the latter.

Experimental Section

General Procedures. NMR spectra were obtained by using a Varian T-60 and EM-390 (90-MHz) spectrometers. Mass spectra were measured by H. L. Hung by using an hp 5985 GC/MS system. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected.

Microanalyses. Microanalyses were carried out by Micro-Tech Laboratories, Inc., Skokie, IL. The analyses for 9,9-disubstituted fluorenes often have been found to give low values for carbon despite the use of a Carlo-Erba furnace, which operates at a high combustion temperature. Several of these analyses are reported herein, but NMR and mass spectral data provide more useful structural information.

Materials. The sources and/or preparations of 9-substituted fluorenes and the measurement of their equilibrium acidities in Me_2SO solution have been described in earlier papers.[9] Commercial samples of 3-chloropropene, (**1**), and 3-chloro-1-butene, (**2**) were distilled twice prior to use. Commercial crotyl chloride was fractionally distilled 3 times through a short Vigreux column, and the fraction, bp 82–83 °C, was used as 1-chloro-2-butene (**4**), a mixture rich in cis isomer, lit.[32] bp 84 °C.) 3-Chloro-3-methyl-1-butene (**3**) was prepared by adding hydrogen chloride to 2-methyl-2-butene according to the method of Ultée.[33] Fractional distillation gave a sample >98% pure by NMR and GLC; bp 30–31 °C/120 mmHg (lit.[33] bp 32 °C/120 mmHg). 1-Chloro-3-methyl-2-butene (**5**) was prepared by refluxing **3** at 110 °C for 10–20 h or by allowing **3** to remain in contact with HCl for several days at 0 °C. Fractional distillation gave **5**, bp 110 °C, >98% pure by NMR and GLC.

Kinetic Measurements. Preparation of solutions and kinetic measurements were performed as described previously.[9] All S_N2 reactions demonstrated good second-order kinetics through 2–4 half-lives. All Me_2SO solutions of allylic chlorides were used shortly after preparation to avoid solvolysis or isomerization. It is essential to avoid contamination of **3** with **5**, which reacts at a faster rate with 9-G-Fl^- ions. Chloride **3** was used in 1.5–8-fold excess and added neat to minimize solvolysis. Larger excesses were used for chlorides less subject to solvolysis.

Product Studies. The product studies were carried out in Me_2SO as described earlier,[34] except where noted. Separations were carried out on product aliquots by HPLC by using a Waters Associates Liquid Chromatograph Model 440 with use of a Whatman Partisil M9 10/50 PAC preparative column.

9-Methyl-9-allylfluorene was obtained in 79% yield as a colorless oil from the reaction of 9-$MeFl^-$ ion with allyl chloride in Me_2SO; ^1H NMR ($CDCl_3$) δ 2.5 (d, 2 H), 4.65 (m, 1 H), 5.2–5.7 (m, 1 H), 7.05 (m, 11 H), 7.45 (m, 2 H); MS (70 eV), *m/e* 220 (M^+), 179 (loss of C_3H_5).

9-Phenyl-9-allyl-γ-d_1-fluorene. Allyl-γ-*d* alcohol, obtained by the reaction of propargyl alcohol with $LiAlH_4$ and D_2O by the method of McMichael,[35] was converted to allyl-γ-d chloride by treatment with Ph_3P and CCl_4.[36] Separation of the product from CCl_4 and $CHCl_3$ was achieved only after repeated distillation through a Vigreux column. The $DCH{=}CHCH_2Cl$ obtained (27% yield) was better than 95% pure by ^1H NMR [$CDCl_3$ δ 3.9 (d 2 H), 4.9 (m, 1 H), 5.6 (m, 1 H)]. Reaction of allyl-d_1 chloride with an equivalent amount of 9-$PhFl^-$ in Me_2SO gave a 75% yield of 9-phenyl-9-allyl-γ-d_1-fluorene as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.5 (d, 2 H), 4.65 (m, 1 H), 5.2–5.7 (m, 1 H), 7.05 (m, 11 H), 7.5 (m, 2 H); MS (70 eV), *m/e* 283 (M^+), 241 (loss of C_3H_4D).

9-Phenyl-9-(2-butenyl)fluorene was obtained from the reaction of 9-$PhFl^-$ ion with 1-chloro-2-butene (**4**) in 90% yield as colorless crystals: mp 55 °C (EtOH); ^1H NMR ($CDCl_3$) δ 1.2 (d, 3 H), 2.9 (d, 2 H), 4.9 (q, 1 H), 5.6 (m, 1 H), 6.9 (m, 11 H), 7.4 (m, 2 H); MS (70 eV), *m/e* 296 (M^+), 241 (loss of C_4H_7). Anal. Calcd for $C_{23}H_{20}$: C, 93.14; H, 6.76. Found: C, 92.56; H, 6.90.

Reaction of 9-phenylfluorenide ion with 3-chloro-1-butene (2) gave a mixture of two products. The product mixture was adsorbed on silica gel (grade 950, mesh size 60–200) and eluted with 5% ether/95% hexane to bring through 9-phenyl-9-(2-butenyl)fluorene (**6**) identical with the sample isolated from the reaction of 9-phenylfluorenide ion with 1-chloro-2-butene. Continued elution gave a mixture of this compound contaminated with a small amount of a second product. Later fractions obtained on elution with 6% ether/94% hexane were rich (85–90% by NMR) in the second compound, 9-phenyl-(1-methyl-2-propenyl)fluorene (**7**), which was isolated as a colorless solid: mp 85–88 °C; ^1H NMR ($CDCl_3$) δ 0.7 (d, 3 H), 3.6 (m, 1 H), 4.7–4.9 (m, 2 H), 5.2–5.7 (m, 1 H) 7.0 (m, 11 H), 7.4 (m, 2 H); MS (70 eV) *m/e* 296 (M^+), 241 (loss of C_6H_7).

The overall yield of the two products was 83% of which 60% was 9-phenyl-9-(2-butenyl)fluorene. The isolated yield correlated well with the 65:35 ratio estimated by NMR analysis of the crude reaction mixture.

Reaction of 9-methylfluorenide ion with 3-chloro-1-butene (2) gave a mixture of products estimated by NMR analysis to contain about 70% of 9-methyl-9-(3-methyl-1-propenyl)fluorene (**7**, G = Me) with the remainder being 9-methyl-9-(2-butenyl)fluorene (**6**). Attempts to separate the products by column chromatography were unsuccessful.

9-*o*-Tolyl-9-(2-butenyl)fluorene (6, G = *o*-tol) was formed in 61% yield from the reaction of the 9-*o*-tolylfluorenide ion with 3-chloro-1-butene (**2**) as a clear oil: ^1H NMR ($CDCl_3$) δ 1.1 (s, 3 H), 1.3 (d, 3 H), 2.9 (d, 2 H), 4.6–4.8 (m, 1 H) 5.3–5.8 (m, 1 H), multiplet centered on 6.9 (10 H), multiplet centered at 7.4 (2 H); MS (70 eV), *m/e* 310 (M^+), 255 (loss of C_4H_7).

Reactions of 9-*tert*-Butylfluorenide Ion with 3-Chloro-1-butene (2) and with 1-Chloro-2-butene (4). A mixture of 0.42 g (1.9 mmol) of 9-*tert*-butylfluorene and 0.21 g (1.8 mmol) of (sublimed) potassium *tert*-butoxide was dissolved in 5 mL of dimethyl sulfoxide under an argon atmosphere. To the stirred solution was added 2.1 mL of a Me_2SO solution containing 2.1 mmol of 3-chloro-1-butene (Aldrich, bp 63 °C). After stirring overnight the orange-red color of the *t*-$BuFl^-$ ion had almost completely faded. The solution was quenched with water, extracted 3 times with ether, and dried over $MgSO_4$. Removal of the solvent by

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[28] Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049–3050. Jorgensen, W. L., private communication.

[29] Catchpole, A. G.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1948**, 8–17.

[30] The *minimum* pK_a of methane in a solvent like Me_2SO is estimated to be 50,[31] and the actual pK_a could be appreciably higher. A β chlorine atom would be expected to lower the pK_a by no more than 5 units.

[31] Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024–5026.

[32] Young, W. G.; Clement, R. A.; Shih, C.-H. *J. Am. Chem. Soc.* **1955**, *77*, 3061–3067.

[33] Ultée, A. J. *J. Chem. Soc.* **1948**, 530.

[34] (a) Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035–1036, **1982**, *47*, 2510–2516.

[35] McMichael, K. D. *J. Am. Chem. Soc.* **1967**, *89*, 2943–2947.

[36] Snyder, E. I. *J. Org. Chem.* **1972**, *37*, 1466.

rotoevaporation gave a quantitative yield of crude 9-*tert*-butyl-9-(2-butenyl)fluorene (**6**, G = *t*-Bu), mp 99–101 °C, after crystallization from 85% ethanol (65% yield): ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 9 H), 2.83 (d, 2 H), 1.07 (d, 3 H), 4.35 (m, 1 H), 4.96 (m, 1 H), 6.9–7.65 (m, 8 H). Anal. Calcd $C_{21}H_{24}$: C, 91.25; H, 8.75. Found: C, 89.57; H, 8.69.

Reaction of **4** with 9-*t*-BuFl$^-$ under the conditions described for **2** gave a quantitative yield of crude product and 53% of crystallized product, mp 99–101 °C. The crystalline products obtained from **2** and **4** were identical as determined by NMR, mixed melting points, and thin-layer chromatography (identical R_f values on a silica plate prepared with $CHCl_3$ and developed with CCl_4). This result is sufficient to establish the regiochemistry but is surprising since one would expect a different proportion of isomers to be formed from **2** and **4**. Reactions of **2** with dialkylamines have been found to give almost exclusively the *E* isomer.[25]

Reaction of 9-Phenylfluorenide Ion with 3-Chloro-3-methyl-1-butene (3). A stock solution of 115 mmol of $MeSOCH_2K$ in 8.5 mL of Me_2SO was neutralized with a Me_2SO solution of 9-PhFlH (242 mg) and treated with a twofold excess of **3**. After processing in the usual manner, 285 mg (82%) of 9-Ph-9-($Me_2C{=}CHCH_2$)Fl (**8**) was obtained as a yellow solid. Recrystallization from EtOH gave colorless crystals, mp 98.5–99 °C. This product was identical by NMR, mp, and mixed mp with that obtained from a similar reaction of 9-PhFl$^-$ ion with $Me_2C{=}CHCH_2Cl$ (**5**) reported below.

Isomerization of 3-Chloro-3-methyl-1-butene (3). This tertiary chloride isomerized in Me_2SO solution to the corresponding primary chloride, 4-chloro-2-methyl-2-butene (**5**), in the presence of hydrogen chloride in about 2 days at 0–4 °C. Isomerization was very slow in the absence of acid. A mixture of equal amounts of 3-chloro-3-methyl-1-butene (>90%) and Me_2SO-d_6 was kept at room temperature in an NMR tube and monitored periodically. The results are summarized in Figure 2. During kinetic work Me_2SO solutions of 3-chloro-3-methyl-1-butene were stored frozen and kept for a maximum of 3 days.

9-Phenyl-9-(3-methyl-2-butenyl)fluorene (8) was obtained from the reaction of 9-PhFl$^-$ ion with 4-chloro-2-methyl-2-butene (**5**) in 78% yield as colorless needles: mp 98–99 °C (EtOH), ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3 H), 1.43 (s, 3 H), 3.09 (d, 2 H), 4.72 (t, 1 H), 7.07–7.47 (m, 11 H), 7.67–7.83 (m, 2 H); MS (70 eV), *m/e* 310 (M^+), 241 (loss of C_5H_9). Anal. Calcd $C_{24}H_{22}$: C, 92.90; H, 7.09. Found: C, 91.79; H, 7.20. (Carbon analyses are frequently low for 9,9-disubstituted fluorenes, presumably due to loss of carbon by fragmentation during combustion.)

Reaction of 9-Cyanofluorenide Ion with 5. Reaction of 9-CN-Fl$^-$ with **5** gave an essentially quantitative yield of crude 9-cyano-9-(3-methyl-2-butenyl)fluorene. Purification by HPLC gave colorless crystals: mp 50.5–51.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 3 H), 1.67 (s, 3 H), 2.72 (d, 2 H), 5.18 (t, 1 H), 7.06–7.75 (m, 8 H); MS (70 eV), *m/e* 259 (M^+), 191 (loss of C_6H_5 + H). Anal. Calcd $C_{19}H_{17}N$: C, 87.99; H, 6.61. Found: C, 87.95; H, 6.72.

Reaction of 9-Cyanofluorenide Ion with 3 in Me_2SO and in MeOH. Reaction of 9-CN-Fl$^-$ with **3** in Me_2SO gave a 90% yield of a crude product consisting of 80% of S_N2' and 20% of S_N2 product by NMR analysis. Separation by HPLC gave a major (S_N2') product, mp 49–51 °C, identical (NMR and mmp) with that obtained from 9-CN-Fl$^-$ and **5**, and a minor (S_N2) product, mp 87.8–88.2 °C: NMR ($CDCl_3$) δ 1.04 (s, 6 H), 5.05 (m, 2 H), 6.14 (q, 1 H), 5.20 (t, 1 H), 7.03–7.70 (m, 8 H). Anal. Calcd $C_{19}H_{17}N$: C, 87.99; H, 6.61; Found: C, 87.89; H, 6.60.

Reaction of 9-CN-Fl$^-$ with **3** in MeOH gave 87% yield of crude $C_{19}H_{17}N$ products. NMR analysis of the mixture indicated the presence of 65% S_N2' and 35% S_N2 product. (Small amounts of methanolysis product may have been lost in the workup.)

Reaction of 9-(Phenylthio)fluorenide Ion with 3. An 88% yield of 9-(phenylthio)-9-(3-methyl-2-butenyl)fluorene was obtained from the reaction of 9-PhS-Fl$^-$ with **3**. None of the S_N2 product was formed, as judged by NMR. Purification by HPLC gave a nearly colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 6 H), 3.02 (d, 2 H), 4.78 (t, 1 H), 6.63–7.66 (m, 13 H); MS (70 eV), *m/e* 342 (M^+), 273 (loss of C_5H_9) 233 (loss of PhS). Anal. Calcd $C_{24}H_{22}S$: C, 84.18; H, 6.48. Found: C, 83.33; H, 6.29.

Reactions of 9-(Methoxycarbonyl)fluorenide Ion with 5 and 3. Reaction of 9-CO_2MeFl$^-$ ion with **5** gave an essentially quantitative yield of 9-(methoxylcarbonyl)-9-(3-methyl-2-butenyl)fluorene as colorless crystals, mp 48.6–49.4 °C (EtOH): ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H); 1.45 (s, 3 H); 2.93 (d, 2 H), 3.45 (s, 3 H), 4.77 (t, 1 H), 7.07–7.73 (m, 8 H); MS (70 eV), *m/e* 292 (M^+), 224 (loss of C_5H_9). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 82.20; H, 6.89.

Reaction of 9-CO_2MeFl$^-$ ion with **3** gave an 89% yield of a mixture of products which was analyzed by NMR. The major product (S_N2', 80%) gave NMR signals at δ 1.35 (s, 3 H), 1.45 (s, 3 H), 2.93 (d, 2 H), 3.45 (s, 3 H), and 4.75 (t, 1 H) characteristic of the product obtained from **5**. The minor (S_N2, 20%) product gave δ 1.00 (s, 6 H), 3.60 (s, 3 H), 4.91 (q, 2 H), and 6.10 (q, 1 H) expected for the S_N2 product.

Reactions of 9-*tert*-Butylfluorenide Ion with 3 and 5. Reaction of 9-*t*-BuFl$^-$ ion with **3** gave a small amount of isoprene, identified by NMR from a $CDCl_3$ extract, and about 15% of 9-*t*-BuFlH (identified by NMR). The major product (85% by NMR) was separated from the 9-*t*-BuFlH and purified by HPLC to give a colorless oil: NMR ($CDCl_3$) δ 0.91 (s, 9 H), 1.22 (s, 3 H), 1.52 (s, 3 H), 2.93 (d, 2 H), 4.03 (t, 1 H), 7.07–7.71 (m, 8 H); MS (70 eV), *m/e* 290 (M^+), 233 (loss of *t*-Bu), 221 (loss of C_5H_9). Anal. Calcd $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 90.97; H, 8.93. A liquid product identical (by NMR) with the S_N2' product obtained from **3** was prepared in 85% yield from **5** by reaction with 9-*t*-BuFl$^-$ ion.

General Procedure for Solvolysis Studies. The usual procedure for kinetic measurements in Me_2SO was followed. The weakly basic and sterically hindered 4-nitro-2,6-di-*tert*-butylphenoxide ion was used to trap the cationic intermediate(s), unless otherwise noted. The kinetics were followed by monitoring the absorbance decay of the trapping anion, usually for less than 1 half-life. The extinction coefficient of the phenoxide ion was determined for each run by titration since it is used in the rate evaluation. The kinetics for relatively reactive chlorides, such as **3** and **5**, were determined by using small excesses of electrophile to trapping agent. Larger excesses were used for less reactive chlorides. The first-order rate constants were evaluated by making a plot of the indicator decay vs. time. The slope of this plot, Abs/t, was divided by the extinction coefficient, ϵ, of the indicator at the wavelength used for the measurements; ϵ was determined by dividing the absorbance of the indicator anion by the CH_3SOCH_2K concentration. Division by the concentration of the electrophile yielded the rate constant, k, in s^{-1}. The rates of solvolysis obtained by this method agreed reasonably well with those obtained by using weakly basic 9-G-Fl$^-$ ions as trapping agents or those obtained by NMR (Table VI).

Solvolyses in methanol were carried out in a similar manner; neat samples of reactive chlorides were used. The rate constant obtained for methanolysis of *tert*-butyl chloride agreed well with the literature value (Table VI).

Solvolyses in MeOH-d_4 and in Me_2SO-d_6. A mixture of **3** and Me_2SO-d_6 (ca. 1:8) was placed in an NMR tube at room temperature and monitored periodically. After 4 days 17% of **5** and 32% of isoprene were formed, and 50% of **3** remained (Figure 2). The estimated rate, based on the percent changes in **3** and the products with time, was 1.8×10^{-6} s^{-1}. The reaction of **3** in MeOH-d_4 was followed in a similar manner.

Reaction of 9-CN-Fl$^-$ Ion with 3 in Me_2SO and in MeOH. The rate in Me_2SO was followed by 2 half-lives by using chloride **3** in two- to four-fold excess. The calculated rate constant of 3.95×10^{-6} s^{-1} at 25 °C ($R^2 = 0.999$) is comparable to the solvolysis rate in Me_2SO. The rate was independent of [9-CN-Fl$^-$].

An optical cell was alternatively flushed with argon and evacuated 3 times. Degassed anhydrous MeOH (3 mL) was then added through an airtight syringe, and the cell was weighed. A stock solution of $CH_3SOCH_2^-K^+$ (2–3 drops ([CH_3SOCH_2K] $\simeq$ 150 mmol)) was added, followed by an excess of a 9-CN-FlH solution in MeOH. Neat **3** was then added in slight excess, and the reaction was followed by monitoring the decay of the colored anion. The rate was independent of [9-CN-Fl$^-$].

Reaction of 9-CN-Fl$^-$ Ion with *t*-BuCl in MeOH. The rate of reaction, which was measured as described above, was found to be independent of [9-CN-Fl$^-$]. The first-order rate constant of 1.03×10^{-6} s^{-1} at 25 °C ($R^2 = 0.9998$) for the first half-life obtained under pseudo-first-order conditions is close to the methanolysis rate (0.79×10^{-6} s^{-1}).

A 71% yield of solid product was obtained from the reaction of 9-CN-Fl$^-$ ion with *t*-BuCl in MeOH for 75 h at room temperature (88% reaction based on the kinetics). The major product (83% by NMR) was 9-CN-FlH, formed from the elimination of HCl. The minor product (17% by NMR) was a new compound, which was identified as 9-cyano-9-*tert*-butylfluorene: NMR ($CDCl_3$) δ 1.05 (s, 9 H), 7.25–7.83 (m, 8 H); MS 70 (eV), *m/e* 247 (M^+), 191 (-C_4H_9 + H), 165 (-C_4H_9 and CN + H). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93. Found: C, 84.57, H, 6.89. The reaction of 9-CN-Fl$^-$ with *t*-BuCl in Me_2SO gave only elimination products.

Reaction of 9-CN-Fl$^-$ Ion with $PhCH_2Cl$ in MeOH. The rate of reaction was measured under the conditions described above to give a second-order rate constant of $5.85 \pm 0.05 \times 10^{-2}$ M^{-1} s^{-1} at 25 °C ($R^2 = 0.9998$).

Reaction of 9-CO_2MeFl$^-$ with 3 in Me_2SO. The rate of reaction was found to be independent of [9-CO_2MeFl$^-$]. The first-order rate constant was 4.5×10^{-6} s^{-1} ($R^2 = 0.9985$).

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Registry No. 2, 563-52-0; **3**, 2190-48-9; **4**, 591-97-9; **5**, 503-60-6; **6** (G = *o*-tol), 106358-47-8; **6** (G = *t*-Bu), 106358-49-0; **7**, 106358-45-6; **8**, 106358-50-3; *t*-BuCl, 507-20-0; 9-CNFlH, 1529-40-4; $PhCH_2Cl$, 100-44-7; 9-MeFl$^-$·K$^+$, 64918-34-9; 9-*o*-tolFl$^-$·K$^+$, 106358-46-7; 9-*t*-BuFl$^-$·K$^+$, 106358-48-9; 9-PhFl$^-$·K$^+$, 106358-43-4; 2-Cl-9-MeFl$^-$·K$^+$, 106358-57-0; 2,7-Br$_2$-9-MeFl$^-$·K$^+$, 106358-58-1; 2-Br-9-*t*-BuFl$^-$·K$^+$, 106358-59-2; 2,7-Br$_2$-9-*t*-BuFl$^-$·K$^+$, 106358-60-5; 9-*p*-MeSO$_2$-*o*-tolFl$^-$·K$^+$, 106358-61-6; 9-*m*-ClC$_6$H$_4$Fl$^-$·K$^+$, 106358-62-7; 9-*p*-MeSO$_2$C$_6$H$_4$Fl$^-$·K$^+$, 106358-63-8; 9-*p*-BrC$_6$H$_4$SFl$^-$·K$^+$, 106358-64-9; 2-Br-9-PhSFl$^-$·K$^+$, 106358-65-0; 2,7-Br$_2$-9-PhSFl$^-$·K$^+$, 106358-66-1; DCH═CHCH$_2$Cl, 89275-39-8; allyl chloride, 107-05-1; 9-phenyl-9-(2-butenyl)fluorene, 106358-44-5; 9-cyano-9-(3-methyl-2-butenyl)fluorene, 106358-51-4; potassium 9-cyanofluorenide, 57643-25-1; potassium 9-(phenylthio)fluorenide, 106358-52-5; 9-(phenylthio)-9-(3-methyl-2-butenyl)fluorene, 106375-42-2; potassium 9-(methoxycarbonyl)fluorenide, 57643-28-4; 9-(methoxycarbonyl)-9-(3-methyl-2-butenyl)fluorene, 106358-53-6; 9-cyano-9-*tert*-butylfluorene, 94004-10-1; 9-methyl-9-allylfluorene, 34163-29-6; 9-phenyl-9-allyl-γ-d_1-fluorene, 106358-54-7; 9-cyano-9-(1,1-dimethyl-2-propenyl)fluorene, 106358-55-8; 9-(methoxycarbonyl)-9-(1,1-dimethyl-2-propyl)fluorene, 106358-56-9.

How Does an Allene Distort to Accommodate Negative Charge? 1,1,3,3-Tetraphenylallene

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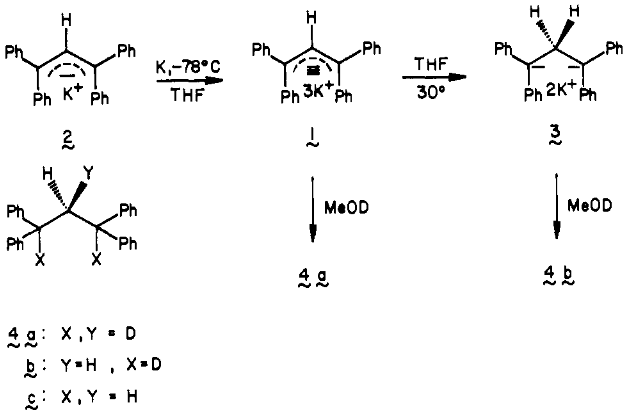
Abstract: Treatment of 1,1,3,3-tetraphenylallene with lithium at low temperature in ethereal solvents leads to a dilithium allenide which apparently consists of two equilibrating 2-lithioallyllithium structures **6a**. Reduction with sodium leads to an analogous, though less stable, species **6b**. Reduction with potassium does not allow detection of the analogous dipotassium allenide **6c**. Rather, protonation by solvent yields 1,1,3,3-tetraphenylallylpotassium (**2c**) which, in the presence of excess potassium, is further reduced to the corresponding trianion **1**. The use of ^{13}C-enriched material and ^{13}C–^{13}C coupling constants allows a determination of the structure of the hydrocarbon framework. Even in the trianion, substantial residual π-bond order is evident.

With the increased availability of modern computational, crystallographic, and spectroscopic techniques, the study of carbanions or, more correctly, alkali metal derivatives of hydrocarbons has taken a more quantitative turn. We have been engaged in a study of how a three-atom system containing stabilizing groups, e.g., tetraphenylallene, distorts to accommodate excess negative charge.[2] To a first approximation, addition of electrons to such a system mimics the excited state, in that antibonding molecular orbitals are being populated. Thus we have reported that the D_{2d} tetraphenylallene lowers its symmetry to C_2 upon formation of the dilithium derivative.[2] We now report that the corresponding dipotassium derivative cannot be observed directly, but it undergoes rapid protonation by solvent at low temperature to produce the 1,1,3,3-tetraphenylallyl anion. We might ask how this system in turn responds to the presence of three negative charges, i.e., the allyl "trianion" formed by reduction of the monoanion. On the one hand, the lack of degeneracy in the allyl π^* provides no impetus for a Jahn–Teller distortion for the trianion as it does in the allene dianion. On the other hand, population of the allyl π^*-orbital might be expected to result in zero bond order, thus leading to a perpendicular orientation of the benzhydryl groups. In fact, Hückel molecular orbital calculations indicate a substantial residual bond order ($\rho > 0.4$) when two or more phenyl groups further delocalize the π^* orbital. Of course, the strong counterion dependence for the dianion cannot be ignored in the trianion. Since the one-bond ^{13}C–^{13}C and ^{13}C–^{1}H coupling constants are generally accepted as measures of the s-character in the associated atomic orbitals,[3] direct observation of the ^{1}H and ^{13}C NMR spectra of a ^{13}C-enriched trimetallopropane derivative appeared to be essential both for establishing the existence of the species and determining its structure. We now report (1) spectroscopic evidence indicating that 1,1,3,3-tetraphenylallyl trianion (**1**) does in fact maintain the allyl geometry insofar as the hydrocarbon framework is concerned, (2) additional low-temperature NMR data in dimethyl ether for dilithium and disodium tetraphenylallenides (**6a,b**) to confirm the previous conclusion about the geometry of the hydrocarbon framework,[2] and (3) full experimental details on both

Scheme I. Protonation of 1,1,3,3-Tetraphenylallyl Trianion



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[2] (a) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 2969. (b) Rajca, A.; Streitwieser, A., Jr.; Tolbert, L. M. *J. Am. Chem. Soc.*, following paper in this issue.

[3] (a) Bingel, W. A.; Lüttke, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 899. (b) For examples see: Wardeiner, J.; Lüttke, W.; Bergolz, R.; Machinek, R. *Ibid.* **1982**, *21*, 872. Kamieńska-Trela, K.; Biedrzycka, Z.; Machinek, T.; Knierem, B.; Lüttke, W. *Org. Magn. Reson.* **1984**, *22*, 317. (c) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177.

0002-7863/87/1509-1782$01.50/0