H), 3.78 (s, 3 H), 5.58 (d, 1 H, J = 7.5 Hz), 5.87 (d, 1 H, J = 3.0 Hz), 6.52–7.07 (m, 6 H), 7.53–7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.43 (q), 29.94 (q), 34.58 (t), 40.37 (d), 47.70 (d), 51.55 (s), 55.11 (q, 2 C), 56.91 (d), 57.54 (s), 60.52 (d), 90.85 (d), 113.14 (d, 2 C), 113.33 (d, 2 C), 129.64 (d, 2 C), 129.85 (s), 130.46 (d, 2 C), 131.87 (d), 136.48 (s), 136.85 (d), 140.53 (s), 146.72 (s), 158.13 (s), 158.46 (s).

Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.13; H, 7.29. Found: C, 81.01; H, 7.53.

TPP$^+$-Sensitized Irradiation of Cage Alcohol 12 in the Presence of TMB. A mixture of **12** (31.1 mg, 7.5 × 10^{-5} mol), TPP$^+$ (3.5 mg, 8.6 × 10^{-6} mol), and TMB (15.9 mg, 8.0 × 10^{-5} mol) in 5 mL of dichloromethane was irradiated for 1 h under the same conditions as those in the absence of TMB. Thin-layer chromatography (9:1 *n*-hexane–ether) gave recovered **12** (12.3 mg, 40% yield) and **14** (17.3 mg, 56% yield), which was recrystallized from ethanol: mp 129.5–130 °C; IR (KBr) 3600–3300, 3000–2800, 1505, 1240, 1230, 1175, 1165, 1040, 835 cm^{-1}; UV (CH_2Cl_2) 231 nm (log ε 4.36), 280 (3.51); mass spectrum (25 eV), m/e (relative intensity) 415 (M$^+$ + 1, 24), 414 (M$^+$, 100), 322 (19), 201 (19), 200 (25), 199 (93), 198 (19), 188 (13), 187 (77), 186 (93), 185 (19), 135 (12), 121 (26), 108 (21); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.99 (s, 3 H), 1.23 (s, 3 H), 1.30 (dd, 1 H, J = 7.0, 6.0 Hz), 1.38 (dd, 1 H, J = 6.5, 0.5 Hz), 1.59 (br d, 1 H, J = 6.0 Hz), 2.09 (ddd, 1 H, J = 6.0, 4.5, 0.5 Hz), 2.11 (ddd, 1 H, J = 19.0, 3.4, 2.0 Hz), 2.33 (dd, 1 H, J = 6.5, 4.5 Hz), 2.36 (dddd, 1 H, J = 19.0, 7.0, 3.4, 2.0 Hz), 2.94 (d, 1 H, J = 6.0 Hz), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.69 (ddd, 1 H, J = 10.0, 2.0, 2.0 Hz), 5.86 (ddd, 1 H, J = 10.0, 3.4, 3.4 Hz), 6.77–6.97 (m, 4 H), 7.22–7.37 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.49 MHz) δ 19.39 (d), 20.50 (q, 2 C), 24.94 (t), 37.86 (d), 40.08 (s), 42.17 (d), 42.56 (d), 42.82 (s), 44.19 (s, 2 C), 55.16 (q, 2 C), 84.27 (d), 113.19 (d, 2 C), 113.65 (d, 2 C), 125.07 (d), 128.01 (d, 2 C), 130.82 (d, 2 C), 132.12 (s), 136.95 (d), 138.91 (s), 157.58 (s), 157.90 (s).

Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.13; H, 7.29. Found: C, 80.84; H, 7.57.

Direct Irradiation of Ketone 7a. A solution of 634 mg (1.54 mmol) of **7a** in 400 mL of dichloromethane was irradiated through a Pyrex filter with Rayonet RUL-3500 Å lamps under nitrogen bubbling for 90 min. Removal of the solvent followed by recrystallization from dichloromethane–ethanol gave 524 mg (83% yield) of **8** as colorless crystals: mp 121–122 °C; IR (KBr) 2950, 2850, 1750, 1610, 1515, 1465, 1280, 1240, 1175, 1025, 825 cm^{-1}; UV (CH_2Cl_2) 237 nm (log ε 4.18), 278 (3.47), 286 (3.40); mass spectrum (25 eV), m/e (relative intensity) 413 (M$^+$ + 1, 23), 412 (M$^+$, 72), 384 (6), 200 (11), 199 (64), 198 (6), 187 (15), 186 (100); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.60 (s, 3 H), 1.26 (s, 3 H), 1.52 (ddd, 1 H, J = 12.5, 2.0, 1.5 Hz), 1.59 (ddd, 1 H, J = 12.5, 5.0, 3.5 Hz), 2.48 (ddd, 1 H, J = 8.0, 5.0, 1.5 Hz), 2.96 (dd, 1 H, J = 8.0, 8.0 Hz), 3.34 (dddd, 1 H, J = 5.0, 5.0, 3.5, 2.0 Hz), 3.42 (ddd, 1 H, J = 8.0, 5.0, 3.0 Hz), 3.50 (dd, 1 H, J = 3.0, 3.0 Hz), 3.53 (dd, 1 H, J = 5.0, 3.0 Hz), 3.65 (s, 3 H), 3.70 (s, 3 H), 6.27–6.50 (m, 6 H), 6.92–7.00 (m, 2 H).

Anal. Calcd for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84. Found: C, 81.50; H, 7.06.

TPP$^+$ Fluorescence Quenching. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrophotometer. The quenching experiments were carried out in air by monitoring the changes in the intensity at 464 nm of fluorescence as a function of concentration of quencher. The slope of I^0/I vs [quencher], which equals $k_q\tau$, was determined by a least-squares method.

Quantum Yield Determinations. Samples were irradiated with a Ushio 150-W xenon lamp on a Hitachi MPF-4 spectrometer (λ_{ex} = 392 ± 10 nm). The number of photons incident on the sample were determined by using a potassium ferrioxalate actinometer. The formation of **7a** was followed by liquid chromatography (column, Merck silica 150; solvent, 95:5 *n*-hexane–ethyl acetate; flow rate, 1.0 mL/min).

Nucleophilic Attacks on Carbon–Carbon Double Bonds. 34.[1,2] Intramolecular Element Effect in Competitive Expulsion of Two Halide Nucleofuges as a Tool for Investigating the Rapid Step of Nucleophilic Vinylic Substitution

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Abstract: The substitution of 9-(bromochloromethylene)fluorene (**8**) and β,β-bis(*p*-nitrophenyl)-α-bromo-α-chloroethylene (**9**) by *p*-toluenethiolate and *p*-cresolate ions gives the monobromo, the monochloro, and the disubstitution products. The [monochloro]/[monobromo] substitution product ratios were determined in CD_3CN, DMSO-d_6, and DMSO-d_6–CD_3OD under conditions where the disubstitution was negligible. The ratios were 2.0–3.2, were slightly higher for **8** than for **9**, and showed no discernible solvent dependence. The ratios did not change in the presence of radical traps although an ESR spectrum was observed with **8** and p-$MeC_6H_4S^-$. The "intermolecular element effects" k_{Br}/k_{Cl} derived from competitive substitution of **8** or **9** with their dibromo or dichloro analogues were 1.2–1.76. The results were interpreted in terms of a multistep nucleophilic vinylic substitution proceeding via an intermediate carbanion, which may be formed either directly or by an initial single-electron transfer followed by combination of the anion radical and the radical. The ratios of the products were hence identified as the ratios of the rate constants for expulsion of Br^- and Cl^- ($k_{el}(Br)/k_{el}(Cl)$—the "intramolecular element effect") from the carbanion. The low ratios and their relative insensitivity to the solvent and to the delocalizing ability of negative charge of the β-substituents were ascribed to an early transition state for the expulsion of halide ions from the carbanion. Generalizations concerning the expulsion of poor and good nucleofuges from carbanions substituted by poor and good electron-withdrawing groups are discussed.

Recent accumulating evidence[4-6] on the mechanism of bimolecular nucleophilic vinylic substitution,[7] which involves a rate-determining nucleophilic attack on C_α where C_β carries two electron-withdrawing groups Y and Y′ (eq 1), suggests that the

$$\underset{\mathbf{1}}{RC_\alpha(X){=}C_\beta YY'} + Nu^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{2}}{RC(Nu)(X){-}\bar{C}YY'} \xrightarrow{k_{el}} RC(Nu){=}CYY' + X^- \quad (X = Cl, Br) \quad (1)$$

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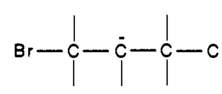
reaction is a multistep process.[7b,c] Amine catalysis,[4] partial or complete stereoconvergence in the substitution,[1,5] and leaving-group effects[6] corroborate this conclusion. The evidence is less clear-cut when only a single activating group[7c] is present, since the stereochemistry can be interpreted either in terms of a concerted (single step) substitution or as a multistep process via carbanion **2**, which undergoes a 60° intramolecular rotation before leaving-group expulsion.[8] The strongest evidence for a multistep process in this case is the analogy with the more activated systems, and especially the "element effect". For a rate-determining nucleophilic attack that does not involve C–X bond cleavage, the relative rate ratios for halide nucleofuges should be $k_F/k_{Cl} \gg 1$ and $k_{Br}/k_{Cl} \sim 1$ since increased electrophilicity of C_α by electron withdrawal by X plays the most important role. For a single-step process, the strength of the C–X bond is as important, and $k_F/k_{Cl} \ll 1$ and $k_{Br}/k_{Cl} > 1$ ratios are expected. The observation of $k_F/k_{Cl} \gg 1$ and $k_{Br}/k_{Cl} \sim 1$ ratios in almost all cases studied[4,6,7,9] is the strongest argument for the multistep route in these cases.

The goal of investigating a reaction mechanism is to understand the details of each step in a multistep process. In eq 1, where k_1 is rate determining, neither the kinetics nor the products give any information on the rapid second step, which is the expulsion (k_{el}) of the nucleofuge from the intermediate carbanion. The amine catalysis[4] and the partial stereoconvergence[1,5] give qualitative information on the competition between the rapid expulsion of the nucleofuges Cl and Br and other rapid processes such as deprotonation with an external base or intramolecular rotation, but other information on k_{el} is as yet not available. None of the several methods used for estimating k_{el} of poorer nucleofuges than the halogens in related processes[10] is applicable to our systems, whereas an isotope effect study of the nucleofuge requires very high accuracy.

The success of the element effect in accounting for the details of the first step of the substitution suggests the use of a similar probe for delineating the details of the rapid step. A stereochemical approach that investigates the extent of stereoconvergence on changing the nature of a good nucleofuge will be reported elsewhere.[11] A complementary method is the comparison of the competitive leaving ability of two good nucleofuges in the same system. If these are Cl and Br (or F) this will give an "intramolecular element effect". Comparison of the observed rate ratio with the value expected based on assumptions concerning the ease of the C–X bond cleavage or its hyperconjugative ability with the carbanionic center may give information on the rapid step.

Two ways for investigating such an intramolecular competitive expulsion of Cl^- and Br^- can be envisioned. First, the two nucleofuges can be on two different vicinal positions to the charge as in **3**. This approach, which will give what we called the "vicinal element effect",[7b] was applied in the substitution of polyhalocyclobutenes,[12] but the competition between Br^- and Cl^- expulsion from **3** was never investigated.



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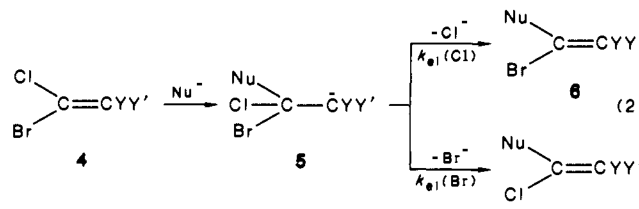
In the second approach, which we report here, the two halogens are geminal to one another in the precursor **4**. Nucleophilic attack gives carbanion **5**, which then may either expel Cl^- to give **6** or Br^- to give **7** (eq 2). Since both eliminations are first-order



(2)

processes, the experimentally measured [**7**]/[**6**] product ratio will be equal to the $k_{el}(Br)/k_{el}(Cl)$ ratio (eq 3) if both eliminations

$$[\mathbf{7}]/[\mathbf{6}] = k_{el}(Br)/k_{el}(Cl) \qquad (3)$$

have an identical ground state (i.e., **5**) and the k_{el} process is rate determining. In this situation the $k_{el}(Br)/k_{el}(Cl)$ ratio should reflect the extent of cleavage of the C–X bonds: When it is extensive the $k_{el}(Br)/k_{el}(Cl)$ ratio will be large as in S_N1 reactions, and when it is low the ratio will be small. However, information on this question could not be achieved when k_{el} is not rate determining, e.g., when the ground states for Br^- and Cl^- expulsion are different. We note that the transition states for Cl^- and Br^- expulsion differ not only in the group displaced but also in the group that remains behind.

Nucleophilic substitution of several β,β-dihalo-α-activated systems was previously investigated.[13] In most cases the two halogens were identical,[13a–i,n] but β-chloro-β-fluoro systems were also studied,[13j–m] although conclusions regarding the position of the transition state were not given. For the β-chloro-β-iodo system[13o,p] the structure was disclaimed.

Three considerations were applied in choosing our systems. First, the products **6** and **7** are expected to be structurally similar and separation problems are anticipated. Hence, we avoided a further complication from formation of geometrical isomers in spite of the useful mechanistic information that it can give, and systems **4** where Y = Y′ were chosen. Second, differences in the $k_{el}(Br)/k_{el}(Cl)$ ratios as a function of Y and Y′ may be observed. Hence, at least two systems differing in the negative charge dispersal abilities of Y and Y′ and therefore probably in the k_{el} values[7c] should be studied. Third, since the $k_{el}(Br)$ (or $k_{el}(Cl)$) ratios differ for oxygen and thio nucleophiles as deduced from the different extents of stereoconvergence for reactions with the two nucleophiles,[1,5] study of a pair of analogous thio and oxygen nucleophiles may be beneficial.

All these requirements are fulfilled by the 9-(bromochloromethylene)fluorene (**8**) and the β,β-bis(*p*-nitrophenyl)-α-

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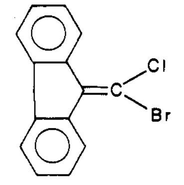
bromo-α-chloroethylene systems that were studied with the p-$MeC_6H_4X^-$ ($TolX^-$, X = S, O) nucleophiles.



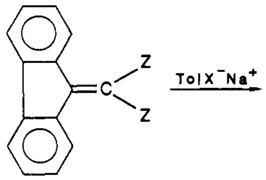
8

$(p\text{-}O_2NC_6H_4)_2C{=}C(Cl)Br$

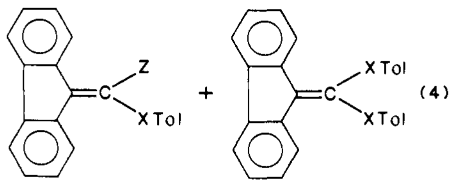
9

Results

Synthesis of the Substitution Products. The mixed dihalides **8** and **9** were prepared from 9-diazofluorene and $(p\text{-}O_2NC_6H_4)_2C{=}N_2$ and bromochlorocarbene, which was generated from $CHClBr_2$ and *t*-BuOK according to Reimhinger et al.[14] Initial experiments showed that substitution of **8** or **9** by *p*-toluenethiolate or by *p*-cresolate ion gives both monosubstitution products and the disubstitution product. Separation difficulties were avoided by preparing the substitution products from the dichlorides **10** and **12** and from the dibromides **11** and **13**. The reactions were usually conducted in acetonitrile by using an equimolar amount or a small excess of sodium *p*-toluenethiolate or *p*-cresolate. Deep blue colors were observed immediately with compounds **9**, **12**, and **13** and a pale pink color was observed with **10** and **11** with p-$MeC_6H_4O^-$. With p-$MeC_6H_4S^-$, **9** and **13** gave deep red to violet colors and **10–12** gave yellowish-green solutions. When no further progress of the reaction was observed, due to complete consumption of the nucleophile, the reaction was worked up. In each case, the corresponding precursor (**10–13**), the monosubstitution product (**14–17**, **20–23**), and the disubstitution product (**18**, **19**, **24**, **25**) were present (eq 4 and 5).



10, Z = Cl
11, Z = Br



14, X = S, Z = Cl
15, X = S, Z = Br
16, X = O, Z = Cl
17, X = O, Z = Br

18, X = S
19, X = O

$(p\text{-}O_2NC_6H_4)_2{=}CZ_2 \xrightarrow{TolX^-Na^+}$

12, Z = Cl
13, Z = Br

$(p\text{-}O_2NC_6H_4)_2C{=}C(XTol)Z + (p\text{-}O_2NC_6H_4)_2C{=}C(XTol)_2$ (5)

20, X = S, Z = Cl
21, X = S, Z = Br
22, X = O, Z = Cl
23, X = O, Z = Br

24, X = S
25, X = O

The spectral properties of the substitution products are given in Table I and their analytical data are given in Table IV.

The following reactions suggested that OAc^-, N_3^-, CN^-, and $t\text{-BuO}^-$ are unsuitable nucleophiles for studying the intramolecular element effects: (a) Reaction of **8** and **11** with NaOAc in AcOH for 48 h at room temperature or for 72 h at reflux did not give any product. **11** gave no reaction, but after reflux for 15 min, ca. 15% fluorene is formed. Fluorene (identified by NMR, mass spectra, and melting point) is also the main reaction product of **8** and **11** after 18 h at reflux. (b) Reaction of **10** with NaN_3 in DMF gave 9-azido-9-cyanofluorene, which on further reaction gives 10-cyanophenanthridine as reported by Smolinsky and Pryde.[15] Neither **10** nor **11** gave any product with NaN_3 in CH_3CN or in 5:2 CH_3CN–MeOH at room temperature. (c) Reaction of **8** or **11** with KCN for 50 h at reflux in MeCN or at room temperature in the presence of dibenzo-18-crown-6 is very slow (as judged by GC) and gives a large number of products. (d) Reaction of **8**, **10**, or **11** with solid $t\text{-BuO}^-K^+$ in MeCN gave mainly fluorenone together with several other products, which according to their GC retention times may inlcude mono- and disubstitution products.

Product Distribution in the Substitution. The formation of disubstitution products **18**, **19**, **24**, and **25** even before complete consumption of the precursor dihalides **10–13** indicated that substitution of the monosubstitution products **14–17** and **20–23** competes effectively with substitution of **10–13**. The same applies for substitution of the bromochloro compounds **8** and **9** since an appreciable amount of the disubstitution product was formed even with an equimolar amount of the dihalide and the nucleophile. This is an obstacle for determination of the kinetically controlled chlorine to bromine substitution products since a preferential loss of one of them from their mixture will change the kinetically controlled ratio to an extent that will be substrate, nucleophile, and reaction time dependent. Hence, the nucleophile was added portionwise to the substrate at concentrations that ensured that at least at the first points analyzed the dihalide was in large excess. Under these conditions the percentage of disubsitution products was nil or relatively low and the ratio of the monosubstitution products remained nearly constant. It did not change very much even when appreciable amounts of disubstitution product were formed, although the substitution of the monobromo compound seems slightly faster than that of the monochloro compound (see below and footnotes to Table III).

Due to the low solubilities of the product salts (NaCl, NaBr) in the organic media the reaction mixtures became heterogeneous with the progress of the reaction.

Three analytical techniques were used for determining the extent of reaction and the product distribution: ^1H NMR was used for studying almost all the reactions, and each system was studied also either by HPLC or by GC. With the latter methods the retention times of the independently prepared samples were used, and the formation of the substitution products was corroborated by peak enhancement experiments, but the compounds were not isolated from the chromatographic columns. Although δ's of the aromatic methyl signals of the TolX (X = O, S) moiety of the mono- and disubstitution products differ, they were not used for the analysis since the methyl signal of traces of the free ArXH overlapped these signals. In the fluorene system the two lower field doublets of H-1 and H-8 were sufficiently separated in the precursor, the two monosubstitution products, and the disubstitution products to enable analysis of the product distributions. The same applies for the signals of the ortho protons to the double bond in the bis(nitrophenyl)-substituted systems. However, with the progress of the reaction, the intensity of these signals increased, the overlap started to be important, and the accuracy of the analysis was reduced, especially in the reaction of p-$MeC_6H_4S^-$ with **9**. This is one reason that the calculated $k_{el}(Br)/k_{el}(Cl)$ ratios at higher reaction percentages (more disubstitution products) increased appreciably; i.e., most of the increase is an artifact of the calculation.

The errors due to integration of small signals at early reaction percentages and to overlap at higher reaction percentages led to the need for corroboration of the results by the chromatographic techniques. These methods are more accurate in determination of the monosubstitution products since they are most sensitive at low reaction percentages, and we regard the HPLC and the GC $k_{el}(Br)/k_{el}(Cl)$ ratios as more reliable. However, the disubstitution products appear as broad signals and the error in their percentage

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Table I. Spectroscopic Data of the Substitution Products

compd	λ_{max}^{MeCN}, nm (log ϵ)	ν_{max}^{Nujol}, cm^{-1}	δ(CDCl$_3$)[a] Tol	δ(CDCl$_3$)[a] Ar$_2$C	m/z (rel %, assignment)[e]
14	243 (4.66), 253 (4.61), 262 (4.66), 285 (4.18), 347 (4.36)	1520	2.36 (Me), 7.08, 7.20 (Ar, J = 9 Hz)	7.32 (4 H, m, H-2,3,6,7), 7.76 (2 H, 2 d, H-4,5), 7.92 (1 H, d, H-8), 8.29 (1 H, d, H-1)	336, 334 (22, 58, M), 319 (17, M − Me), 299 (21, M − Cl), 298 (15, M − HCl), 284 (52, M − Cl − Me), 266 (24, M − HCl − S), 208 (18, FlCS), 163 (17, Fl − 3 H), 135 (B, TolCS)
15	232 (4.56), 253 (4.57), 262 (4.62), 276 (4.17), 286 (4.16), 350 (4.23)	1520	2.37 (Me), 7.32 (Ar)[b]	7.32 (4 H, m, H-2,3,6,7), 7.71 (2 H, d, H-4,5), 8.80 (1 H, d, H-8), 8.88 (1 H, d, H-1)	380, 378 (27, 27, M), 299 (75, M − Br), 284 (B, M − Br− Me), 266 (24, M − Br − SH), 208 (22, FlCS), 165 (15, Fl − H), 135 (4, TolCS)
16	229 (4.63), 248 (4.52), 256 (4.60), 271 (4.25), 307 (4.24), 319 (4.30)[c]	1625	2.36 (Me), 7.08, 7.29 (Ar)	7.32 (4H, m, H-2,3,6,7), 7.77 (2 H, 2 d, H-4,5), 7.92 (1 H, d, H-8), 8.29 (1 H, d, H-1)	320, 318 (30, 89, M), 255 (68, M − CO − Cl), 200, 198 (34, 100, Ar$_2$CCl − H), 164 (67, Ar$_2$C), 119 (49, TolCO)
17	228 (4.55), 238 (4.42), 248 (4.45), 256 (4.55), 283 (4.16), 308 (4.19), 320 (4.25)[d]	1615	2.35 (Me), 7.09, 7.16 (Ar, J = 9 Hz)	7.25 (4 H, m, H-2,3,6,7), 7.75 (2 H, 2 d, H-4,5), 7.93 (1 H, d, H-8), 8.50 (1 H, d, H-1)	364, 362 (68, 67, M), 255 (88, M − CO − Br), 164 (B, Ar$_2$C), 119 (34, TolCO)
18	240 (4.68), 254 (4.57), 263 (4.56), 352 (4.26)	1520	2.33 (2 Me), 7.06 (4 H, d, J = 12 Hz, TolS-H ortho to Me), 7.08 (4 H, d, J = 12 Hz, TolS-H, ortho to S)	7.30 (4 H, m, H-2,3,6,7), 7.73 (2 H, d, H-4,5), 8.95 (2 H, d, J = 6 Hz, H-1, 8)	422 (43, M), 299 (57, M − TolS), 284 (B, M − TolS − Me), 164 (B, Fl − 2 H), 163 (18, Fl − 3 H), 135 (24, TolS), 123 (14, TolS)
19	232 (4.71), 254 (4.40), 294 (4.38), 321 (4.37)	1670, 1595	2.15 (2 Me), 6.81 (8 H, m, ArS)	7.23 (4 H, m, H-2,3,6,7), 8.08 (2 H, d, H-4,5), 8.20 (2 H, d, H-1,8)	390 (24, M), 255 (B, M − TolO − CO), 164 (86, Ar$_2$C)
20	206 (4.54), ca. 220 sh, (4.30), 257 (4.41), 330 sh (4.13)	1600, 1590	2.37 (Me), 7.23, 7.33 (Ar)	7.49, 8.22 (8 H, 2 AB q, J = 9 Hz)	427, 425 (35, 100, M − 1), 345 (37, M − Cl − NO$_2$?), 176 (52, C$_{14}$H$_8$), 84 (59)
21	203 (4.43), ca. 220 sl. (4.30), 267 sh (4.23), 292 (4.27)	1595	2.38 (Me), 7.20, 7.32 (Ar)	7.49, 8.22 (8 H, 2 AB q, J = 9 Hz)	472, 470 (55, 48, M), 391 (75, M − Br), 345 (B, M − Br − NO$_2$), 284 (32), 123 (64, TolS), 91 (31, C$_7$H$_7^+$)
22	204 (4.50), 221 (4.43), 307 (4.23)	1585	2.35 (Me), 6.99, 7.20 (Ar, J = 9 Hz)	7.43, 8.12 (4 H, AB q, J = 9 Hz, Ar trans to Cl), 7.56, 8.29 (4 H, AB q, J = 9 Hz, Ar cis to Cl)	412, 410 (25, 9, M), 411, 409 (100, 36, M − 1), 256 (20, Ar$_2$C), 91 (74, C$_7$H$_7^+$)
23	206 (4.51), 223 (4.45), 305 (4.33)	1585	2.35 (Me), 7.00, 7.20 (Ar, J = 9 Hz)	7.44, 8.11 (4 H, AB q, J = 9 Hz, Ar trans to Cl?), 7.56, 8.30 (4 H, AB q, J = 9 Hz, Ar cis to Cl?)	456, 454 (43, 44, M), 268 (12, M − Br − OTol), 164 (29, Ar$_2$C), 163 (40, Ar$_2$C − H), 119 (22, TolCO), 91 (B, C$_7$H$_7$)
24	207 (4.57), 262 (4.44), 354 (4.05)	1595	2.30 (2 Me), 7.0 (8 H, s, Ar)	7.38, 8.11 (8 H, 2 AB q, J = 9 Hz)	514 (84, M), 391 (80, M − TolS), 345 (B, M − TolS − NO$_2$), 123 (62, TolS)
25	205 (4.52), 223 (4.43), 335 (4.27)	1630, 1585	2.27 (2 Me), 6.84, 7.03 (2 Ar, J = 8.4 Hz)	7.48, 8.50 (8 H, 2 AB q, J = 9 Hz)	482 (53, M), 347 (B, Ar − TolO − CO), 272 (24, Ar$_2$CO), 150 (25, ArCO)

[a] Tol = p-MeC$_6$H$_4$; Me groups appear as 3 H singlets. Tol and Ar groups appear as a 4 H quartet with J = 8 Hz, unless otherwise stated. [b] The quartet is buried under the multiplet of fluorene H-2,3,6,7. [c] λ_{max}^{DMF} = 321 nm (4.28). [d] λ_{max}^{DMF} = 323 nm (4.30). [e] Fl = fluorene.

Table II. Examples of Substitution of **8** and **9**[a]

Reaction of **8** with p-MeC$_6$H$_4$O$^-$Na$^+$

	in CH$_3$CN (analyzed by GC)						in CD$_3$CN (analyzed by NMR)				
% reaction[b]	4	10	31	39	47	63	9	17	29	40	46
% **16**	2.5	7	20	23	29	29	6	11.5	20	28	30
% **17**	1.2	3	10	10	11	10	3	5	7	7	9
% **19**			1	6	7	24		0.5	2	5	7
k_{el}(Br)/k_{el}(Cl)	2.1	2.3	2.0	2.3	2.6	2.9	2.0	2.3	2.9	4.0	3.3

Reaction of **9** with p-MeC$_6$H$_4$S$^-$Na$^+$

	in CD$_3$CN (analyzed by NMR)					in CH$_3$CN (analyzed by HPLC)				
% reaction[b]	9	14.5	50	60	80	8.5	21	31.5	43	72
% **20**	6	10	33	38	50	6	15	22	30	48
% **21**	3	4	14	18	22	2.5	6	9	12	19
% **24**		0.5	3	4	8		0.3	0.5	1	5
k_{el}(Br)/k_{el}(Cl)	2.0	2.5	2.4	2.1	2.3	2.4	2.5	2.4	2.5	2.5

[a] Portionwise addition of the nucleophile. [b] Based on the precursor reacted.

is significant. Except for these products, the agreement between the results of the GC and HPLC methods and the NMR method was mostly satisfactory within the experimental errors. Examples of two sets of experiments followed by two methods, which show the near constancy of the ratios, are given in Table II. The appreciable difference in the reported amount of disubstitution products in these and other cases is due not only to the experimental error but also to the fact that their amount depends on the concentration of the nucleophile added at each point, which differs in the different experiments.

A summary of the ratios of the monochloro to monobromo products at the beginning of the reaction at reaction percentages that were determined by the disappearance of the precursor, together with the corresponding errors estimated either from the changes of the ratios within the experiment or from parallel experiments, is given in Table III. Also given are the derived k_{el}(Br)/k_{el}(Cl) ratios under the various conditions and their average values for each substrate/nucleophile combination regardless of the solvent. The main conclusion is that the ratios of 2.0–3.2 are nearly substrate, nucleophile, and solvent independent.

Table III. Product Distributions and $k_{el}(Br)/k_{e}(Cl)$ Ratios

substrate	nucleophile[a]	solvent	% reaction[b]	analytical method	[mono Cl]/[mono Br] ratio	$k_{el}(Br)/k_{el}(Cl)$	
8	TolO⁻	CH_3CN	4–47	GC	70:30	2.3 ± 0.2	
		CD_3CN	9–29[d]	NMR	71:29	2.4 ± 0.3	
		$(CD_3)_2SO$	32–56[e]	NMR	74:26	2.9 ± 0.2	2.5 ± 0.4[c]
		9:1 $(CD_3)_2SO$–CD_3OD	6–29	NMR	71:29	2.5 ± 0.8	
	TolS⁻	CH_3CN	6–83[f]	GC	68:32	2.1 ± 0.2	
		CD_3CN	33–58[g]	NMR	75:25	(3.0 ± 0.1)	2.8 ± 0.6[c]
		1:1 CD_3CN–$CDCl_3$	10–28	NMR	76:24	3.2 ± 0.4[h]	
		9:1 $(CD_3)_2SO$–CD_3OD	16–37[i]	NMR	74:26	2.9 ± 0.2	
9	TolO⁻	CH_3CN	5–40	HPLC	67:33	2.0 ± 0.1	
		CH_3CN	4–21	GC	68:32	2.1 ± 0.1[j]	
		CD_3CN	6–23	NMR	69:31	2.2 ± 0.1	2.1 ± 0.2[c]
		$(CD_3)_2SO$	45–52[k]	NMR	68:32	2.1 ± 0.3	
		9:1 $(CD_3)_2SO$–CD_3OD	16–40	NMR	68:32	2.1 ± 0.2	
	TolS⁻	CH_3CN	8.5–7.2[d]	HPLC	71:29	2.5 ± 0.1	
		CD_3CN	9–80[d]	NMR	70:30	2.3 ± 0.1	2.4 ± 0.2[c]

[a]The nucleophile was added portionwise; Tol = *p*-MeC_6H_4; sodium salts were used. [b]Percentage reaction for which the $k_{el}(Br)/k_{el}(Cl)$ ratios were calculated. Unless otherwise stated, the percentages of disubstitution products at these reaction percentages were ≤8% and negligible in most cases. [c]Average value under all conditions. [d]See Table II. [e]At 56% reaction, 9% of disubstitution product **19** is formed. At 95% reaction, **19** is 54% of the product, and $k_{el}(Br)/k_{el}(Cl) = 3.3$. [f]No disubstitution product **18** up to 83% reaction. When **18** is 19% (98–100% reaction of **8**, $k_{el}(Br)/k_{el}(Cl)$ = 3.4 ± 0.4. [g]**18** is already 19% at 58% reaction. It increases to 52% at 96% reaction when $k_{el}(Br)/k_{el}(Cl) = 5$. [h]Increases to 3.7 at 70% reaction, when **18** is 24%. [i]At 37% and 91% reaction, 10% and 47% of **18** are formed and $k_{el}(Br)/k_{el}(Cl)$ = 3.5 and 2.7, respectively. [j]2.3 ± 0.1 at 65–89% reaction when the disubstitution product **25** is 21–49%. [k]**25** is formed in 15–21%.

Development of Colors during the Reaction. The color development when 0.0025 mol L^{-1} of **9** reacted with 0.025 mol L^{-1} of $TolS^-Na^+$ in DMSO was followed simultaneously at the two newly rapidly formed maxima at 432 and 572 nm, where neither **9** nor the substitution products absorb. The maxima are apparently due to two species. After 2.5 min the optical density (OD) was 0.99 at 572 nm and it increased approximately linearly ($\Delta OD/\Delta t$ = 0.031 min^{-1}) to 1.61 after 22.5 min. A slower increase led to a plateau with OD = 2.0 after 70 min. The higher absorption at 432 nm was developed more rapidly: the corresponding OD values were 3.46, 3.71, and 3.84.

At identical concentrations of **9** and $TolO^-Na^+$ in DMSO maxima were developed at 508 and 572 nm. Again, they reached a high value during 2.5 min (OD = 1.35 and 1.56, respectively) and increased slowly in parallel (OD = 1.45 and 1.72, respectively, after 1 h). The longer wavelength maximum was displaced to 588 nm with OD_∞ = 1.84 and the second maximum became a shoulder with OD_∞ = 1.52.

In a similar experiment with 0.0025 mol L^{-1} of both **9** and *p*-TolO⁻ ion, the maxima appear at 510 and 599 nm, with OD's of 0.46 and 0.41 after 2.5 min. They increased rapidly and approximately linearly ($\Delta OD/\Delta t$ = 0.058 and 0.064 min^{-1}) up to 12.5 min, and OD_∞ = 1.23 and 1.54, respectively, after 60 min. The values started then to decrease slowly.

Since the color persisted even when **9** nearly disappeared, we investigated the parallel reactions of the mono- and diproducts. Reaction of **22** and **23** with TolO⁻ resulted in the appearance of two flat maxima: at 516 and 582 nm with an ϵ ratio of 0.8 from **22** and at 514 and 584 nm with an ϵ ratio of 0.8 from **23**. The two spectra seem identical within experimental error. The diproduct **25** gave λ_{max} = 550 nm with a shoulder at 510 nm with relative intensities of 1.05. The diproduct **24** and the monobromo product **21** gave a single new maximum at 567 nm with *p*-TolS⁻ ion; the monochloro compound **20** did not show any such new maxima above 400 nm.

ESR Measurements. In order to probe the possibility of a single-electron transfer, a few reactions were followed by ESR. Equal volumes of 0.02 mol L^{-1} solutions of either **8** or **9** and the nucleophile in DMSO were mixed immediately before the measurements. The ESR spectrum was taken after 10–15 min, the time required for calibration of the spectrometer.

In the reaction between **8** and *p*-$TolS^-Na^+$ identical spectra (Figure 1) were obtained after 15 and 90 min, but after 150 min no ESR spectrum was obtained. The reactants did not give any ESR signal. Solutions of the two monosubstitution products with and without thiolate ion gave an ESR spectrum, which immediately disappeared, only in the reaction of **15** with *p*-$TolS^-Na^+$.

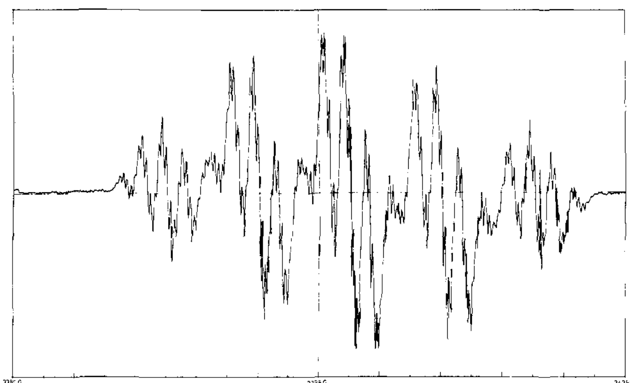


Figure 1. ESR spectrum obtained from the reaction of **8** and *p*-$MeC_6H_4S^-Na^+$ in DMSO.

In the reaction of **8** with *p*-TolO⁻ and of **9** with *p*-TolO⁻ and *p*-TolS⁻ no ESR spectrum was observed.

Substitution in the Presence of Radical Traps. Substitution of **8** with *p*-$MeC_6H_4S^-Na^+$ in acetonitrile was conducted in parallel in the absence or the presence of an equimolar amount of hydroquinone. GC analysis gave identical (2.1) [**14**]/[**15**] ratios. Substitution of **9** with *p*-$MeC_6H_4S^-Na^+$ in acetonitrile in the presence of *N,N*-dimethyl-*p*-nitrosoaniline gave a [**20**]/[**21**] ratio of 2.5, regardless of whether the nucleophile was added in solution or portionwise as a solid. The ratio is identical with the ratio obtained without *N,N*-dimethyl-*p*-nitrosoaniline.

Electrochemical Measurement. A cyclic voltammogram of **8** and **9** was taken with a Pt button electrode and Ag/AgCl reference electrode with Bu_4NBF_4 as the electrolyte in DMF. The mono- and the disubstitution potentials respectively were −1.3 and −1.5 V for **8** and −0.9 and ≤−1.8 V (solvent reduction interferes) for **9**.

Intermolecular Element Effect. Competition experiments with excess vinyl halides were conducted for evaluating the intermolecular element effects. Sodium *p*-toluenethiolate was added portionwise to mixtures containing a [**12**]/[**9**] ratio of 0.88 or a [**13**]/[**9**] ratio of 0.91 in acetonitrile. Samples were taken between 1.3 and 96% reaction, and the product ratios were analyzed by HPLC. Only **20**, **21**, and <2% of **24** were formed up to 50% reaction. The average [**20**]/[**21**] ratios obtained in the two experiments were up to 50% reaction 5.0 ± 0.1 and 0.67 ± 0.04, respectively. At 92% disappearance of the vinyl halides in the competition between **9** and **12**, 19% of **24** was formed and the [**20**]/[**21**] ratio was 6.1. The [**20**]/[**21**] ratio was 1.7 after 96%

disappearance of the vinyl halides in the competition of **9** and **13**, where **24** consisted of 25% of the product.

In another experiment, sodium *p*-cresolate was added portionwise to a 33:37:30 mixture of **8**, **10**, and **11** in DMF. Up to 23% reaction, the disubstitution product **19** was <1%. The normalized decrease in the concentration of the dihalides followed the order **10** > **8** > **11**; e.g., the **8**:**10**:**11** ratios were 26.8:29.4:25.7 and 25.5:26.1:25.3 at 17 and 23% reaction, respectively. The average [**16**]/[**17**] ratios were 2.1 ± 0.2.

The intermolecular element effect for elimination of Br^- from **9** vs elimination Cl^- from **12** ($k_{Br}(\mathbf{9})/k_{Cl}(\mathbf{12})$ = (EEE)$_1$) can be calculated from eq 6, since **20** is formed by both k_{Cl} from **9** and

$$[\mathbf{21}]/[\mathbf{20}] = k_{Cl}(\mathbf{9})/k_{Br}(\mathbf{9}) + 2Ak_{Cl}(\mathbf{12}) \quad (6)$$

$$[\mathbf{21}]/[\mathbf{20}] = (2Bk_{Br}(\mathbf{13}) + k_{Cl}(\mathbf{9}))/k_{Br}(\mathbf{9}) \quad (7)$$

k_{Cl} from **12**, taking into account the presence of two chlorines in **12** and the initial [**12**]/[**9**] ratio (A), whereas **21** is formed only via k_{Cl} from **9**. Similarly, the intermolecular element effect for the **13**/**9** pair ($k_{Br}(\mathbf{13})/k_{Cl}(\mathbf{9})$ = (EEE)$_2$) is obtained from eq 7, where B is the initial [**13**]/[**9**] ratio.

Equations 6 and 7 lead to eq 8 and 9, where IEE = $k_{Br}(\mathbf{9})/k_{Cl}(\mathbf{9})$ is the intramolecular element effect, X = [**21**]/[**20**] in the competition between **9** and **12**, and Y = [**21**]/[**20**] in the competition between **9** and **13**.

$$(\mathrm{EEE})_1 = 2AX(\mathrm{IEE})/(1 - X(\mathrm{IEE})) \quad (8)$$

$$(\mathrm{EEE})_2 = (Y(\mathrm{IEE}) - 1)/2B \quad (9)$$

The intermolecular element effects for the **9**/**12** pair and for the **9**/**13** pair are 1.76 and 1.51, respectively.

The analogous reaction scheme for the fluorenylidene systems is eq 10.

$$\mathbf{11} \xrightarrow{2k_{Br}(11)} \mathbf{17} \xleftarrow{k_{Cl}(8)} \mathbf{8} \xrightarrow{k_{Br}(8)} \mathbf{16} \xleftarrow{2k_{Cl}(10)} \mathbf{10} \quad (10)$$

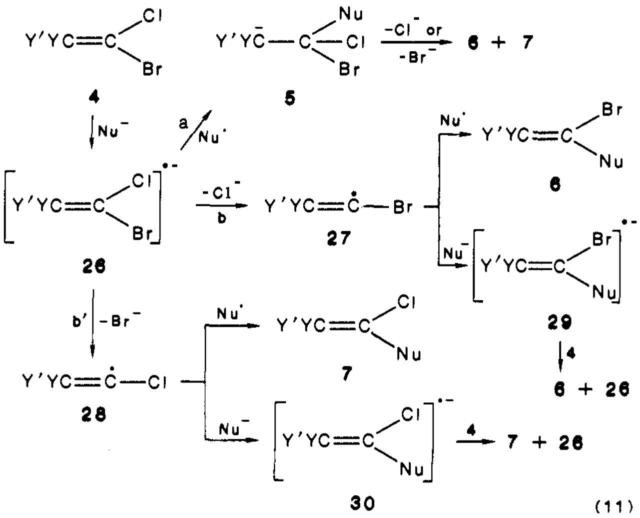
Since **16** and **17** are formed simultaneously from **8** and **10** and **8** and **11**, respectively, the intermolecular element effects $k_{Br}(\mathbf{8})/k_{Cl}(\mathbf{10})$ and $k_{Br}(\mathbf{11})/k_{Cl}(\mathbf{8})$ cannot be obtained independently from the [**16**]/[**17**] ratio. They were calculated from the decrease in the concentrations of **8**, **10**, and **11**, after normalization to identical concentrations, using statistical correction for the presence of two identical halogens in **10** and **11** and applying the intramolecular element effect of 2.5 from Table III. The two intermolecular element effects were 1.2 ± 0.1. The [**16**]/[**17**] ratios calculated from this value were within ±15% of the experimental value.

Discussion

Our main result is that all the values of the intramolecular element effects are 2.0–3.2, being practically independent of the β-activating group, the nucleophile, and the solvent. Before these values are discussed in terms of the second step of eq 2, the possibility of alternative substitution routes should be raised, since if these operate, the intramolecular element effect may be irrelevant to the elimination step presented in eq 2 and 3.

Possibility of a Substitution Involving a Single-Electron Transfer. Inspection of the many vinylic substitution mechanisms[16] indicates that the main possible competing substitution routes of **8** and **9** involve an initial single-electron-transfer (SET) step. This should be considered for three reasons. First, the importance of such a step in substitution of saturated and unsaturated halides has been recognized in recent years.[17,18] Moreover, system **9** carries *p*-nitrobenzyl moieties, and the *p*-nitrobenzyl group is known to participate in SET steps, especially with easily reducing nucleophiles such as thiolate ions.[1] Second, an ESR signal was observed in the reaction of **8** with $p\text{-MeC}_6H_4S^-$. Third, the colors appearing during the reaction may be due to a SET step.

When the monoreduction potentials of **8** (−0.9 V) and **9** (−1.3 V) are compared with the oxidation potential of $p\text{-MeC}_6H_4S^-Na^+$)[19] it is clear that a SET from $p\text{-MeC}_6H_4S^-$ to **4** (i.e., **8** or **9**) generating the ion radical **26** and Nu• is feasible. Further reactions leading to a multiplicity of substitution routes are shown in eq 11: cage recombination of **26** with Nu• gives anion **5** (route



(11)

a), which gives the monosubstitution products **6** and **7** according to eq 2. Loss of Cl^- or Br^- from **26** (routes b and b′) gives halovinyl radicals **27** and **28**, which can then give respectively **6** and **7** either by recombination with Nu^- or via an $S_{RN}1$ reaction involving **29** and **30**. Radicals **27** and **28** can also dimerize.

During the cyclic voltammetry of **12** and **13** the concentration of the anion radicals remained constant, suggesting that $\mathbf{12}^{\bullet-}$ and $\mathbf{13}^{\bullet-}$ do not cleave during the measurement. The [**6**]/[**7**] ratios derived from **26** will be determined by the [**27**]/[**28**] ratio, but the relative rates of Br^- to Cl^- loss from analogous chloro and bromo aromatic radical anions are much higher ($k_{Br}/k_{Cl} > 10^2$) than those in Table III.[21] Consequently, substitution via routes b and b′ of eq 11 seems unlikely.

The ESR spectrum observed in the reaction of **8** with $p\text{-MeC}_6H_4S^-Na^+$ shows similarity with the spectra of the fluorenyl radical anion[22a] or cation.[22b] Hence the radical anion contains the fluorenyl moiety, but its structure is not clear. The possibility that the species observed is an anion radical derived from dimerization of **28**[23] is unlikely since dimers are not observed and the implicit appreciable preferential loss of Br^- from **26** is not reflected in the [**14**]/[**15**] ratio. The persistence of the spectrum after the reaction is finished suggests that the species observed is not on the reaction coordinate for the substitution.

The anion radical derived from **9** seems to be more stable than that derived from **8**, but an ESR spectrum was not observed in the reactions of **9**. The explanation may be similar to that of Russell.[24] The difference in stability between the anions derived from **8** and **9** may be larger than that between the corresponding anion radicals, so that formation of the anion from **9** and formation

(16) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309.

(17) E.g.: Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212 and references therein. Norris, R. K. In *The Chemistry of Functional Groups. Supplement D*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapter 16, p 681.

(18) Kornblum, N. In *The Chemistry of Functional Groups. Supplement F*; Patai, S., Ed.; Wiley: Chichester, 1982; Chapter 10, p 361.

(19) The reduction potential for the $Mn^{III} \rightarrow Mn^{II}$ porphyrin pair is −0.25 V and the reduction is carried out by $p\text{-MeC}_6H_4S^-$ (Harriman, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1979**, 1532. Fuhrhop, J. H. *Struct. Bonding (Berlin)* **1974**, *18*, 1).

(20) Preliminary experiment by Prof. V. D. Parker.

(21) Parker, V. D. *Acta Chem. Scand., Ser. B* **1981**, *B35*, 595, 655. Aalstad, B.; Parker, V. D. *Ibid.* **1982**, *B36*, 47. Parker, V. D. *Adv. Phys. Org. Chem.* **1983**, *19*, 131. For example, the k_{Br}/k_{Cl} ratio for expulsion of Br^- and Cl^- from the 4-halogenobenzophenone ion radicals in acetonitrile is 648; In the substitution of PhCl and PhBr by the acetone enolate ion via $S_{RN}1$ where the C–X bond cleavage is rate determining, k_{Br}/k_{Cl} = 450 (Bunnett, J. F. *Acc. Chem. Res.* **1977**, *11*, 413).

(22) (a) Rothwell, E. J.; Tabner, B. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1384; **1983**, 145. (b) Bethell, D.; Handoo, K. L.; Fairhurst, S. A.; Sutcliffe, L. H. *Ibid.* **1979**, 707.

(23) Bethell, D., personal communication.

(24) Russell, G. A.; Jansen, E. G.; Bemis, A. G.; Geels, E. J.; Moye, A. J.; Mak, S.; Strom, E. T. *Adv. Chem. Ser.* **1965**, *No. 51*, 112. Russell, G. A.; Bemis, A. G.; Geels, E. J.; Jansen, E. G.; Moye, A. J. *Ibid.* **1968**, *75*, 174.

of the anion radical from **8** are the preferred processes.

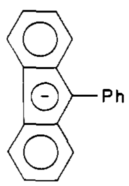
The insensitivity of the product distribution to the presence of the radical traps *N*,*N*-dimethyl-*p*-nitrosoaniline or hydroquinone indicates that if **27** and **28** are formed, their capture rates by the radical traps are similar.

We therefore conclude that if a SET to form **26** takes place, the main substitution course is not via radicals **27** or **28**. Additional support for this is the lack of sensitivity of the [**6**]/[**7**] ratio to the nucleophile. The SET ability of our nucleophiles is p-$MeC_6H_4S^-$ > p-$MeC_6H_4O^-$,[25] and the SET-involving route should be more pronounced with p-$MeC_6H_4S^-$ and this should presumably be reflected by a different [**6**]/[**7**] ratio than that in the other routes.

However, a SET followed by a (cage) recombination of **26** and $Nu^\bullet$ (eq 11, route a) leads to **5**. Since the route by which **5** is formed is probably irrelevant to the product-forming step of eq 2,[26] any conclusion regarding the nucleofuge expulsion step in nucleophilic vinylic substitution remains valid regardless of whether the first step of the substitution is a single nucleophilic attack (**4** → **5**) or a sequence of two steps (SET–recombination; **4** → **26** → **5**).

Nature of the Colored Solutions. The colors formed during the reaction could have been due to an anion radical formed by SET. However, they change during the reaction and persist after its completion, and the absence of an ESR signal in the blue solution formed from **9** and p-$MeC_6H_4O^-$ excludes this possibility.

Anion **31** is orange[27] and anion **32** is blue.[27b] The blue color (λ_{max} 525 nm) observed in the *t*-BuO^--promoted dehydrofluorination of **33** was first ascribed to the anion **34**[28] but recent evidence suggests that the color is not due to **34** but to a further cleavage to 4,4′-dinitrobenzophenone.[30]



31

$(p\text{-}O_2NC_6H_4)_3C^-$

32

$(p\text{-}O_2NC_6H_4)_2CHCF_3$

33

$(p\text{-}O_2NC_6H_4)_2\bar{C}CF_3$

34

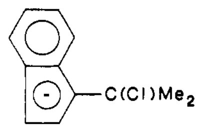
The spectral behavior of our reactions resembles that described above. The colors develop more slowly than the displacment of the nucleofuge, they persist for a long time after the reaction, and the disubstitution products also generate colors, which persist for days to weeks, with the nucleophiles. We conclude that the colors are not due to carbanion **5**, but they are likely to be formed from anions such as $Y'YC^-CNu_3$ in the basic solution.

k_{Br}/k_{Cl} Ratio as a Possible Probe for Evaluating the Position of the Transition State along the Reaction Coordinate. For using the intramolecular element effect as a transition state probe for the elimination step in our reactions, three closely related prerequisites should be fulfilled. (a) It has to be shown that the addition–elimination type substitution is a two-step process where the C–X bond cleavage occurs in the second step. (b) It should be shown that the k_{Br}/k_{Cl} ratio is indeed related to the extent of bond cleavage in the transition state and if this is so, a calibration of the magnitude of the ratio is required in order to make the terms "high" and "low" mechanistically useful. (c) It should be shown that the intramolecular element effect is still a measure of the extent of C–X bond cleavage in the transition state, in spite of the interaction of the two halogens in **5**.

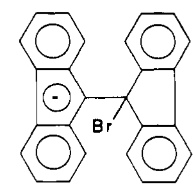
Evidence for a Two-Step Mechanism. The evidence for a two-step mechanism is threefold and stronger for the substitution of **9**. The intermolecular element effects of 1.6 ± 0.15 for **9** and of 1.2 ± 0.1 for **8** obtained from the competition experiments are of the order ascribed to a rate-determining nucleophilic attack in vinylic substitution and used as evidence for the multistep mechanism (see below).[7] Whereas the stereochemical tool is not available for **8** and **9**, the partial stereoconvergence observed during the substitution of p-$MeC_6H_4C(Br){=}C(CO_2Me)CO_2Bu$-*t* by p-$MeC_6H_4O^-$ [1] shows that species activated by two ester groups react via a multistep route. According to the qualitative correlation between the pK_a's of CH_2YY' and the observation of stereoconvergence,[7c] the multistep route applies also for **9**. Finally, evidence for the $(ElcB)_I$ mechanism, involving intermediate β-halocarbanions **35**,[31] **36**,[32] and **37**,[33] was presented (see below). The feasibility of the existence of **35** and **37** is consistent with formation of the analogous **5** as discrete intermediates in our reactions.

$(p\text{-}O_2NC_6H_4)_2\bar{C}CHCl_2$

35



36



37

k_{Br}/k_{Cl} Ratio as a Mechanistic Probe. The previous use of the k_{Br}/k_{Cl} intermolecular element effect (i.e., the comparison of rates of RBr and RCl) as a mechanistic probe for the extent of C–X bond cleavage rests on two assumptions. (i) The electronic effects of Cl and Br on a reaction that does not involve C–halogen bond cleavage are similar.[34,35] (ii) For a rate-determining C–halogen bond cleavage, the reaction of the bromo compound will be faster.

k_{Br}/k_{Cl} ratios that do not differ appreciably from unity are therefore ascribed to reactions where the rate-determining step does not involve C–X bond cleavage. Examples are many nucleophilic aromatic substitutions,[34,36] many nucleophilic vinylic substitutions,[7] a few $(E1cB)_I$ reactions[33,37a] (e.g., in the dehydrohalogenation of the conjugate acid of **37**, k_{Br}/k_{Cl} = 1.9),[33] and substitution of 1-halobicyclo[1.1.0]butane-3-carbonitrile by MeO^- or CN^-, where k_{Br}/k_{Cl} ratios are 0.25[38a] and 0.71,[38b] respectively. Even k_{Br}/k_{Cl} ratios of 2 belong to this category,[7] and we therefore ascribed this route for **8** and **9**. However, we are aware of the difficulty in distinguishing between a multistep route where the C–X bond is "completely unbroken" and a concerted route where the same bond is "almost completely unbroken".[37]

(25) This is based on the (surprisingly small) differences in ionization potentials (IP) of PhS^- (5.26 eV) and PhO^- (5.42 eV) in water (Pearson, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 6109). Note, however, that an opposite order of the IP's was given by Ritchie (Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313).

(26) Whereas in the E1cB process the C–X orbital can be aligned with the incipient carbanionic orbital to benefit most from hyperconjugation, this is not the case in vinylic substitution.

(27) (a) Leffler, J. E. *The Reactive Intermediates of Organic Chemistry*; Interscience: New York, 1956; p 177. (b) Bowden and Stewart (Bowden, K.; Stewart, R. *Tetrahedron* **1965**, *21*, 261) reported λ_{max} of 582 nm (basic EtOH) to 703 nm (basic EtOH–DMSO).

(28) Kurzawa, J.; Leffek, K. T. *Can. J. Chem.* **1977**, *55*, 1696. Leffek, K. T.; Schroeder, G. *Ibid.* **1982**, *60*, 3077.

(29) Jarczewski, A.; Schroeder, G.; Galezowski, W.; Leffek, K. T.; Maciejewska, U. *Can. J. Chem.* **1985**, *63*, 576. Jarczewski, A.; Waligorska, M.; Leffek, K. T. *Ibid.* **1985**, *63*, 1194.

(30) Leffek, K. T., private communication.

(31) (a) Grout, A.; McLennan, D. J.; Spackman, I. H. (a) *J. Chem. Soc., Chem. Commun.* **1976**, 775. (b) Grout, A.; McLennan, D. J.; Spackman, I. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1758.

(32) Ölwegard, M.; McEwan, I.; Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1985**, *107*, 7494.

(33) Carey, E.; More O'Ferrall, R. A.; Vernon, N. M. *J. Chem. Soc., Perkin Trans 2* **1982**, 1581.

(34) Bunnett, J. F.; Garbisch, E. W., Jr.; Pruitt, K. M. *J. Am. Chem. Soc.* **1957**, *79*, 385.

(35) Based on the small difference between the σ_I and σ_R values of Cl and Br.

(36) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: London, 1968.

(37) (a) Fiandanase, V.; Maffeo, C. V.; Naso, F.; Ronzini, L. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1303 (for $TolSO_2C(Ph)CH(Ph)X$, k_{Br}/k_{Cl} = 4.9 (90 °C) for the erythro isomer and 1.64 for the threo isomer with Et_3N in benzene and 1.67 and 2.2 at 25 °C, respectively, with MeO^-/MeOH). (b) Cann, F. P.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 820. Bordwell, F. G. *Acc. Chem. Res.* **1970**, *3*, 281. Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

(38) (a) Hoz, S.; Auerbach, D. *J. Org. Chem.* **1984**, *49*, 4144. (b) Hoz, S.; Auerbach, D. *J. Am. Chem. Soc.* **1983**, *105*, 7685.

Since bromine is a better nucleofuge than chlorine, intuition suggests that "crudely, a large sensitivity to the nature of the leaving group may normally be taken as indicating a large degree of leaving group bond breaking in the transition state".[39,40] The main criticism of this notion is that of Bird and Stirling,[41] who dissected the k_{Br}/k_{Cl} ratio into three contributions, the homolytic bond energies (73 and 60 kcal mol^{-1} for C–Cl and C–Br, respectively), the electron affinities (–83.3 and –77.6 kcal mol^{-1} for Cl and Br, respectively[42]), and the solvation energies in water (–84.2 and –77.8 kcal mol^{-1} for Cl^- and Br^-, respectively). Consequently, the heterolytic bond dissociation energies $RX \rightarrow R^+ + X^-$, which are 6–8 kcal mol^{-1} higher for aliphatic chlorides than for bromides,[43] are nearly completely compensated by the solvation energies. At complete ionization the k_{Br}/k_{Cl} ratio will be ca. unity and "superimposition of the three factors gives a bell-shaped dependence of bromide:chloride ratio on bond extension" for a solvent "in which solvation of halide ions is important".[41]

In spite of the relevance of this analysis to the use of k_{Br}/k_{Cl} ratios as mechanistic probes, we did not find any serious confirmation or rebuttal of these ideas. The only comment that we want to make *in relation to our system* is that k_{Br}/k_{Cl} values close to unity cannot reflect a very late transition state. First, the assumption that the full solvation energy is obtained even at a very late transition state seems unjustified in view of the desolvation of the nucleophile required in the reverse reactions of cation–anion recombination, S_N2 reactions, and presumably E2C reactions. Second, the value of $\Delta\Delta G°_{solvation} = \Delta G°(Cl^-) - \Delta G°(Br^-)$ in water differs from those in our solvents (CD_3CN, $(CD_3)_2SO$, $(CD_3)_2SO$–CD_3OD). $\Delta G°$ values of transfer of these ions from water to these solvents (in kcal mol^{-1}) are as follows: Cl^-, 10 (MeCN), 9.6 (DMSO), 3.2 (MeOH); Br^-, 7.5 (MeCN), 6.6 (DMSO), 2.7 (MeOH).[44] These values indicate both that the ratio, according to Stirling analysis,[41] is not expected to be unity in our solvents and that it should change appreciably by the solvent change MeCN → 9:1 DMSO-d_6–CD_3OD, in contrast to what was observed. Finally, it seems very unlikely that the reverse reaction, the slow (and mostly unobservable) attack of halide nucleophile on an electrophilic double bond, will have a very early transition state.

The problem is to choose a process with k_{Br}/k_{Cl} values that can be regarded as "high". There are many k_{Br}/k_{Cl} ratios in processes that are assumed to involve a rate-determining C–X bond cleavage, e.g., S_N1, S_N2, E2, or substitutions of X—CO or X—C═N bonds. The values vary with the system and the solvent, and it seems that the C—X bond cleavage, which occurs in an S_N1 monomolecular process, is the most appropriate model for our k_{el} step in spite of the difference in charge type of both reactions. The k_{Br}/k_{Cl} ratios for S_N1 of several tertiary halides are 32–58,[45] and in solvolysis of triarylvinyl halides they are 5–42 in AcOH.[45] In dipolar aprotic solvents the ratios are higher, as expected, and for t-BuX they are 500–527 in DMF and $MeNO_2$[46a,b] and 361 in 9.7% H_2O in H_2O–DMSO.[46c] Even if we take values that are 1 order of magnitude lower than those as measures of "appreciable" bond cleavage,[47] the inescapable conclusion is that the transition state for our process is "early", *provided that prerequisite c below is fulfilled and that the C–X bond cleavage is rate determining.*

Is the Intramolecular Element Effect an Appropriate Measure of the C–X Bond Cleavage? The answer to this question depends on the answer to the questions whether the presence of the second halogen affects strongly the cleavage of the bond of the first halogen to carbon and whether the C–X bond cleavage is rate determining. The effects that should be analyzed in this respect are the anionic hyperconjugation and the anomeric effect.[48]

The anionic hyperconjugation is the net difference between the stabilizing two-electron interaction between the doubly occupied donor carbanionic 2p orbital and the acceptor π^*_{C-Cl} and π^*_{C-Br} orbitals and the destabilizing four-electron interaction between the π_{C-Cl} (or π^*_{C-Br}) and the $2p(C^-)$ orbitals.[49] In the expulsion of nucleofuges from carbanions these interactions are present in the ground states and may lead to rate-determining internal rotations to the carbanionic conformers involved in the C–Cl and C–Br bond cleavages. These interactions are present also in the transition states and if the ability of the noncleaved C–Br bond to affect the cleavage of the C–Cl bond differs from that of the C–Cl bond to affect the cleavage of the C–Br bond, a unique interaction term to the intramolecular element effect is present.

The anomeric effect in a system XCH_2Y is the interaction between the donor π_{C-X} orbital and the acceptor π^*_{C-Y} orbital when Y is more electronegative than X.[50] In the carbanion **5** such interactions exist between the C–Nu, C–Cl, and C–Br orbitals. The interaction unique to the intramolecular effect is between the C–Br and C–Cl orbitals.

Calculations showed that the magnitude of the anomeric effect strongly decreases when Y is in a lower row in the periodic table, and the values for interactions involving third-row substituents are low.[51] For example, the calculated anomeric stabilizations for H_2NCH_2F and H_2NCH_2Cl are 17.6 and 10.5 kcal mol^{-1} and the value for H_2NCH_2Br is expected to be lower.[51] In our systems it is expected that the Br–C–Cl interaction will be small, and since the interaction with the carbanionic orbital will be much more important,[52] the differential contribution from this effect to the two transition states can be neglected.

Are the hyperconjugative π^*_{C-X}–$2p(C^-)$ stabilizations (HSE) different for X = Cl or Br? A value for the rotational barrier in $\bar{C}H_2CH_2Cl$, which is proportional to the HSE for X = Cl is available[8] but there is no such calculation for X = Br. We will therefore review the indirect data related to this question.

Calculations for the $\bar{C}H_2CH_2X$ carbanions show a decrease in the HSE on going from the second to the third row in the periodic table (HSE values in kcal mol^{-1}: CH_3, 2.1; SiH_3, 0.1; NH_2, 4.8; PH_2, 4.1; OH, 11.5; SH, 9.2).[8] The F (HSE = 10.1), Cl (HSE = 16.7) pair is an exception. The HSE increases with the overlap of the two orbitals, and the interaction will be higher when X is more electronegative. It was suggested that the energy of π^*_{C-Br} is slightly lower than that of π^*_{C-Cl} in neutral systems,[53] since Cl is slightly more electronegative than Br. These data suggest that the difference between the HSE's for C–Cl and C–Br bonds is

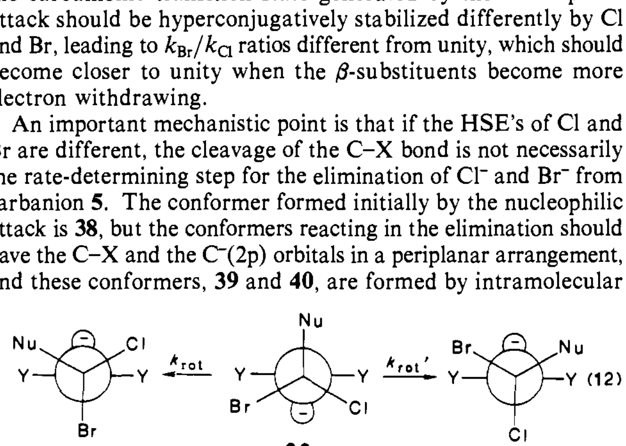
(39) More O'Ferrall, R. A. In *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Wiley-Interscience: 1973; Part 2, Chapter 9, pp 609–675.
(40) Bunnett, J. F.; Baciocchi, E. *J. Org. Chem.* **1970**, *35*, 76.
(41) Bird, R.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1221. For an analysis that shows that the k_{OTs}/k_{Br} ratios are also not a linear function of the extent of bond cleavage in the transition state, see: Cockerill, A. F. *Tetrahedron Lett.* **1969**, 4913.
(42) Rosenstock, H. M.; Draxel, K.; Steiner, B. W.; Henon, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1.
(43) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn and Bacon: Boston, 1983; p 21.
(44) Marcus, Y. *Ion Solvation*; Wiley-Interscience: Chichester, 1985; p 168.
(45) Rappoport and Gal (Rappoport, Z.; Gal, A. *J. Chem. Soc., Perkin Trans 2* **1973**, 301) give a list of k_{Br}/k_{Cl} values with references for S_N1 reactions.
(46) (a) Ross, S. D.; Labes, M. M. *J. Am. Chem. Soc.* **1957**, *79*, 4155. (b) Gelles, E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1954**, 2918. (c) Pocker, Y. *Ibid.* **1960**, 1972. (d) Heinonen, K.; Tommila, E. *Suom. Kemistil. B* **1965**, *38*, 9.
(47) Most values for E2 reactions or S_N2 reactions are in the range >10 but <100 (e.g., Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 30 and ref 40).
(48) Strictly, these interactions cannot be separated from one another, but since the negative hyperconjugation is the dominant effect, their separation in a qualitative discussion seems justified.
(49) (a) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221. (b) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, *39*, 1141. (c) For a recent review of anionic hyperconjugation, see: Nobes, R. H.; Poppinger, D.; Li, W.-H.; Radom, L. In *Comprehensive Carbanion Chemistry, Part C*; Buncel, E.; Durst, T., Eds.; Elsevier: Amsterdam, 1987; pp 1–92.
(50) (a) Anet, F. A.; Yavari, J. *J. Am. Chem. Soc.* **1977**, *99*, 6752. (b) Kirby, A. G. *The Anomeric Effect and Related Stereoelectronic Effects of Oxygen*; Springer Verlag: Berlin, 1983. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. *Ab Initio Molecular Orbital Theory*; Wiley: Chichester, 1986; pp 355–360.
(51) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.
(52) Judged by the values of the corresponding stabilization energies in ref 8 and 52.
(53) Bingham, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 6743.

small. In our systems where Y and Y′ are electron-withdrawing groups, the HSE's and therefore their differences are expected to be strongly reduced compared with the values for the $\bar{C}H_2CH_2X$ carbanions as demonstrated by the following HSE values (in kcal mol^{-1}): $\bar{C}H_2CH_2F$ (10.1), $(NC)_2\bar{C}CH_2F$ (5.5); $\bar{C}H_2CH_2OCl$ (29.4), $(NC)_2\bar{C}CH_2OCl$ (6.3); $\bar{C}H_2CH_2CH_2Cl$ (10.0), $NC\bar{C}HCH_2CH_2Cl$ (3.9).[8,54]

A different opinion is implicitly expressed by Thibblin.[55] In the analysis of the borderline between E2 and $(E1cB)_I$ routes for H–C_α–C_β–X systems, a plot of log $k_{ionization}(C_\alpha\text{–H})$ vs $\sigma^*_{CH_2X}$ is linear for nonnucleofugic X's as well as for poor nucleofuges X reacting via $(E1cB)_I$. Positive deviations from this line of better β-nucleofuges (e.g., Cl, Br) were ascribed to E2 elimination.[56] However, Ahlberg and Thibblin suggested[57] that the good nucleofuge enhances the ionization rate of the α-H by stabilization of the incipient carbanion by negative hyperconjugation. Thibblin[55] therefore suggested a four-parameter equation, log $(k^{el}/k_0^{el}) = \rho^*\sigma^* + lL$, where the L parameters are the leaving-group abilities and reflect the hyperconjugative abilities of the good nucleofuges. L values calculated from the above-mentioned relationship are 0.68 (determined indirectly) for F and 1.32, 2.16, and 3.14 for Cl, Br, and I, respectively.[57] Hence, the k_{Br}/k_{Cl} ratios of 10–100 for systems suspected to react via this mechanism are ascribed to the higher hyperconjugative ability of the C–Br bond compared with the C–Cl bond. However, More O'Ferrall[33] suggested an $(E1cB)_I$ process for elimination from 9-halogeno-9,9′-bifluorenyls, and the observed k_{Br}/k_{Cl} ratio of 1.9 was ascribed to carbanion formation, which is not assisted by C–X hyperconjugation.

Since the inductive and resonance effects of Cl and Br are similar, the fact that the k_{Br}/k_{Cl} ratios for the intermolecular element effect in nucleophilic vinylic substitution are almost always around unity regardless of the delocalizing ability of negative charge by the β-substituents[7] could be used as a supportive argument for similar HSE for Cl and Br. By Thibblin's argument, the carbanionic transition state generated by the nucleophilic attack should be hyperconjugatively stabilized differently by Cl and Br, leading to k_{Br}/k_{Cl} ratios different from unity, which should become closer to unity when the β-substituents become more electron withdrawing.

An important mechanistic point is that if the HSE's of Cl and Br are different, the cleavage of the C–X bond is not necessarily the rate-determining step for the elimination of Cl^- and Br^- from carbanion **5**. The conformer formed initially by the nucleophilic attack is **38**, but the conformers reacting in the elimination should have the C–X and the $C^-(2p)$ orbitals in a periplanar arrangement, and these conformers, **39** and **40**, are formed by intramolecular



39 **38** **40**

Y = p-$O_2NC_6H_4$ or Y′YC = fluorenyl

60° rotations. Conformer **39** benefits maximally from C–Br/$C^-(2p)$ hyperconjugative stabilization, and conformer **40** benefits likewise from the C–Cl/$C^-(2p)$ hyperconjugation. Their relative rates of formation will be determined by the relative hyperconjugative + steric (eclipsing interaction between α- and β-substituents during the rotation) barriers. The Curtin–Hammett principle is applicable here. If elimination from **39** and **40** is faster than rotation, the product composition will be determined by the relative populations of **39** and **40**, i.e., by the k_{rot}/k_{rot}' value. If internal rotation is faster than elimination, i.e., if **39** and **40** equilibrate before elimination, the ground state for the elimination is identical and the $k_{el}(Br)/k_{el}(Cl)$ ratio reflects the difference in the rotational barriers.

The steric barrier of the rotation leading to **39** involves a Cl/Y interaction and is therefore lower than the steric barrier leading to **40** which involves a Br/Y interaction.[58] If the hyperconjugative ability of the C–Cl and C–Br orbitals is similar, the hyperconjugative component of the barrier will be very low,[59] and the overall barrier will also be low. However, if the HSE of Br is appreciably higher than that of Cl, a k_{Br}/k_{Cl} ratio $\gg 1$ is expected if the rotation is rate determining. This seems not to be the case in view of the observed k_{Br}/k_{Cl} ratios of 2.0–3.2. We note, however, that since the rotational barriers seem to be low, even if the rotations of eq 12 are rate determining for the expulsion of X^-, the $k_{el}(Cl)$ and $k_{el}(Br)$ values will be so high that the transition state for the elimination is bound to be early.

The conclusion from the above discussion is that the k_{Br}/k_{Cl} ratios indeed measure the competition between rate-determining $k_{el}(Br)$ and $k_{el}(Cl)$ according to eq 2 and 3.

An Early Transition State for the Halide Ion Expulsion. Generalization Concerning the Transition States for Expulsion of Nucleofuges from β-Nucleofuge-Substituted Carbanions. Comparison of our k_{Br}/k_{Cl} ratios with the values for appreciable bond cleavage in the transition state leads to the conclusion that the transition state for the halide ion cleavage from the carbanion **5** is early, with only a slight extension of the C–X bond over that in the ground state. This is consistent with the Hammond postulate since the process is probably exothermic and especially with the low sensitivity of the ratios to external factors such as the solvent and to internal structural factors such as the delocalizing ability of the β-substituents and the nature of the nucleophilic moiety. The average $k_{el}(Br)/k_{el}(Cl)$ values are slightly higher for **8** than for **9** (Table III), but in view of the error in determining the product distribution, we will not try to analyze this difference in the present work.

Higher HSE's of X are associated with increased transfer of the negative charge to the C–X bond and with a more extended C–X bond. Consequently, since HSE(Cl) (and probably HSE(Br)) is one of the highest known,[8] the C–X bond is appreciably extended in the carbanion ground state, thus increasing its similarity to the transition state for X^- expulsion. This factor can be an important contributor to the nucleofugality order of nucleofuges from carbanions (see below).

The availability of good and poor nucleofuges (LG) and of highly and slightly negative charge delocalizing β-substituents in the carbanion $YY'\bar{C}CR^1R^2LG$ leads to four different nucleofuge/activating group combinations. Expulsions of the nucleofuge in two of these situations were previously encountered,[10] and the nature of the transition state was discussed in one of them. The present work complements the picture.

Our two reasonable assumptions are that the transition state is earlier for the better nucleofuge and that since part of the driving force for nucleofuge expulsion is the charge concentrated on C_β, increased negative charge delocalization leads to a more product-like transition state.

The second step of E1cB reactions (eq 13)[60] resembles our k_{el}

(54) Apeloig, Y.; Karni, M.; Rappoport, Z. *J. Am. Chem. Soc.* **1983**, *105*, 2784.

(55) Thibblin, A. *Chem. Scr.* **1980**, *15*, 121.

(56) (a) More O'Ferrall, R. A.; Warren, P. J. *J. Chem. Soc., Chem. Commun.* **1975**, 483. (b) More O'Ferrall, R. A. *Acta Univ. Ups.* **1977**, 209. (c) More O'Ferrall, R. A.; Larkin, F.; Walsh, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1573.

(57) Ahlberg, P. *Chem. Scr.* **1973**, *3*, 183. (b) Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1977**, *99*, 7926; **1979**, *101*, 7311.

(58) The effect of a change of Cl to Br in CFYClCClBrX (Y = Br, H; X = Cl, Br) on the intramolecular rotational barrier is negligible (Weigert, F. J.; Winstead, M. B.; Garrels, J. I.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7359). We are indebted to a referee for this reference.

(59) The hyperconjugative barrier for internal rotation in a system carrying two chlorine nucleofuges (or Cl and Br when they have identical HSE's) is low. Using the previously calculated HSEs (in kcal mol^{-1})[8] for Cl (16.7), OH (12.6), and SH (9.2), we calculated rotational barriers for $^-CH_2C(Nu)Cl_2$ in the gas phase (neglecting anomeric effects) of 4 and 7.4 kcal mol^{-1}, respectively, for Nu = OH and SH. These values are expected to be reduced appreciably by the β-substituents and the solvent.

(60) For a recent review on elimination reactions which include k_{Br}/k_{Cl} values and a detailed discussion and examples of E1cB reactions, see: Baciocchi, E. In *The Chemistry of Functional Groups. Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Part 2, Chapter 23, pp 1173–1227.

except that usually $R^1, R^2 \neq$ Nu. Stirling and co-workers have

$$B + Y'YCH{-}CR^1R^2LG \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y'Y\bar{C}{-}CR^1R^2LG + BH^+$$

$$Y'Y\bar{C}{-}CR^1R^2LG \xrightarrow{k_{el}} Y'YC{=}CR^1R^2 + LG^- \quad (13)$$

investigated an extensive number of systems with Y = H, Y′ = SO_2R,[10c] COPh,[10b] and CN,[10b] which reacted via the $(ElcB)_R$ variant, where $k_{-1}[BH^+] > k_{el}$ and $k_{obsd} = k_1k_{el}/k_{-1}[BH^+]$. By independent evaluation of k_1/k_{-1} they were able to construct a scale of nucleofugality, defined as "ranks" (= log k_{el}) extending over 14 log k_{el} values[10e] from moderately good nucleofuges ($PhSe^-$, $PhNMe_2$, >10) to very poor nucleofuges (CN^-, $CMe(SO_2Et)_2^-$, <0.5). The low sensitivity of the ranks to the nature of Y, the solvent (as in our systems), and the substituent in ArO^- was interpreted as due to an early transition state in which a very small degree of bond extension to the nucleofuge takes place.[10b,e] Consequently, with *relatively* moderately charge-delocalized substituted carbanions (i.e., with more concentrated charge on the C^-(2p) orbital) the transition state is early for both moderately good and good nucleofuges.

k_{el} values are also available for carbanions with better delocalizing Y and Y′ carrying poor and moderately good nucleofuges.[10a,f–j] A direct measure of the expulsion rate of CN^- from carbanions **41** and **42** gave a $k_{el}^{42}(CN)/k_{el}^{41}(CN)$ ratio of ≥560 in

$$\underset{\mathbf{41}}{An_2C(CN){-}\bar{C}(NO_2)_2} \qquad \underset{\mathbf{42}}{AnC(Me)(CN){-}\bar{C}(CN)_2}$$

$$An = p\text{-}MeOC_6H_4$$

MeCN.[10a] Bernasconi and co-workers[10f–i] measured k_1 and $k_{el}(NHR^1R^2)$ values for the equilibrium process of eq 14 and found

$$NHR^3R^4 + R^1R^2C{=}CYY' \underset{k_{el}}{\overset{k_1}{\rightleftharpoons}} R^1R^2C(\overset{+}{N}HR^3R^4){-}\bar{C}YY' \quad (14)$$

a strong dependence of the k_{el} values on Y and Y′. E.g., for R^1R^2NH = morpholine the following k_{el} values were found in 1:1 DMSO–H_2O at 20 °C: $PhCH(^+NHR^1R^2){-}^-C(COMe)_2$, 2.78; $Ph_2C(^+NHR^1R^2){-}^-C(NO_2)_2$, 2400; $PhCH(^+NHR^1R^2){-}^-C(CN)_2$, 260 000; and $PhCH(^+NHR^1R^2){-}^-C(CN)(p\text{-}O_2NC_6H_4)$, 811 000. The high sensitivity of k_{el}(CN) and $k_{el}(NHR^1R^2)$ values to Y and Y′ in these systems and the higher ρ value for ArO^- than in Stirling's systems[10h] indicate a much "later" transition state for these highly delocalized carbanions than for Stirling's less delocalized carbanions for both moderately good and poor nucleofuges.

Data on expulsion of very good nucleofuges (e.g., Br, Cl) from relatively localized (only Y is electron withdrawing) carbanions are not available. The transition state should be the "earliest" of all the Y,Y′/LG combinations. However, the $(E1cB)_R$ probe is not available in these cases since the reaction is either E2 or $(E1cB)_I$.[10c,d] The fact that the k_{el} step becomes so rapid as to make the carbanion shorter lived or nonexistent is consistent with an early transition state. This is supported by calculations on $\bar{C}H_2CH_2Cl$[61] and $\bar{C}H_2CH_2F$[49b] that show that these anions (in the gas phase) are not minima on the potential energy surfaces. For the latter anion the C–F bond elongation shows no evidence for a barrier in the calculation.[49b]

The present work complements the picture by showing that the transition state for expulsion of good nucleofuges remains early even when the delocalizing ability of Y and Y′ increases. The evidence for an $(E1cB)_I$ mechanism in the reactions proceeding via carbanions **35**–**37**[31–33] and in the elimination from 1,1-diaryl-2,2,2-trichloroethanes[62] indicates that even a rapid protonation of the carbanions cannot compete with the nucleofuge expulsion. A corollary is that the transition state is early.

There is, however, one study where, in spite of the $(E1cB)_I$ mechanism, information on the nucleofuge expulsion which is very relevant to our work was obtained. The intramolecular chlorine isotope effect for the dehydrochlorination of **43** (eq 15) was determined by McLennan and co-workers,[31] and a $k_{el}(^{35}Cl)/k_{el}(^{37}Cl)$ value of 0.99995 ± 0.00026 was deduced.[63] The absence of a chlorine isotope effect was interpreted in terms of an early transition state for Cl^- expulsion. The agreement between the results for a similar step, using slightly different probe processes[64] studied by two different techniques, and the fewer assumptions involved in the isotope effect study give strong support to our conclusion.

$$\underset{\mathbf{43}}{(p\text{-}O_2NC_6H_4)_2CH{-}CHCl_2} \xrightarrow[MeOH]{MeO^-}$$

$$\underset{\mathbf{35}}{(p\text{-}O_2NC_6H_4)_2\bar{C}{-}CHCl_2} \xrightarrow{k_{el}(Cl)} (p\text{-}O_2NC_6H_4)_2C{=}CHCl \quad (15)$$

The overall picture emerging from the experimental data agrees with the predictions. For singly activated systems (only Y is strongly electron withdrawing) the transition state for the elimination is early regardless of the nature of the nucleofuge. For highly activated systems (both Y and Y′ are strongly electron withdrawing) the transition state is still early for the expulsion of the very good Br^- and Cl^- nucleofuges but it becomes less reactant-like for moderate and poor nucleofuges. An obvious future extension of the present study would be to study the intramolecular element effect with systems where Y and Y′ are much more electron withdrawing (e.g., NO_2) where a shift of the transition state in the product direction may result in higher $k_{el}(Br)/k_{el}(Cl)$ ratios than in the present work.

Spectral Properties of the Substitution Products. The UV spectra of the monobromo and the monochloro substitution products resemble each other, and in the fluorene series also that of the disubstitution product. In the bis(*p*-nitrophenyl) derivatives the λ_{max} of the disubstitution products is shifted to long wavelengths, which is consistent with the complementary nature of the α- and β-substituents.

Two features are noteworthy in the mass spectra. First, the nature of the base peak changes for almost all the compounds. Second, the base peaks in the spectra of the disubstitution products with $p\text{-}MeC_6H_4O^-$ correspond to the cations $Ar_2C^+{-}Tol$ (*m/z* 255 and 347 for **19** and **25**, respectively). These are probably formed by the sequence of eq 16, which involves a tolyl group migration in the carbene–cation hybrid of an intermediate vinyl cation.

$$Ar_2C{=}C(OTol)_2^{\cdot +} \xrightarrow{-TolO^\cdot} Ar_2C{=}\overset{+}{C}{-}OTol \leftrightarrow$$

$$Ar_2\overset{+}{C}{-}\ddot{C}{-}OTol \xrightarrow{\sim Tol} Ar_2C(Tol){-}\overset{+}{C}{=}O \xrightarrow{-CO} Ar_2\overset{+}{C}{-}Tol \quad (16)$$

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Ultraviolet and visible spectra were measured with Varian Techtron 635 and UVIKON 820 spectrophotometers. IR spectra were taken with a Perkin-Elmer 157 G spectrometer. Mass spectra were determined with a MAT 311 instrument. ^1H NMR spectra were recorded with Bruker WH300 and Bruker WP200 SV pulsed FT spectrometers operating at 300.133 and 200.133 MHz, respectively. Tetramethylsilane was used as the reference. The ESR spectrum was measured with a Varian X-band E-12 instrument. Gas chromatographic separations were done on a Hewlett-Packard 417 instrument with a flame ionization detector, and HPLC separations were conducted with a Tracor 970 A instrument with a UV detector attached to a Merck-Hitachi D-2000 Chromato Integrator.

(61) Cohen, D.; Bar, R.; Shaik, S. S. *J. Am. Chem. Soc.* **1986**, *108*, 231. See also: Bach, R. D.; Wolber, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 1401. However, neither paper deals with comparison of bromine and chlorine nucleofuges.

(62) McLennan, D. J.; Wong, R. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1373, 5262.

(63) Appropriate control experiments showed that the analytical method is reliable and k_{35}/k_{37} values of 1.002–1.003 are obtained for reactions where the C–Cl bond is cleaved in the rate-determining step.

(64) The difference in the substituents on the C–X bond (H in **35**, Nu in **5**, Y = Y′ = $p\text{-}O_2NC_6H_4$) is not expected to shift appreciably the position of the transition state.

Table IV. Analytical Data for the Substitution Products

				anal.										
				calcd, %						found, %				
compd	mp, °C	color	crystallization solvent	C	H	N	Hal	S	formula	C	H	N	Hal	S
14	103	white	hexane	75.34	4.48		10.61	9.57	$C_{21}H_{15}ClS$	75.11	4.56		10.78	9.56
15	88	light yellow	hexane	66.49	3.96		21.11	8.44	$C_{21}H_{15}BrS$	66.10	3.93		20.50	8.41
16	90	white	hexane	79.12	4.71		11.14		$C_{21}H_{15}ClO$	79.23	4.28		11.29	
17	103	white	MeOH	69.42	4.13				$C_{21}H_{15}BrO$	69.20	4.05			
18	123	yellow	hexane	79.62	5.21				$C_{28}H_{22}S_2$	79.60	5.28			
19	89	white	petroleum ether	86.15	5.64				$C_{28}H_{22}O_2$	86.24	5.56			
20	126–127	yellow	CCl_4–petroleum ether	59.15	3.52	6.57		7.51	$C_{21}H_{15}ClN_2O_4S$	59.20	3.56	6.36		7.49
21	115–116	yellow	CCl_4–petroleum ether	53.50	3.18				$C_{21}H_{15}BrN_2O_4S$	53.52	3.21			
22	119–120	brown	CCl_4–petroleum ether	61.39	3.65				$C_{21}H_{15}ClN_2O_5$	61.50	3.60			
23	153	yellow	benzene–petroleum ether	55.38	3.30	6.15			$C_{21}H_{15}BrN_2O_5$	54.97	3.46	5.94		
24	152–153	green	CCl_4–petroleum ether	65.37	4.28				$C_{28}H_{22}N_2O_4S_2$	65.20	4.34			
25	150–160	brown	CCl_4–petroleum ether	69.71	4.56	5.81			$C_{28}H_{22}N_2O_6$	69.67	4.64	5.59		

The electrochemical experiments were conducted with a BAS cyclic voltammetry instrument.

Materials and Solvents. Compounds **8–13** were prepared according to Reimhinger.[14] Sodium *p*-toluenethiolate and sodium *p*-methylphenolate were precipitated from the reactions of *p*-toluenethiol and *p*-cresol, respectively, with sodium hydride in dry ether. The solid salts were washed with ether, dried, and used without further purification. Fresh salts were prepared every few weeks.

Acetonitrile was distilled from P_2O_5, and the middle fraction was used. Deuteriated solvents (CD_3CN, DMSO-d_6, CD_3OD (Aldrich)) were used without further purification.

Preparation of the Substitution Products. To a solution of **10**, **11**, **12**, or **13** (1.5 mmol) in dry acetonitrile (25 mL) was added sodium *p*-toluenethiolate or sodium *p*-methylphenolate (1.8 mmol, 1.2 molar ratio to the dihaloethylene) with stirring. The solutions immediately turned a light pink in the reaction of **10** and **11** and deep blue with **12** and **13** with p-$MeC_6H_4O^-$. In the reactions with p-$MeC_6H_4S^-Na^+$ the solutions turned yellow-green with **10–12** and deep red to violet with **13**. Stirring at room temperature was continued for <1 h, until 50–70% of the starting material was reacted (as indicated by NMR or TLC). The solvent was evaporated, and the reaction mixture was chromatographed on a silica gel column, using gradient petroleum ether (40–60 °C)–CH_2Cl_2 as the eluent. The two monosubstitution products **14–17** and **20–23** were separated in this way from the unreacted starting material and from the small amount of the disubstitution products (**18**, **19**, **24**, and **25**) and crystallized. The yields and the analytical data are given in Table IV, and the spectroscopic data are listed in Table I. For formation of the disubstitution products the same procedure was repeated with 2 molar equiv of the sodium salt. Stirring was continued for ca. 1 h. TLC showed that the reaction was nearly complete under these conditions. Use of higher molar ratios of salt to dihaloolefin resulted in formation of a brown solution, which showed several spots in the TLC. The disubstitution product was obtained by chromatography over silica gel with gradient petroleum ether–CH_2Cl_2 as the eluent. Crystallization from petroleum ether or from CCl_4–petroleum ether gave pure **18**, **19**, **24**, and **25**. Yields and analytical and spectroscopic data are in Tables I and IV.

Determination of the Products and the Product Distributions. (a) By ^{1}H NMR. The reactions were conducted in the deuteriated solvent in an NMR tube. Sodium *p*-toluenethiolate or sodium *p*-methylphenolate was added in small portions to the sample, and the composition of the mixture and the percentage of the reaction was determined by ^{1}H NMR after each addition. For analysis of the substitution of the fluorenylidene system **8**, integration of the signals that were most influenced by the substituents and differed in their positions in the precursors and the products (Table I) was used. These signals were assigned to the 1 and 8 hydrogens on the assumption that the closer protons to the substituents will be most influenced by them. The signal of the methyl group of the tolyl moiety was occasionally used. In the reaction of **9** with the *p*-methylphenolate ion in CD_3CN the signals for the ortho hydrogens to the nitro group at low field of the various compounds were integrated. In the reaction in DMSO-d_6 the signals at δ ca. 8.18 were used. In the reaction with *p*-toluenethiolate the hydrogens ortho to the sulfur were integrated due to overlap of other signals, but overlap became extensive, especially at high reaction percentages. We estimate the accuracy of the ratios derived from ^{1}H NMR as ±10% except for the reaction of **9** with p-$MeC_6H_4S^-$, where the error in the NMR-determined ratios could be ±15%.

(b) By HPLC. Analysis by HPLC was found to be the most accurate method in analysis of the reaction products of **9**. The reaction was conducted with 0.004 mol L^{-1} of **9** in MeCN (43.5 mg of **9** in 25 mL of MeCN) with a portionwise addition of the nucleophile. Samples were taken at the appropriate intervals, the solvent was rapidly driven off with a stream of nitrogen, and the residue was dissolved in CH_2Cl_2 (1 mL)–hexane (9 mL), filtered, and used for the analysis. The best separation of the two monosubstitution products with *p*-toluenethiolate was obtained on a LiChrosorb CN (250-4) column, and for the products of *p*-methylphenolate either on the CN column or on a LiChrosorb Diol (125-4) column. Each chromatography took ca. 40 min and the signals were identified by peak enhancement experiments using the isolated samples. At 254 nm the products of each reaction have nearly identical ϵ values, and only a small correction was required for determination of the percentage reaction based on the concentration of **9**. The following retention times (in min) were obtained: on the CN column using 98:2 hexane–CH_2Cl_2 at 2 mL min^{-1}, **9** (9.3), **20** (11), **21** (11.7), **24** (12.6); on the CN column using hexane at 2 mL min^{-1}, **9** (17), **22** (20), **23** (21), **25** (25); on the diol column using hexane at 0.4 mL min^{-1}, **9** (25), **22** (27), **23** (29), **25** (31). The signals for the disubstitution product were slightly broader than the signals of the monosubstitution products.

(c) By GC. Samples from reaction mixtures obtained by portionwise addition of the nucleophiles to 0.004 mol L^{-1} of **8** or **9** in CH_3CN (25 mL) were directly injected into an Apiezone N 2% column ($^1/_4$ in., 80 cm on GCQ 80-100), which was found to be the best column for separation of the monosubstitution products. The retention times (in min) were as follows: **8**, 14; **14**, 20.5; **15**, 22; **16**, 18; **17**, 19.5; **18**, 36; **19**, 27; and **9**, 13.5; **20**, 21.5; **21**, 23; **22**, 19;, **23**, 20; **24**, 40; **25**, 28. Each chromatogram took ca. 40 min (programming from 160 °C (5 min) at 8 °C/min till 270 °C (25 min)). The signals were identified by peak enhancements with the pure samples.

Reduction Potentials. Cyclic voltammetry with a Pt button electrode and a Ag/AgCl reference electrode in DMF with 0.1 N tetrabutylammonium tetrafluoroborate as electrolyte was used in order to estimate the reduction potentials of **8** and **9**.

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Registry No. 8, 91960-72-4; **9**, 110223-38-6; **14**, 110223-37-5; **15**, 110223-39-7; **16**, 110223-40-0; **17**, 110223-41-1; **18**, 110223-42-2; **19**, 110223-43-3; **20**, 110223-44-4; **21**, 110223-45-5; **22**, 110223-46-6; **23**, 110241-64-0; **24**, 110223-47-7; **25**, 110223-48-8.