Table I

Carbon-13 Nmr Shifts of Fluorine Exchanging Fluorocarbenium Ion Systems[a]

$CH_3CF_2CH_3$ (IV)	$-CF_2$	$-CH_3$	CH_3CHF_2	$-CHF_2$	$-CH_3$
IV in SO_2ClF at −40°	+68.2	+167.4	X in SO_2ClF at −60°	+77.5	+174.6
IV in HF (excess)–SbF_5–SO_2ClF at −60°	+67.7	+168.1	X in HF (excess)–SbF_5–SO_2ClF at −60°	+71.8	+145.2
IV in HF–SbF_5–SO_2ClF (5/1 mol/mol) at −60°	−91.0	+157.3	X in HF–SbF_5–SO_2ClF (5/1 mol/mol) at −60°	−59.1	+140.4
IV in excess SbF_5–SO_2ClF at −60°	−142.0	+155.0			

[a] Carbon-13 shifts are in parts per million from external CS_2.

Varian Associates Model A-56-60A spectrometer equipped with variable temperature probes. Probe temperatures were calibrated before use. TMS and $CFCl_3$ in a capillary were used for proton and fluorine references, respectively. Carbon-13 spectra were obtained by the INDOR method described previously.[15]

Preparation of Ions.—Solutions of ions were prepared as described previously in this series, with concentrations and conditions given in text.

Registry No.—IV, 420-45-1; VI, 14665-81-7; X, 75-37-6; XI, 29526-61-2; HF, 7664-39-3; SbF_5, 7783-70-2; SO_2ClF, 13637-84-8.

Acknowledgment.—Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are also indebted to Dr. Gheorge D. Mateescu and Dr. William E. Heyd for their contribution in calculating the theoretical spectra.

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[15] A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).

Vinylic Cations from Solvolysis. X. SN1 and Nucleophilic Addition–Elimination Routes for 9-(α-Haloarylidene)fluorenes

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The solvolysis of α-anisyl-β,β-diphenylvinyl chloride and bromide (1-Cl and 1-Br) in 80% EtOH in the presence of acetate, hydroxide, benzylthiolate, and *p*-toluenethiolate ions is mechanistically SN1. The solvolysis of 9-(α-haloarylidene)fluorenes (2 and 4) in 80% EtOH in the presence of acetate ion also follows the SN1 route. However, 2 and 4 react in the presence of *p*-toluenethiolate and benzylthiolate ions *via* the nucleophilic addition–elimination substitution route. Various criteria (the substituent effect, the solvent effect, the "element effect," the dependency on the nucleophile, and the kinetics) for differentiation between the two routes were investigated and discussed and the behavior of compounds 1 and 2 is compared.

Two of the important mechanisms of nucleophilic vinylic displacement of the leaving group X by the nucleophile Nu^- are the nucleophilic addition–elimination route[1-3] (Ad$_N$–El, eq 1) and the SN1 route[1,2,4,5]

$$RCX{=}CYR' + Nu^- \xrightarrow{\text{slow}} RCX(Nu)\overset{-}{C}YR' \longrightarrow RC(Nu){=}CYR' + X^- \quad (1)$$

(eq 2). Other mechanisms such as the "elimination–

$$RCX{=}CR'R'' \xrightarrow[-X^-]{\text{slow}} R\overset{+}{C}{=}CR'R'' \xrightarrow{Nu^-} RC(Nu){=}CR'R'' \quad (2)$$

addition" routes[1-3] are dependent on the presence of an allylic or a vinylic hydrogen and are less general. The two mechanisms differ by many mechanistic criteria. The rate of the SN1 route is of a first order and is independent of added nucleophiles. This route is activated by electron-donating α substituents R, and it shows an "element effect" of the leaving group X and is accelerated by polar solvents. Both cis and trans isomers give the same product mixture.[6] The Ad$_N$–El route is of a second order and its rate is strongly nucleophile dependent. The reaction is activated by electron-attracting groups Y from the β position, it shows a small k_{Br}/k_{Cl} element effect, and its stereochemical outcome is retention of configuration.[1-3] No system which reacts by both routes is known. Competition between the powerfully SN1 activating α-*p*-dimethylaminophenyl group and the two Ad$_N$–El activating β-cyano groups of *p*-$Me_2NC_6H_4C(Cl){=}C(CN)_2$ resulted in the Ad$_N$–El route alone.[7] Indeed, the SN1 route often competes with the electrophilic addition–elimination route,[8] while the Ad$_N$–El route often competes with the elimination–addition routes.[1-3]

It was of interest to find a system capable of reacting under different conditions by both the SN1 and the Ad$_N$–El routes. Since triarylvinyl halides are known

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[1] S. Patai and Z. Rappoport in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, p 469.

[2] Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969).

[3] G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).

[4] M. Hanack, *ibid.*, **3**, 209 (1970).

[5] G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971). We thank Professor Modena for a preprint of this paper.

[6] (a) Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, **91**, 6734 (1969); (b) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970); **93**, 1941 (1971).

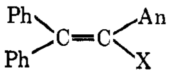
[7] Z. Rappoport and R. Ta-Shma, *J. Chem. Soc. B*, 871, 1461 (1971).

[8] Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, **92**, 4985 (1970); Z. Rappoport and J. Kaspi, *Tetrahedron Lett.*, 4039 (1971).

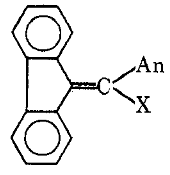
to react *via* the SN1 route,[6a,9-12] a logical starting point is the replacement of the two β-aryl groups by a fluorenyl moiety. This group is much more suitable than the two β-phenyl groups to carry the partial negative charge formed in the transition state of the Ad_N–El route.[13]

Results

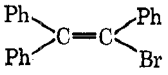
Synthesis.—The triarylhaloethylenes **1**-Cl, **1**-Br, and **3**-Br were prepared by halogenation–dehydrohalogenation of the corresponding ethylenes without isolation of the α,β-dihalides.[9,11,14] The fluorenylidene derivative **4**-Br was prepared similarly from the isolated α,β-dibromide. The dibromide **5**-Br and the corresponding dichloride **5**-Cl were prepared by adding the halogen to 9-anisylidenefluorene, but their analysis and nmr showed that both compounds partially eliminate hydrogen halide rather rapidly.



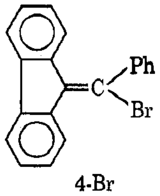
1-Cl, X = Cl
1-Br, X = Br
1-OTs, X = OTs



2-Cl, X = Cl
2-Br, X = Br
2-OTs, X = OTs
2-OAc, X = OAc



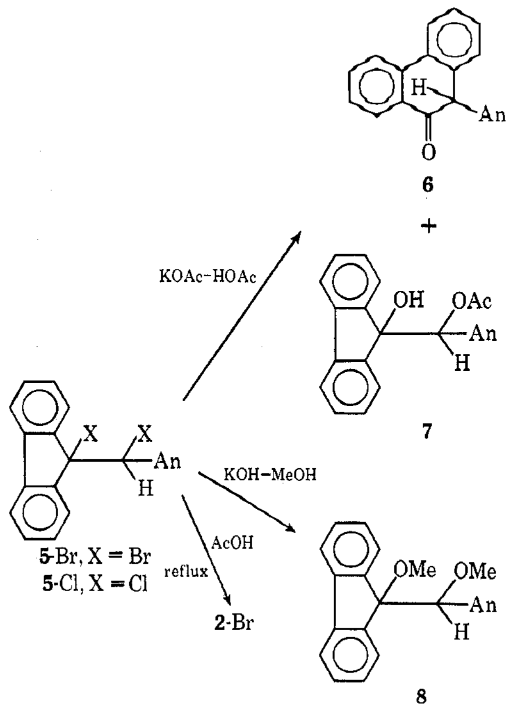
3-Br



4-Br

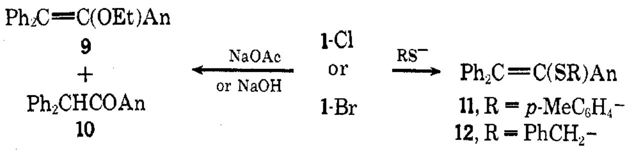
An = p-$MeOC_6H_4$–

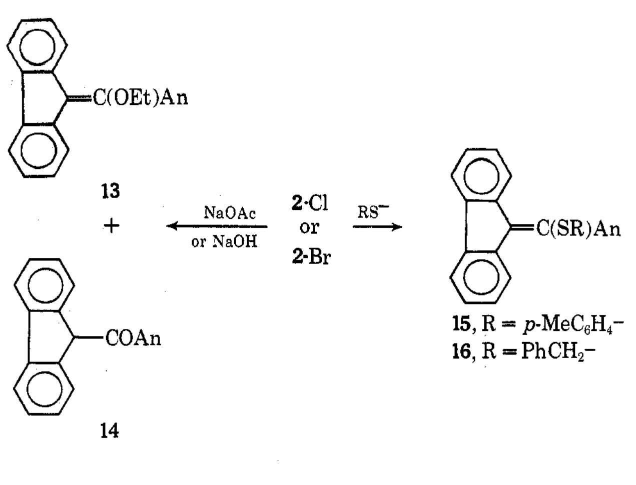
In attempts to prepare **2**-Br by dehydrobromination of **5**-Br with KOAc in acetic acid, the ring enlargement product, 9-anisyl-9,10-dihydro-10-oxophenanthrene (**6**), was formed and identified by analysis, uv, ir, mass spectrum (base peak at M − HCO), and nmr (H-9 at δ 9.55). A small amount of 9-hydroxy-9-(α-acetoxy-p-methoxybenzyl)fluorene (**7**) (or its isomer in which the OH and the OAc groups exchange places) was also formed. The dimethyl ether **8** was formed on attempted dehydrobromination with methanolic KOH. **2**-Br was finally obtained as the main product by reflux of **5**-Br in acetic acid without added base, and **6** was the minor product. Similarly, **2**-Cl was the main product and **6** a minor product in the dehydrochlorination of **5**-Cl in acetic acid.



Formation of **6**, **7**, and **8** is accounted for by the initial formation of the substituted p-methoxybenzyl carbonium ion, followed by either capture by the solvent or a Wagner-Meerwein rearrangement followed by solvolysis of the second halogen. **2**-Br is not a precursor to **6** or **7** since it was recovered unchanged after reflux for 2 hr in KOAc–HOAc. Under these conditions, the **5** → **6** + **7** reaction takes place.

Solvolysis Products.—Solvolysis of **1**-Cl and **1**-Br in the presence of 0.18 M NaOAc gave the vinyl ether **9** and the ketone **10** (by ketonization of the initially formed enol). In 80% EtOH the **9**:**10** ratios (determined by nmr) are 52:48 from **1**-Br and 50:50 from **1**-Cl, and in 90% EtOH the ratio from **1**-Br is 72:28 at 120°. Similarly, the ether **13** and the ketone **14** are formed from **2**-Br and **2**-Cl. **14** was also prepared independently by the base-catalyzed hydrolysis of the acetate, **2**-OAc, which was obtained in turn by the





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[9] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, **91**, 5246 (1969).

[10] Z. Rappoport and A. Gal, *Tetrahedron Lett.*, 3233 (1970); (b) Z. Rappoport and Y. Apeloig, *ibid.*, 1845 (1970); (c) Z. Rappoport and Y. Apeloig, *ibid.*, 1817 (1970).

[11] L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

[12] W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969); **90**, 5457 (1970).

[13] This is judged by the difference in the pK_a's of fluorene and diphenylmethane: D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapters 1 and 2; K. Bowden, A. F. Cockerill, and J. R. Gilbert, *J. Chem. Soc. B*, 179 (1970).

[14] C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 2045 (1932).

TABLE I

SOLVOLYSIS OF **1** AND **2** IN AQUEOUS ETHANOL

Compd	Concn, $M \times 10^3$	Added base	Concn, $M \times 10^2$	Solvent, % EtOH	T, °C	$k_1 \times 10^4$ sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[b] eu
1-Br	35	$NaSCH_2Ph$	20	80	120.0	2.02 ± 0.16[c]		
	33–43	$NaSC_6H_4Me$-*p*	11–20	80	120.3	1.97 ± 0.09[d]		
	43	$NaSC_6H_4Me$-*p*	13	80	120.3	1.81 ± 0.03		
	35	$NaSC_6H_4Me$-*p*	20	80	120.7	2.19 ± 0.13		
	29	$NaSC_6H_4Me$-*p*	8	80	128.2	3.21 ± 0.24	22.0	−20
	57	$NaSC_6H_4Me$-*p*	8	80	128.2	3.62 ± 0.20		
	29–40	NaOH	30–50	80	120.3	1.92 ± 0.04[d]	22.3[d]	−19[d]
	40	NaOH	44	80	127.8	3.05 ± 0.04		
	20–40	NaOH	29–44	80	127.8	3.48 ± 0.02[d]		
	57	NaOH	27	80	127.8	2.97 ± 0.06		
	40–57	NaOH	29–36	80	139.8	7.75 ± 0.14[d]		
	35	NaOAc	8.6	80	120.3	1.56 ± 0.02	21.6	−22
	35	NaOAc	8.6	80	140.3	6.24 ± 0.07		
	35	NaOAc	11.5	90	140.6	2.70 ± 0.03		
1-Cl	35	NaOAc	18	80	140.2	0.117 ± 0.002	25.5	−21[e]
	35	NaOAc	18	80	155.4	0.368 ± 0.005		
2-Br	35	NaOAc	20	70	140.3	6.03 ± 0.12		
	35	NaOAc	36	70	140.2	6.27 ± 0.10		
	35	NaOAc	8.6	80	120.3	0.63 ± 0.002[f]		
	35	NaOAc	17	80	120.3	0.64 ± 0.01		
	35	NaOAc	50	80	120.3	0.61 ± 0.01		
	35	NaOAc	17	80	140.3	2.94 ± 0.02	24.0	−17
	35	NaOAc	11.5	90	140.6	1.08 ± 0.03		
	35	NaOH	50	80	120.5	2.27 ± 0.10[g]		
	35	NaOH	50	90	120.3	4.6 ± 0.2[h]		
2-Cl	35	NaOAc	18	80	140.2	0.039 ± 0.001		
	35	NaOAc	36	80	140.3	0.039 ± 0.001		
	35	NaOAc	18	80	155.4	0.128 ± 0.003	26.7	−20[e]

[a] Estimated ±1 kcal/mol. [b] Estimated ±3 eu; $\Delta S^{\ddagger}$ at 120°. [c] The observed infinity of 82% was used. [d] From ref 9. [e] $\Delta S^{\ddagger}$ at 140°. [f] Extrapolated values: 10^4k_1 = 0.047, 0.19, and 9.05 sec^{-1} at 90.2, 105, and 155.5°, respectively. [g] Based on five points at 25–67% reaction. [h] Based only on two points.

AgOAc-catalyzed solvolysis of **2**-Br in AcOH. The **13**:**14** ratios from **2**-Br in 90, 80, and 70% EtOH are 92:8, 70:30, and 52:48, respectively. A small signal at the δ expected for the acetoxy signal of the acetate **2**-OAc was also observed, but thin layer chromatography revealed the presence of only **13** and **14**. **2**-Cl gave >85% of **13** (by nmr) in 80% EtOH, and ir showed the formation of **14** in <5%.

While **1**-Br was reported to give a 1:1 ratio of **9** to **10** with sodium hydroxide in 80% EtOH at 140°,[9] the solvolysis of **2**-Br in 80% EtOH with excess NaOH gave very black reaction mixtures which after several half-lives showed none of **13** and **14** in the nmr. The only signals observed are for methoxyl and aromatic protons in a ratio of 3:16. The reaction mixture from **4** also blackened with NaOH and, in addition to the aromatic signals, several new signals appeared at δ 2.1–2.5 and 4.0–4.7. These reactions were not investigated further.

Reactions of **1**-Br in 80% EtOH in the presence of sodium benzylthiolate and sodium *p*-toluenethiolate gave exclusively the vinyl thiolates **11** and **12** which were isolated in a quantitative yield. **9** and **10** were not formed. Similarly, **2**-Cl and **2**-Br gave the vinyl thiolates **15** and **16** with the two thiolate anions. Their quantitative formation is verified by the uv of the kinetic runs at infinity, which corresponded to 100% reaction. **4**-Br gave quantitatively the analog of **16** in the presence of sodium benzylthiolate.

Kinetics.—Compounds **1**–**4** were solvolyzed in 80% EtOH in the presence of excess NaOAc and occasionally in 70 or 90% EtOH in the presence of NaOH. The formation of the halide ion was followed titrimetrically. In the reaction of **1**-Br in the presence of sodium *p*-toluenethiolate the excess thiolate ion had to be precipitated by $Cu(NO_3)_2$ before titration.[9] As reported earlier,[9] under these conditions the calculated infinity was not achieved and the k_1 values were calculated by using the observed infinity.

In solvolysis of **2**-Br in the presence of NaOH the reaction mixtures began to blacken after 10–15% reaction and side reactions took place (see above). Although the titrimetric k_1 was good, only few experiments were conducted. The loss of hydroxide ion by reaction with the glass ampoules under conditions similar to ours was recently reported.[15]

The reaction of **1**-Br under solvolytic conditions in the presence of sodium benzylthiolate was followed titrimetrically (see below).

All these reactions were first order in the substrate and zero order in the added base (NaOAc, NaOH, $NaSCH_2Ph$, $NaSC_6H_4Me$-*p*) with correlation coefficients for the first-order plots over 0.99. The data are summarized in Table I.

One point solvolyses of 0.035 *M* **3**-Br and **4**-Br in the presence of 0.18 *M* NaOAc gave 10^7k_1 values of 1.7 and 5.7 sec^{-1} at 140 and 155.5° for **3**-Br and 2.9 sec^{-1} at 155.5° for **4**-Br. The last two values are for kinetic points at ⩽10% reaction, and the values should be considered as upper limits for k_1.

The reaction of **2**-Br with excess of an equimolar mixture of *p*-toluenethiol and NaOH in 80% EtOH

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(15) J. MacMillan and R. J. Pryce, *J. Chem. Soc. B*, 337 (1970).

Table II

Rate Data for the Reactions of **2**-Cl, **2**-Br, and **4**-Br with Thiolate Ions in Aqueous Ethanol

Compd	RSH, $M \times 10^3$	NaOH, $M \times 10^3$	Solvent, % EtOH	T, °C	$k_1 \times 10^4$ sec^{-1}	$k_2 \times 10^2$ M^{-1} sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal/mol	$\Delta S^{\ddagger}$,[b] eu
RSH = p-MeC_6H_4SH								
2-Br[c]	8.0	8.0	80	90.0	4.24	0.53	21	−12
	16.0	16.0	80	90.0	8.88	0.55		
	8.0	8.0	80	105.0	13.6	1.70		
	16.0	16.0	80	105.0	30.0	1.87		
RSH = $PhCH_2SH$								
2-Br[c]	4.0	4.0	80	90.2	0.86 ± 0.03	6.7 ± 0.3	16	−21
	8.0	8.0	80	90.2	2.38 ± 0.09	7.0 ± 0.3		
	16.0	16.0	80	90.2	6.09 ± 0.08	7.0 ± 0.1		
	8.0	8.0	50	105.0	6.29 ± 0.68	18.6 ± 2.0		
	8.0	8.0	70	105.0	5.67 ± 0.02	16.8 ± 0.1		
	8.0	8.0	80	105.0	5.84 ± 0.32	17.3 ± 0.9		
	16.0	16.0	80	105.0	14.9 ± 0.14	17.2 ± 0.2		
2-Cl[c]	8.0	8.0	80	90.2	1.38 ± 0.02	4.1 ± 0.1	15	−25
	16.0	16.0	80	90.2	3.00 ± 0.30	3.5 ± 0.4		
	8.0	8.0	80	105.0	2.97 ± 0.07	8.8 ± 0.3		
	16.0	16.0	80	105.0	7.62 ± 0.50	8.8 ± 0.6		
4-Br[d]	4.0	4.0	80	90.2	0.96 ± 0.01	7.5 ± 0.1	16	−19
	8.0	8.0	80	90.2	2.45 ± 0.20	7.3 ± 0.6		
	16.0	16.0	80	90.2	6.48 ± 0.22	7.5 ± 0.3		
	8.0	8.0	80	105.3	6.80 ± 0.40	20.0 ± 1.2		
	16.0	16.0	80	105.3	16.4 ± 0.1	19.0 ± 0.1		
	4.0	4.0	80	105.1	2.34 ± 0.10	18.3 ± 0.8		
	4.0	8.0	80	105.1	3.21 ± 0.19	16.5 ± 1.0		
	4.0	16.0	80	105.1	4.44 ± 0.27	16.3 ± 1.0		
	4.0	32.0	80	105.1	5.11 ± 0.27	15.5 ± 0.8		

[a] Estimated ±1 kcal/mol. [b] $\Delta S^{\ddagger}$ at 105°; estimated ±3 eu. [c] [**2**] = 2.2 × 10^{-4} M. [d] [**4**-Br] = 2.52 × 10^{-4} M.

was followed spectrophotometrically at 392 nm, a wavelength where only the product **15** has an appreciable absorption. The reaction is first order in both **2**-Br and the thiol and, since the ionization of the latter is practically complete under our conditions, the second-order coefficients k_2 (Table II) are for the reaction of the p-toluenethiolate ion with **2**-Br.

The reactions of **2**-Br, **2**-Cl, and **4**-Br in the presence of excess α-toluenethiol in aqueous alcohol were followed at both the λ_{max} of the vinyl halide and the vinyl thiolates, and the average rate coefficient from both measurements is given. The isosbestic point at 324 nm remained stable along the reaction and up to >10 half-lives, showing that side reactions are unimportant. The reactions were of first order in the vinyl halide but with an apparent order between one and two for the α-toluenethiol. This is due to incomplete ionization of the thiol as shown by the increase of k_1 with the NaOH concentration in the presence of a constant concentration of α-toluenethiol. The actual concentrations of the benzylthiolate anion were calculated by using the value $pK_a = 11.8$ for α-toluenethiol in aqueous ethanol.[16] These concentrations were used for calculation of the second-order coefficients for the reaction of the benzylthiolate anion with the vinyl halide (Table II). The slight deviation from the second-order dependency for **4**-Br probably reflects the approximations used for the calculation of the anion concentrations.[17]

Discussion

It is clear from Tables I and II that the β,β-diphenyl compounds **1** and **3**-Br react by the same mechanism in the presence of all the nucleophiles studied, while the fluorenyl systems (**2** and **4**-Br) react by the same mechanism in the presence of sodium acetate, but by a different route in the presence of the stronger thio nucleophiles. That this is the first example for the operation of the SN1 and the Ad_N–El routes with the same substrate is best shown by inspecting Table III in which several mechanistic criteria are summarized and compared.

SN1 Mechanism.—The solvolysis of 1-anisyl-2,2-diphenylvinyl halides show the rate-product behavior expected for the formation of an intermediate carbonium ion (eq 3). The k_1 is nucleophile independent with four different nucleophiles (OAc^-, OH^-, $PhCH_2S^-$, and p-$MeC_6H_4S^-$) but the products are nucleophile dependent, being the ether and the ketone with the

$$Ph_2C{=}C(An)X \xrightarrow{k_1} Ph_2C{=}\overset{+}{C}An \xrightarrow{Nu^-} Ph_2C{=}C(An)Nu \quad (3)$$

oxygen nucleophiles and the vinyl thiolates with the thio nucleophiles. The $k_{1\text{-Br}}/k_{1\text{-Cl}}$ ratio of 53 (with NaOAc) is similar to those reported for other triarylvinyl halides in 80% EtOH,[9,10b] and their similarity to the ratios reported (32–58) for the solvolyses of

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[16] J. Maurin and R. A. Paris, *C. R. Acad. Sci.*, **232**, 2428 (1951), reported the value 11.8 in aqueous ethanol. B. Dmuchovsky, F. B. Zienty, and W. A. Verdenburgh, *J. Org. Chem.*, **31**, 865 (1966), used this value and showed that the pK_a of α-toluenethiol in 3:1 acetone–water (v/v) is 11.8 and that the pK_a values of several thiols are identical in 75% acetone and in 75% ethanol (v/v). We believe that the slight difference in the solvents is balanced by the temperature difference in our experiments and in the pK_a determination. The pK_a's of thiols decrease slightly with the increase in the temperature.

[17] In calculations of $PhCH_2S^-$ concentrations, the autoprotolysis of the $EtOH$-H_2O solvent was taken as $K = 10^{-14}$. However, except for the reactivity ratio of the two thiolate ions which is slightly dependent on the K and the pK_a ($PhCH_2SH$) values, all the other data of Table III are independent of K and pK_a ($PhCH_2SH$) since comparison of the apparent rate coefficients at a constant $[PhCH_2SH]/[NaOH]$ ratio gives the same results.

TABLE III

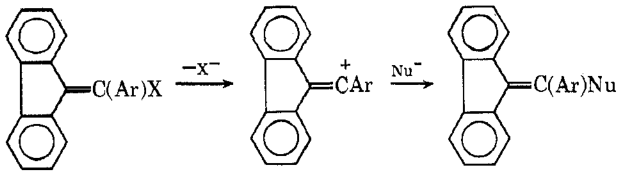
MECHANISTIC CRITERIA FOR THE REACTIONS OF THE β-FLUORENYL AND THE β,β-DIPHENYLVINYL SYSTEMS[a]

System	Order in nucleophile	k_{Br}/k_{Cl}	$k_{\alpha\text{-An}}/k_{\alpha\text{-Ph}}$	m in aq EtOH	$k_{PhCH_2S^-}/k_{p\text{-MeC}_6H_4S^-}$	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]
β,β-Diphenyl with NaOAc	0[d]	53	3670	0.49	1	22	−22
β-Fluorenyl with NaOAc	0	75	3100	0.57		24	−17
β-Fluorenyl with $PhCH_2SNa$	1[e]	1.8–1.9	0.93–0.96	~0	12.6	16	−21

[a] The data summarize the behavior of different substrates in different solvents, at different temperatures. [b] In kcal/mol. [c] In eu. [d] Also with NaOH, $NaSCH_2Ph$, and $NaSC_6H_4Me$-*p*. [e] Also with $NaSC_6H_4Me$-*p*.

isopropyl, *tert*-butyl, neophyl, 1-adamantyl, 3-homoadamantyl, 1-bicyclo[3.3.1]nonyl, and 1-bicyclo[3.2.2]nonyl halides in 80% EtOH[18] suggests an SN1 mechanism. The approximate $k_{\alpha\text{-An}}/k_{\alpha\text{-Ph}}$ ratio of 3670 at 120° which amounts to a ρ of −4.6[19] is higher than the ratio for the 1-aryl-2,2-diphenylvinyl iodides in aqueous DMF (880, ρ = −3.6)[11] or for the 1-aryl-2,2-diphenylvinyl tosylates in 70% acetone (830, ρ = −3.8),[20] but is lower than the ratio for α-bromostyrenes in 80% EtOH (8600, ρ = −5.1).[21] The Winstein–Grunwald m value[22] of 0.49 at 120° is similar to those of other triarylvinyl halides and tosylates in aqueous–organic media. Hindrance to back solvation and the high temperature were suggested to be responsible for the low m values.[9–12,20] However, high m values were found for bridged polycyclic compounds[18c,23] in which the approach of solvent from the back is hindered. Our low m values may be due to a combination of the high temperature and the efficient charge dispersion by the α-anisyl group.[9] Indeed, it was suggested that "the sensitivity of the ionization rate to the solvent change tends to be less for the methoxylated than for the parent structures."[24] The activation parameters for our compounds are also similar to those for related systems solvolyzing *via* the SN1 route.[9,11,12]

The similarity of the reaction order in NaOAc, of the effects of the activating and leaving groups, of the m values, and of the activation parameters of lines 1 and 2 of Table III strongly indicates a similar SN1 mechanism for the solvolyses of the β-fluorenyl derivatives **2** and **4**-Br in the presence of NaOAc (eq 4). The slightly higher m value than that for **1**-Br is probably connected with the different geometries of both systems.



(4)

Additional argument to those brought earlier against the electrophilic addition–elimination mechanism[8–10,12,20] is the constancy of k_1 during a kinetic run, although AcOH is formed by the neutralization of the NaOAc.

The β-fluorenyl systems are 2–3-fold less reactive than the β,β-diphenyl systems in aqueous ethanol, and the reactivity ratio is slightly solvent, activating group, and leaving group dependent. For comparison, the $k_{1\text{-Br}}/k_{2\text{-Br}}$ ratio in acetolysis at 140° is *ca.* 6,[25] and the ratio for the corresponding tosylates $k_{1\text{-OTs}}/k_{2\text{-OTs}}$ in 70% acetone at 75° is 7.5.[26] The available data on the solvolysis of α-anisyl-α-bromoethylenes in 80% EtOH are collected in Table IV which shows that the β-fluorenyl compound is the least reactive of those studied. Table IV also indicates that the inductive effects of alkyl and aryl groups from the β position are relatively small[10c] and that the $k_{1\text{-Br}}/k_{2\text{-Br}}$ ratio can be explained if the β-fluorenyl moiety is slightly more electron attracting than the two β-phenyl groups. However, the large rate differences among pairs of cis–trans isomers were ascribed to a relief of steric strain and to ground state destabilization effects[27,28] These geometrical factors should also be considered for our crowded systems. When the α-anisyl group is twisted from the plane of the double bond, the ground state anisyl double bond conjugation is reduced and the α-anisyl perpendicular cationic orbital interaction in the transition state increases. The rigid fluorenyl moiety of **2** and **4** is more in the plane of the double bond than the β-phenyl groups of **1** and **3** and consequently the α-anisyl group is pushed out of this plane. The dipolar structure **17** contributes electronically to this effect. The appearance of an upfield proton at δ 6.35 in the nmr of **2**-Br (but not in the nmr of **1**-Br) is probably due to the H-1 proton which is cis to the twisted α-anisyl group and in its shielding zone. This is also shown by a model and by analogy to the nmr of 9-benzhydrylidenefluorene.[29] This effect is opposed by the contribution of structure **18**, in which the α-anisyl is buttressed into the double bond plane. In this respect it is noteworthy that the long wavelength λ_{max} and ϵ of **2**-Br are[6a] higher than those for **1**-Br.

While we are unable to dissect the observed $k_{1\text{-Br}}/k_{2\text{-Br}}$ ratio into these contributing factors, its small value argues for the relative unimportance of struc-

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(20) Z. Rappoport and Y. Kaspi, *ibid.*, **92**, 3220 (1970). Recalculation of the data with the aid of a computer program which searches and uses the best infinity gave $k_{\alpha\text{-anisyl}}/k_{\alpha\text{-phenyl}}$ = 630, and ρ = −3.66.

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(26) Z. Rappoport and J. Kaspi, unpublished results.

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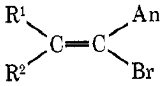
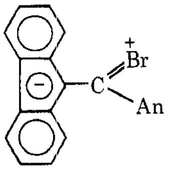
TABLE IV
RELATIVE SOLVOLYSIS RATES IN 80% EtOH AT 120° FOR

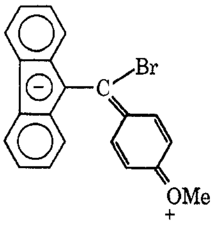


R¹	R²	Rel k_1	Ref	R¹	R²	Rel k_1	Ref
H	H	1.0[a]	21	An	An	1.70[c] (1.48)[b]	9
Me	H	6.43[a,d]	27	An	Ph	1.05[c]	10c
H	Me	0.78[a,d]	27	Ph	An	1.22[c]	10c
Me	Me	3.74[b]	25	Ph	Ph	0.80[c] (0.65)[b]	This work
An	H	13.5[b]	28	Fluorenyl		0.26[b]	This work
H	An	0.29[b]	28				

[a] Base, triethylamine. [b] Base, NaOAc. [c] Base, NaOH. [d] Relative k_1 at 110°.



17



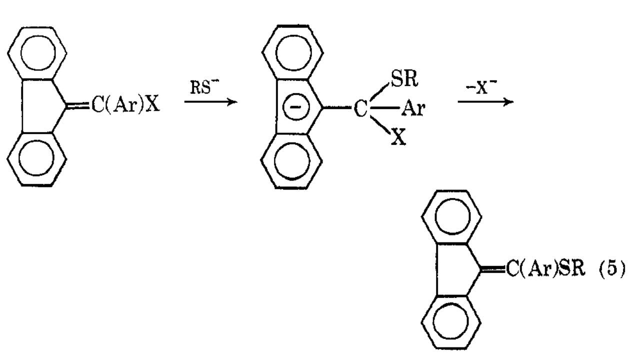
18

tures such as **17** as the main source for the vinylic unreactivity.[9,11,30,31] In view of the enormous differences in the charge-spreading ability of the fluorenyl and the benzhydryl groups,[13] it is highly improbable that an important contribution from **17** would be coincidentally masked by the other factors mentioned above.

Addition–Elimination Route.—The reaction of the β-fluorenyl system with thiolate ions is much faster than with NaOAc. For comparison, the half-lives of **4**-Br are 39 min at 105° in the presence of 0.008 *M* sodium *p*-toluenethiolate and 66 hr at 155.5° in the presence of 0.018 *M* NaOAc. Comparison of lines 2 and 3 of Table III shows that the use of the highly nucleophilic thiolate ions results in their involvement in a rate-determining bond formation. Two possible mechanisms are in-plane SN2 substitution and an Ad$_{\mathrm{N}}$–El route. The SN2 route which predicts inversion of configuration of the substitution product and $k_{\mathrm{F}}/k_{\mathrm{Cl}}$ and $k_{\mathrm{Cl}}/k_{\mathrm{Br}}$ "element effects" was not yet observed in bimolecular nucleophilic vinylic substitutions, which give retention of configuration and high $k_{\mathrm{F}}/k_{\mathrm{Cl}}$ ratios.[2] This route is very unlikely on steric ground since substituents α and β trans to the leaving group prevent approach of the nucleophile to a bonding distance from the α carbon.[2,32] This is especially true in our system where the nucleophile has to attack in-plane a *cis*-stilbene moiety. While we have no stereochemical information, the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratio (see below) and analogies with other nucleophilic vinylic reactions[2] suggest the Ad$_{\mathrm{N}}$–El route.

The reaction is first order in the reactant and in the thiolate nucleophile, provided that the incomplete ionization of α-toluenethiol is taken into account. The $k_{2\text{-Br}}/k_{2\text{-Cl}}$ ratios of 1.8–1.9 are very close to the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratios of 2.2–2.6 for the substitution of α-halo-β-arylsulfonylethylenes with thiophenoxide ion,[33] or to the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratios in the substitutions *via* Ad$_{\mathrm{N}}$–El in the $Ph_2C{=}CHX$ system.[34] These small ratios are ascribed to the operation of similar inductive and resonance effects of the two halogens in the rate-determining addition of the nucleophile to the double bond. The 12.6-fold higher reactivity of the benzylthiolate ion compared with the *p*-toluenethiolate ion at 90° is parallel to the reactivity ratio of 15.5 of these two nucleophiles toward α-chloro-β-*p*-toluenesulfonylethylene in methanol.[35]

The $k_{2\text{-Br}}/k_{4\text{-Br}}$ ratios of 0.93–0.96 give Hammett's ρ values (using σ values) of +0.06 to +0.11. While the sign of ρ is positive as found for other nucleophilic vinylic reactions,[36,37] its absolute value is much lower. This cannot be due to a very highly effective charge spreading into the β-fluorenyl moiety, since the ρ's for nucleophilic vinylic reactions of more electrophilic olefins such as arylidenemalononitriles are 1.1–2.0.[36b,c] We ascribe the $k_{\alpha\text{-anisyl}}/k_{\alpha\text{-phenyl}}$ ratio to the intervention of a small contribution from the SN1 route. Extrapolation of the data of Table I gives the half-lives of the SN1 reaction of **2**-Br at 90 and 105° as 41 and 10 hr, respectively. Therefore, in our conditions the Ad$_{\mathrm{N}}$–El route (eq 5) predominates and the SN1 route contributes only 0.5–1% to the overall rate, but this contribution is sufficient to increase the $k_{\alpha\text{-anisyl}}/k_{\alpha\text{-phenyl}}$ ratio. Indeed, in view of the large differences



(5)

between such ratios for both routes (*ca.* 3000 for the SN1 route *vs.* *ca.* 0.5 for the Ad$_{\mathrm{N}}$–El route) *we suggest that the $k_{\alpha\text{-anisyl}}/k_{\alpha\text{-phenyl}}$ ratios are the most sensitive tool for detecting a small contribution of the SN1 route in a pre-*

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(34) (a) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958); (b) P. Beltrame and G. Favini, *Gazz. Chim. Ital.*, **93**, 757 (1963).

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(37) The use of a combination of σ and σ^+ values suggested recently for similar reactions (ref 36a) does not change much the ρ value.

dominantly nucleophilic addition–elimination substitution. We predict that these ratios will be nucleophile dependent and higher for the less nucleophilic thiolate ions. Further work on this criterion is now in progress.

A lower rate in the more aqueous solvent is predicted for the reaction of the neutral molecules **2** and **4** with the thiolate ions. This was observed with the benzylthiolate ion, although the effect is rather small. This is probably due to the increased dissociation of the α-toluenethiol in the more aqueous solvents[17] in addition to the small contribution from the S_N1 route.

The 3.5-fold faster reaction in the presence of NaOH than with NaOAc may indicate that both routes operate simultaneously.[38] Preliminary experiment showed that the reaction is faster in 90% than in 80% EtOH. Unfortunately, the reaction was not studied further since it is followed by a side reaction which consumes the base.

Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded with Varian T/60 or HA/100D instruments and are given in δ units downfield from internal tetramethylsilane. Mass spectra were recorded with an Atlas C4 instrument and uv on a Perkin-Elmer 450 or on a Beckman DU spectrometer.

Materials.—α-Toluenethiol (Aldrich), bp 195°, and *p*-toluenethiol (Aldrich), mp 42–43°, bp 195°, were distilled before use. 9-Anisylidenefluorene was prepared according to Thiele[39] and 9-benzylidenefluorene dibromide according to Koelsch.[14] 1-Anisyl-2,2-diphenylvinyl 1-*p*-toluenethiolate was prepared earlier.[9]

Solvents.—The 80% ethanol and the aqueous ethanolic mixtures were prepared according to Grob.[21]

9-Anisylidenefluorene Dichloride (5-Cl).—Into 9-anisylidenefluorene (13.5 g, 48 mmol) in dry carbon tetrachloride (100 ml), chlorine gas (3.5 g, 50 mmol) was bubbled and the solution was shaken for 3 min, washed with water, dilute sodium hydroxide solution, and again with water, and dried, (Na_2SO_4), the solvent was evaporated, and methanol (50 ml) was added. After a few minutes of shaking, 15 g (80%) of white crystals, mp 105–106°, was obtained.

Anal. Calcd for $C_{21}H_{16}Cl_2O$: C, 71.03; H, 4.54. Found: C, 71.10; H, 4.72.

Spectra: nmr ($CDCl_3$) δ 3.66 (3 H, s, MeO), 5.60 (1 H, s, CH), 6.43–8.0 (12 H, m, Ar). If the nmr is taken after 2 hr, it showed the presence of *ca.* 30% of **2**-Cl.

α-Chloro-9-anisylidenefluorene (2-Cl).—9-Anisylidenefluorene dichloride (14.5 g, 40 mmol) in acetic acid (100 ml) was refluxed for 1 hr until the evolution of hydrogen chloride ceased. Water was added to turbidity, and the 10 g of crystals which was separated was recrystallized from 95% ethanol giving 4.1 g (31%) of α-chloro-9-anisylidenefluorene, mp 149–150°.

Anal. Calcd for $C_{21}H_{15}ClO$: C, 79.24; H, 4.72; Cl, 10.80. Found: C, 79.11; H, 4.74; Cl, 11.12.

Spectra: nmr ($CDCl_3$) δ 3.87 (3 H, s, OMe), 6.50 (1 H, unsymmetrical d, H-1), 6.77–7.87 (10 H, m, Ar), 8.60–8.76 (1 H, quart, H-8?); λ_{max} (dioxane) 250 nm (ε 31,100), 259.5 (39,000), 317.5 (14,300).

Additional fractions were mixtures (by nmr) of **2**-Cl and **6**.

9-Anisylidenefluorene Dibromide (5-Br).—To 9-anisylidenefluorene (5.8 g, 20 mmol) in dry carbon tetrachloride (100 ml), bromine (1.1 ml, *ca.* 20 mmol) was added at a rate that its color discharged immediately. With the progress of the reaction the yellow solution turned yellow red. The solution was left for additional 10 min at room temperature, washed with water and with dilute sodium hydroxide solution, and dried (Na_2SO_4), the solvent was evaporated, and the oil was triturated with methanol. White solid, mp 128–129° (with evolution of HBr), 7.6 g (85%), was obtained.

Spectra: nmr (CCl_4) δ 3.66 (3 H, s, MeO), 5.82 (1 H, s, CHBr), 6.77 (4 H, quart with 2 H at 6.58 and 2 H at 6.95, *J* = 9 cps, An), 6.87–8.23 (8 H, m, Ar).

The compound eliminates HBr easily and analyses gave various results.

Anal. Calcd for $C_{21}H_{26}Br_2O$: C, 56.80; H, 3.61; Br, 35.98. Found: C, 57.82; H, 3.64; Br, 35.10.

The nmr of these samples showed the presence of **2**-Br.

α-Bromo-9-anisylidenefluorene (2-Br).—9-Anisylidenefluorene dibromide (4.5 g, 10 mmol) in glacial acetic acid (50 ml) was refluxed for 30 min. The yellow solution turned brown and an acidic gas was evolved. After cooling, water was added slowly, and the yellow solid precipitated was recrystallized from ethanol giving 2.2 g (60%) of yellow plates, mp 152–154°.

Anal. Calcd for $C_{21}H_{15}BrO$: C, 69.34; H, 4.02; Br, 21.60. Found: C, 69.40; H, 4.16; Br, 22.00.

Spectra: nmr ($CDCl_3$) δ 3.82 (3 H, s, MeO), 6.35 (1 H, half of a quart, H-1), 6.77–7.76 (10 H, m, Ar), 8.80–8.88 (1 H, m, H-8?); λ_{max} (cyclohexane) 243.5 nm sh (ε 29,400), 251 (33,000), 259 (38,200), 281 sh (11,900), 304.5 (12,300), 317 (15,400); mass spectra, parent peak at *m/e* 362, 364 (81%), base peak at 283 (M − Br), and additional peaks at 268 (30%, M − Br − Me) and 252 (30%, M − Br − OMe); ir (KBr) 1580 cm⁻¹ (C═C).

1-Anisyl-2,2-diphenylvinyl Chloride (1-Cl).—1-Anisyl-2,2-diphenylethylene[11] was prepared by the dehydration of 2-anisyl-1,1-diphenylethanol[9] by reflux for 2 hr in 20% sulfuric acid. To ethylene (5.72 g, 20 mmol) in carbon tetrachloride (50 ml), chlorine (1.6 g, 22 mmol) in carbon tetrachloride (25 ml) was added. When the addition was finished, air was bubbled into the mixture to remove the excess chlorine and hydrochloric acid formed. The solvent was evaporated and the oil was refluxed in acetic acid (50 ml) for 15 min, and, on cooling and addition of few milliliters of water, white crystals of **1**-Cl, mp 119–120° (4.7 g, 73%), were precipitated.

Anal. Calcd for $C_{21}H_{17}ClO$: C, 78.61; H, 5.34; Cl, 11.05. Found: C, 78.46; H, 5.19; Cl, 10.93.

Spectra: nmr ($CDCl_3$) δ 3.65 (3 H, s, OMe), 6.62–7.28 (14 H, m, Ar).

α-Bromo-9-benzylidenefluorene (4-Br) was prepared according to Koelsch:[40] λ_{max} (cyclohexane) 251.5 nm (ε 32,500), 259.5 (41,300), 283 (12,000), 303 (12,600), 316.5 (15,500).

9-Anisyl-9,10-dihydro-10-oxophenanthrene (6).—9-Anisylidenefluorene dibromide (2 g, 4.5 mmol) and potassium acetate (2 g, 20.2 mmol) in acetic acid (50 ml) were refluxed for 2 hr. KBr was precipitated. The mixture was poured into ice-water (200 ml), and the viscous residue was crystallized from methanol giving 1.22 g (90%) of white crystals of 9-anisyl-9,10-dihydro-10-oxophenanthrene, mp 170° (after recrystallization from acetone–chloroform).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.95; H, 5.37. Found: C, 83.63; H, 5.12.

Spectra: nmr ($CDCl_3$) δ 3.70 (3 H, s, MeO), 6.77–7.90 (12 H, m, Ar), 9.55 (1 H, s, CHAn); λ_{max} (cyclohexane) 248 nm (ε 22,500), 256 sh (22,000), 302.5 (5600); ir (KBr) 2800, 2700 (CH), 1715 cm⁻¹ (C═O); mass spectra, parent peak at *m/e* 300 (10%), base peak at 271 (M − HCO), other peaks at 257 (4%, M − HCO − Me), 228 (18%), 226 (18%), 135 (9%, AnCO).

9-(α-Acetoxy-*p*-methoxybenzyl)fluoren-9-ol (7).—Addition of water (200 ml) to the aqueous–acetic mother liquor left from the isolation of **6** above precipitated a solid (100 mg), mp 80°, which after recrystallization from carbon tetrachloride–hexane gave 60 mg (4%) of white crystals, mp 153°.

Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.61; H, 5.59. Found: C, 75.81; H, 5.54.

Spectra: nmr ($CDCl_3$) δ 2.08 (3 H, s, MeCO), 3.65 (3 H, s, MeO), 4.65 (1 H, broad s, OH), 6.20 (1 H, s, CH), 6.42–6.88 (4 H, quart centered at 6.73), 7.08–7.67 (8 H, m, Ar); ir (KBr) 3480, 3420 (OH), 1720 cm⁻¹ (C═O); mass spectra, parent peak at *m/e* 360 (1%), other peaks at 300 (4%, M − HOAc), 239 (9%), 179 (base peak, $AnCHOAc^+$), 180 (53%, dibenzpyran$^+$, ?).

9-Methoxy-9-(α-*p*-dimethoxybenzyl)fluorene (8).—9-Anisylidenefluorene dibromide (2 g, 4.5 mmol) was kept at room temperature in methanol (50 ml) containing KOMe (2 g, 28 mmol) for 24 hr. The mixture was poured into water and the oil formed was separated by decantation and crystallized from methanol giving 1.25 g (80%) of white solid, mp 110°.

Anal. Calcd for $C_{23}H_{22}O_3$: C, 80.21; H, 6.45; MeO, 27.04. Found: C, 79.96; H, 6.17; MeO, 26.56.

Spectra: nmr ($CDCl_3$) δ 2.85 (3 H, s, OMe), 3.25 (3 H, s,

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[38] If the higher reactivity of **2**-Br with NaOH compared with NaOAc is due to the intervention of the Ad_N-El route, the second-order rate coefficient for this route is 3.3×10^{-4} l. mol⁻¹ sec⁻¹.

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[40] C. F. Koelsch, *J. Amer. Chem. Soc.*, **54**, 3384 (1932).

OMe), 3.67 (3 H, s, MeO), 4.50 (1 H, s, CH), 6.43–6.85 (4 H, quart centered at 6.58, J = 9 cps, An), 7.18–8.0 (8 H, m, Ar).

α-Acetoxy-9-anisylidenefluorene (2-OAc).—α-Bromo-9-anisylidenefluorene (1.8 g, 5 mmol) and silver acetate (3 g, 12 mmol) in acetic acid (50 ml) were refluxed in the dark for 3 hr. The hot solution was filtered, the solid was washed with hot acetone, and the organic solvents were combined and evaporated. The remaining oil was dissolved in dichloromethane and filtered, the solvent was evaporated, and the residue crystallized fron 95% ethanol giving 1.4 g (82%) of pale yellow crystals of **2**-OAc, mp 143–144°.

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.40; H, 5.22. Found: C, 80.69; H, 5.30.

Spectra: nmr ($CDCl_3$) δ 2.37 (3 H, s, OCOMe), 3.90 (3 H, s, OMe), 6.92–8.05 (12 H, m, Ar); λ_{max} (cyclohexane) 248 nm (ϵ 26,000), 257 (32,000), 311 (14,000); ir (KBr) 1742 cm^{-1} (C=O).

α-Ethoxy-9-anisylidenefluorene (13).—α-Bromo-9-anisylidenefluorene (128 mg, 0.18 mmol) in 80% ethanol 0.5 N in sodium acetate (10 ml) was kept for 4 days at 140° in an ampoule. On cooling, yellow crystals of **13**, mp 154–156° (50 mg, 41%), were obtained.

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.67; H, 6.18. Found: C, 84.62; H, 6.22.

Spectra: nmr ($CDCl_3$) δ 1.40 (3 H, t, Me), 3.90 (2 H, quart, CH_2), 3.95 (3 H, s, OMe), 6.33–6.48 (1 H, half of a quart, H-1), 6.80–7.90 (10 H, m, Ar), 8.27–8.40 (1 H, m, H-8?).

9-Anisoylfluorene (14).—α-Acetoxy-9-anisylidenefluorene (0.34 g, 1 mmol) and sodium hydroxide (1 g, 25 mmol) in 80% ethanol (50 ml) were refluxed for 90 min. The mixture was poured into water, extracted with chloroform, washed with water, and dried (Na_2SO_4). White needles of **14**, mp 117–118° (from petroleum ether), were obtained (230 mg, 76%).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.95; H, 5.37. Found: C, 83.78; H, 5.08.

Spectra: nmr ($CDCl_3$) δ 3.80 (3 H, s, OMe), 5.50 (1 H, s, CH), 6.73–7.93 (12 H, m, Ar); λ_{max} (cyclohexane) 265 nm (ϵ 30,000), 301 (6100); ir (KBr) 1653 cm^{-1} (C=O); mass spectra, parent peak at m/e 300 (5%) and peaks at 165 ($C_{13}H_9^+$, 14%), 135 (base peak, $AnCO^+$).

α-*p*-Toluenethio-9-anisylidenefluorene (15).—An ampoule containing α-bromo-9-anisylidenefluorene (65 mg, 0.18 mmol) and sodium *p*-toluenethiolate (0.24 M) in 80% ethanol (5 ml) was kept at 140° for 14 hr. On cooling, a yellow solid was separated and on crystallization from 95% ethanol it gave 50 mg (70%) of α-*p*-toluenethio-9-anisylidenefluorene, mp 150–151°.

Anal. Calcd for $C_{28}H_{22}OS$: C, 82.73; H, 5.46; S, 7.89. Found: C, 82.86; H, 5.29; S, 8.16.

Spectra: nmr ($CDCl_3$) δ 2.22 (3 H, s, Me), 3.77 (3 H, s, MeO), 6.32 (1 H, one-half of a quart, H-1), 6.68–7.90 (14 H, m, Ar), 8.95–9.08 (1 H, m, H-8?); λ_{max} (cyclohexane) 237 nm (ϵ 50,000), 254 (30,000), 263 (30,000), 348 (17,800).

α-Benzylthio-9-anisylidenefluorene (16).—α-Bromo-9-anisylidenefluorene (0.3 g, 0.82 mmol) and α-toluenethiol (0.5 g, 4 mmol) in 90% dioxane (50 ml) were kept at 75° for 14 hr. The mixture was poured into water and extracted with 1,2-dichloroethane (50 ml), the solvent was evaporated, the remaining viscous oil was triturated with methanol, and the solid was filtered and recrystallized from methanol giving 170 mg (51%) of yellow crystals of **16**, mp 146–147°. Additional fractions contain large percentages of dibenzyl disulfide (mp 63°, mmp 63°).

Anal. Calcd for $C_{28}H_{22}OS$: C, 82.73; H, 5.46; S, 7.89. Found: C, 82.72; H, 5.48; S, 8.01.

Spectra: nmr ($CDCl_3$) δ 3.65 (2 H, s, CH_2), 3.85 (3 H, s, MeO), 6.08–6.20 (1 H, half of a quart, H-1), 6.68–7.75 (15 H, m, Ar), 8.68–8.85 (1 H, m, H-8?); λ_{max} (dioxane) 255 nm sh (ϵ 21,000), 264.5 (19,600), 350 (17,900).

α-Benzylthio-9-benzylidenefluorene.—A mixture of α-bromobenzylidenefluorene (333 mg, 1 mmol) and α-toluenethiol (620 mg, 5 mmol) in 80% dioxane (50 ml) containing sodium hydroxide (8 mM) was kept at 75° overnight. The mixture was poured into water, extracted (chloroform), washed with water, and dried ($CaCl_2$) and the solvent was evaporated. The remaining oil was crystallized from ethanol giving 200 mg (53%) of yellow crystals, mp 144–145°.

Anal. Calcd for $C_{27}H_{20}S$: C, 86.12; H, 5.35; S, 8.51. Found: C, 86.12; H, 5.34; S, 8.52.

Spectra: nmr ($CDCl_3$) δ 3.66 (2 H, s, CH_2), 6.0–8.9 (18 H, m, Ar); λ_{max} (dioxane) 254 nm (ϵ 24,000), 264 (22,000), 295 (6400), 305 (6200), 350 (22,000).

Kinetics. A. With Benzylthiolate Ion.—Stock solutions of $2–2.5 \times 10^{-4}$ M of **2**-Cl, **2**-Br, and **4**-Br and of a mixture of α-toluenethiol and sodium hydroxide were prepared, mixed, sealed in ampoules, warmed at 75° for equilibration for 1–2 min, and kept at the reaction temperature. At predetermined times the ampoules were cooled and opened, 5-ml samples were withdrawn and diluted 2–2.5-fold with absolute methanol, and the optical density of the samples were measured in a 1-cm cells at 317 nm (λ_{max} of the vinyl halide) using methanol as a reference. After additional dilution the measurement was repeated at 350 nm (λ_{max} of the product). The isosbestic point at 324 nm remained constant during the reaction. The absorptions of the vinyl halide at the λ_{max} of the product and of the vinyl thiolate at the λ_{max} of the vinyl halide were taken into account. With **1**-Br the reaction was followed by titration of the bromide ion after precipitation of the excess thiol with $Cu(NO_3)_2$.[9] Although the calculated infinity was not achieved (the infinities observed are *ca.* 85%), the product was obtained in quantitative yield.

B. With Sodium *p*-Toluenethiolate.—The reaction with **2**-Br was followed essentially as with benzylthiolate above, except that measurements were at 392 nm. The reaction with **1**-Br was again followed titrimetrically with the $Cu(NO_3)_2$ variant. The infinities observed were at *ca.* 80%, but the product was obtained quantitatively.

C. With Sodium Acetate.—The solutions were prepared as described previously.[9] The sodium acetate concentration was determined in water by titration with 0.1 N HCl using a combination of 2,4-dinitrophenol and bromophenol blue indicators (color change, blue-violet → yellow). The bromide was titrated with silver nitrate using an eosin indicator, and the chloride (from **1**-Cl and **2**-Cl) was titrated potentiometrically.

D. With Sodium Hydroxide.—The reactions were conducted as described earlier.[9]

In all cases the first-order rate coefficients were calculated with the aid of a first-order KINDAT program.[41]

Product Analysis.—The product analysis was done usually by nmr in addition to the isolation of the products. The ethers were recognized by their triplet signal for the methyl group and the ketones by the single benzhydrylic proton and by the low-field half-quartet signals for the α-anisyl protons ortho to the carbonyl group. In the case of the vinyl thiolates none of these were observed and the spectra corresponded to that of the vinyl thiolate.

Registry No.—**1** (X = Br), 25354-48-7; **1** (X = Cl), 33686-66-7; **2** (X = Br), 33686-67-8; **2** (X = Cl), 33686-68-9; **2** (X = OAc), 33735-94-3; **4** (X = Br), 33735-95-4; **5** (X = Br), 33686-69-0; **5** (X = Cl), 33686-70-3; **6**, 33686-71-4; **7**, 33735-96-5; **8**, 33686-72-5; **13**, 33686-73-6; **14**, 33735-97-6; **15**, 33686-74-7; **16**, 33686-75-8; acetate, 71-50-1; hydroxide, 14280-30-9; benzylthiolate, 1492-49-5; *p*-toluenethiolate, 26330-85-8; α-benzylthio-9-benzylidenefluorene, 33686-77-0.

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[41] R. C. Williams, *J. Chem. Soc.*, **47**, 129 (1970).