

SUBSTITUTION OF 9-(α -BROMO- α -ARYLMETHYLENE)FLUORENES BY THIOLATE IONS IN AQUEOUS ACETONITRILE†

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The substitution of 9-(α -bromo- α -arylmethylene)fluorenes by MeS^- and $p\text{-TolS}^-$ ions in 80% MeCN–20% H_2O is a second-order reaction. With MeS^- , for the change of the α -aryl group, Hammett's $\rho = 1.07$ in MeCN. The reaction rate decreases on increasing the water content of the medium. The reactions proceed by the $\text{Ad}_\text{N}\text{-E}$ route and no competitive $\text{S}_\text{N}1$ reaction was observed. The expected influence of the changes in the substituent, solvent, nucleophile and nucleofuge on the competition between the $\text{Ad}_\text{N}\text{-E}$ and $\text{S}_\text{N}1$ reactions was analyzed. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

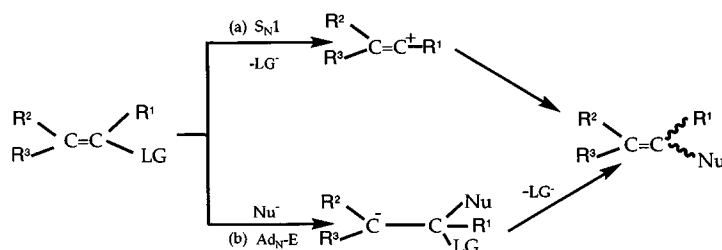
The two most common mechanisms for nucleophilic substitution at a vinylic carbon are the bimolecular addition–elimination and the monomolecular $\text{S}_\text{N}1$ routes.² In contrast with the aliphatic $\text{S}_\text{N}2$ and $\text{S}_\text{N}1$ routes, whose transition states can be regarded as the extremes of a general situation in which the entering nucleophile, the leaving nucleofuge and the attacked carbon are colinear and the routes differ in the extents of bond formation and cleavage,³ the situation differs in vinylic systems. In the $\text{S}_\text{N}1$ route [equation (1), route (a)], the nucleofuge (LG) leaves from the plane of the double bond, and the nucleophile (Nu^-) then reacts with the empty p orbital in the plane.⁴ In the nucleophilic addition–elimination route $\text{Ad}_\text{N}\text{-E}$ [equation

(1), route (b)], the nucleophile attacks and the nucleofuge leaves from a plane perpendicular to the $\text{C}=\text{C}$ plane.⁵ In-plane back-side nucleophilic attack has been discussed in recent years, but an unequivocal example for it is still unavailable.⁶ Consequently, the two routes are independent and a situation can be visualized where both routes proceed simultaneously. It is of interest to study such a situation.

We have shown previously⁷ that the substitution of 9-(α -bromo- α -*p*-methoxyphenylmethylene)fluorene (**1a**) proceeds by either route (a) or (b) under different conditions. In a solvolyzing solvent such as aqueous EtOH, in the presence of the weak nucleophile AcO^- the reaction follows the $\text{S}_\text{N}1$ route. In contrast, in the presence of the strong thio nucleophiles PhCH_2S^- and $p\text{-TolS}^-$, the reaction follows the addition–elimination route.⁷ As expected, route (b) is accelerated when the nucleophile becomes stronger.

Many mechanistic criteria distinguish between the two routes. These involve the kinetics, the effect of solvent, nucleophile and nucleofuge, the nature of the α - and β -substituents and the stereochemistry of the reaction.

The operation of the two routes for **1a** under appreciably



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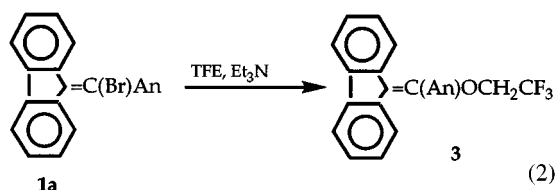
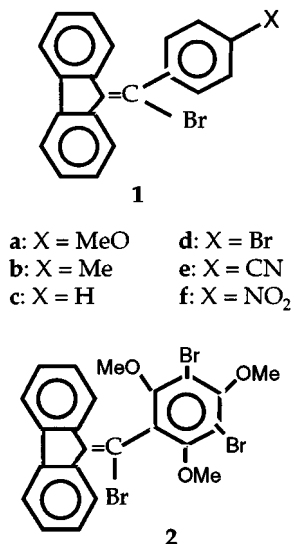
different conditions suggests that **1a** and closely related compounds could be suitable substrates to detect the simultaneous operation of the two nucleophilic vinylic substitution routes. A systematic way to find an appropriate system and conditions is by a gradual variation of one or more of the parameters mentioned above. In the present work, we studied the effect of three parameters on the bimolecular reaction of system **1**: (i) the effect of α -substituents, which range from the electron-donating anisyl (**1a**) to the electron-withdrawing *p*-nitrophenyl (**1f**),⁸ (ii) the effect of the solvent (ranging from 5 to 30% aqueous MeCN) and (iii) the effect of nucleophile (MeS^- and *p*- TolS^-). A preliminary search for conditions for the operation of the $\text{S}_{\text{N}}1$ route was also conducted, both with **1a**, which is the most favorable substrate for this route in the monosubstituted series, and for the polysubstituted compound **2**,⁹ which should be more activated for the $\text{S}_{\text{N}}1$ route.

RESULTS

α -Bromo-9-arylmethylenefluorenes (**1**) were available from the bromination of 9-arylmethylenefluorenes.⁸ ($\alpha,3',5'$ -Tri-bromo-2',4',6'-trimethoxyphenylmethylene)fluorene **2** was obtained from bromination of 9-(2',4',6'-trimethoxyphenylmethylene)fluorene, which was obtained, in turn, from the condensation of fluorene with 2,4,6-trimethoxybenzaldehyde.⁹

Solvolysis

Solvolysis of **1a** in 2,2,2-trifluoroethanol (TFE) containing a three-fold excess of Et_3N gave only the corresponding substitution product, 9-(*p*-methoxyphenyl)- α -trifluoroethoxymethylene)fluorene (**3**) [equation (2)].



In 90% DMSO–10% H₂O or in 75% MeCN–25% H₂O mixtures, solvolysis of **1a** did not take place even at 130 °C after 70 h. Surprisingly, even the addition of 0.05–0.25 molar equivalents of AgNO_3 , Ag_2CO_3 or AgOAc to the solution of **1a** in DMSO did not give the solvolysis product.

From attempted solvolysis of **2**, which is simultaneously activated to solvolysis by three methoxy groups and deactivated by the two bromines, in 70% MeCN–30% H₂O in the presence of a six-fold excess of Et_3N , we isolated both fluorene and fluorenone. We failed to isolate the other cleavage product which should contain the $\text{C}_6\text{Br}_2(\text{OMe})_3$ moiety.

Bimolecular substitution

The reaction of **1a–f** with sodium methanethiolate ($\text{MeS}^- \text{Na}^+$) or sodium *p*-toluenethiolate (*p*- $\text{TolS}^- \text{Na}^+$) in MeOH or EtOH afforded the thioether substitution products **4** in good yield [equation (3)]. In contrast, the starting material was recovered unchanged from reaction of the vinyl bromide **2** with *p*- TolS^- even after 73 h at 130 °C in MeOH in a sealed tube.

The reactions of **1a–f** with MeS^- and of **1d–f** with *p*- TolS^- were followed spectrophotometrically in aqueous MeCN by monitoring the increase of the absorption at the λ_{max} of the substitution products **4** (ca 350 nm), using 13:3- and 33:3-fold excesses of *p*- TolS^- and MeS^- , respectively, over **1**.

The initial pseudo-first-order rate coefficients, divided by the RS^- concentration, gave relatively constant second-order rate coefficients (k_2). Their values in 80% MeCN at several temperatures, together with the derived activation parameters, are given in Table 1. The Hammett's ρ value for the reaction with MeS^- at 40 °C is 1.07 ± 0.03 ($n=6$, $r=0.998$).

The reaction was also investigated for systems with electron-donating (**1a**) and electron-withdrawing (**1e**) substituents in several water–MeCN mixtures (Table 2). The k_2 values decreased on increasing the water content of the medium, by 43-fold from 5% H₂O–95% MeCN to 20%

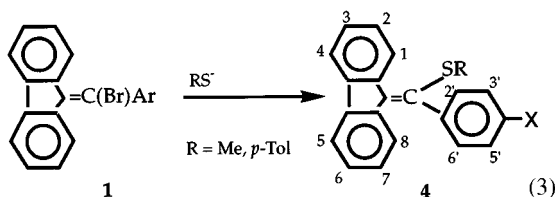


Table 1. Second-order rate coefficients for the reaction of RS^- with 9-(α -bromo- α - p -X-substituted-arylmethylene)fluorenes (**1**) in 80% MeCN–20% H_2O ^a

R	X	Temperature (°C)	$10^2 k_2$ ($\text{M}^{-1} \text{s}^{-1}$)	$\Delta H^\ddagger$ (kcal mol ⁻¹) ^b	$\Delta S^\ddagger$ (kcal e.u.) ^b
Me	MeO	40	(1.34) ^c		
		60	3.22		
		70	4.7	8.3	–51.3
		80	6.95		
Me	Me	40	(1.88) ^c		
		60	4.32		
		70	5.88	7.7	–52.5
		80	8.88		
Me	H	40	3.02		
		50	4.88		
		60	7.42	8.7	–48.4
		70	11.4		
Me	Br	40	5.55		
		50	10.4	11.9	–37.3
		60	18.6		
Me	CN	10	0.94		
		20	2.50	16.5	–22.4
		30	6.55		
		40	14.0		
Me	NO ₂	10	1.32		
		20	4.42	16.0	–23.4
		30	9.72		
		40	18.8		
<i>p</i> -Tol	Br	40	(1.18) ^c		
		70	8.0	7.3	–43.0
		80	11.1		
<i>p</i> -Tol	CN	40	(4.2) ^c		
		50	7.2		
		60	11.4	10.0	–45.7
		70	18.8		
		80	29		
<i>p</i> -Tol	NO ₂	40	(11.4) ^c		
		50	22.8		
		60	48	13.2	–33.3
		70	85		
		80	144		

^a $[\mathbf{1}] = 1.2 \times 10^{-4} \text{ M}$; $[\text{MeS}^- \text{Na}^+] = 4 \times 10^{-3} \text{ M}$; $[\text{p-TolS}^- \text{Na}^+] = 1.6 \times 10^{-3} \text{ M}$; $k_2 \pm 3\%$.^b $\Delta H^\ddagger \pm 1.0 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger \pm 3 \text{ e.u.}$ ^c Extrapolated value from higher temperatures.

H_2O –80% MeCN for **1a** and by 50-fold from 5% H_2O –95% MeCN to 30% H_2O –70% MeCN for **1e**. We found no ionizing parameter Y values for MeCN– H_2O mixtures in the water-rich region. However, Bentley's Y_{OTS} values are available for such mixtures in the water-rich region,^{10a} and they and the value in pure MeCN^{10a} are linearly related to the volume percentage of MeCN in the mixture. A nearly parallel line was found for the solvolysis of AnSO_2Cl in the 0–90% MeCN– H_2O region,^{10b} allowing the estimation of approximate Y_{OTS} values. The $\log k_2$ values were linear with these Y_{OTS} values and their slopes (m) are $m = -0.93$ for **1e** at 30 °C ($r = 0.99$, $\text{SD} = 0.07$) and -1.50 for **1a** at 60 °C ($r = 0.99$, $\text{SD} = 0.11$).

DISCUSSION

The bimolecular $\text{Ad}_\text{N}\text{-E}$ route

The second-order behavior summarized in Table 1 indicates that in 80% MeCN–20% H_2O all six substrates react by the bimolecular $\text{Ad}_\text{N}\text{-E}$ route [equation (1), route (b)] with the thio nucleophiles MeS^- and p-TolS^- at the whole temperature range studied. The positive Hammett's ρ value of 1.07 for the reaction with MeS^- is consistent with formation of a negative charge on C_α in the transition state.

This conclusion is corroborated by the solvent effect (Table 2). A decrease in the reaction rate of an anion with a

Table 2. Second-order rate coefficients for the reactions of **1a** and **1e** with MeS^- in MeCN–H₂O mixtures^a

Solvent(v/v)	$10^2 k_2 \text{ (M}^{-1} \text{ s}^{-1}\text{)}$		Y_{OTS}^b
	1a (60 °C)	1e (30 °C)	
5% H ₂ O–95% MeCN	140	85	–2.60
10% H ₂ O–90% MeCN	50	24.5	–2.25
15% H ₂ O–85% MeCN	17	12.5	–1.90
20% H ₂ O–80% MeCN	3.22	6.6	–1.52
25% H ₂ O–75% MeCN		2.4	–1.16
30% H ₂ O–70% MeCN		1.7	–0.80

^a $[\mathbf{1}] = 1.2 \times 10^{-4} \text{ M}$; $[\text{MeS}^- \text{Na}^+] = 4 \times 10^{-3} \text{ M}$; $k_2 \pm 3\%$.
^b Estimated values. See text and Ref. 10.

neutral molecule with increase in the dielectric constant of the medium is the expected outcome.

For both electron-donating and -withdrawing substituents, the increase in the dielectric constant on addition of water to the acetonitrile decreased significantly the substitution rate, and more so for **1a** with the electron-donating *p*-anisyl group. Consequently, Winstein–Grunwald slopes (*m*) based on the estimated Y_{OTS} values have appreciable negative values.

Although MeS^- reacts faster than $p\text{-TolS}^-$, the reactivity difference (based mostly on extrapolated k_2 values at 40 °C) are mostly small: $k_{\text{MeS}^-}/k_{p\text{-TolS}^-} = 1.65$, 3.3 and 4.7 for reactions of **1f**, **1e** and **1d**, respectively. By extrapolation, the ratio for **1a** is expected to be 10–15. Indeed, PhCH_2S^- shows a 12.6-fold higher reactivity than $p\text{-TolS}^-$ with **1a** in 80% EtOH.⁷

Since for the $S_{\text{N}}1$ route a large negative ρ value for the change of α substituents and a positive m value for the change of the solvent are predicted, this route is unequivocally excluded for our system.

Conditions for competition of routes (a) and (b)

Since the change in the α -substituent effect and the solvent did not lead to competition of routes (a) and (b), it is worth analyzing the conditions under which such a competition is expected.

The half-life for the $\text{Ad}_{\text{N}}\text{-E}$ reaction of the slower substrate **1a** with 0.004 M MeS^- is approximately 1 h at 80 °C in 80% MeCN–20% H₂O. Based on the increase in the $k_{\text{MeS}^-}/k_{p\text{-TolS}^-}$ ratio from 1.65 for **1f** to 4.70 for **1d**, we will use a rough extrapolated ratio of 15 for **1a**. The rate increase for **1e** from 75% MeCN–25% H₂O to 80% MeCN–20% H₂O is 2.8. Consequently, the half-life for the reaction of **1a** with 0.004 M $p\text{-TolS}^-$ in 75% MeCN–25% H₂O at 80 °C will be at most 42 h. At a 1:1 $[p\text{-TolS}^-]/[\mathbf{1a}]$ molar ratio of 1.2×10^{-4} , the half-life will be ca 1400 h.

In 75% MeCN–25% H₂O, no solvolysis of **1a** (by $S_{\text{N}}1$) is observed at 130 °C after 70 h. Assuming (a) that 2% of the solvolysis product would have been detected and (b) a

2⁵-fold rate increase from 80 to 130 °C, the half-life for the $S_{\text{N}}1$ solvolysis of **1a** in 75% MeCN–25% H₂O at 80 °C will be $\leq 4.5 \times 10^4$ h.

Consequently, even with the lowest reasonable thio nucleophile concentration and with the most favorable substrate studied, the $S_{\text{N}}1$ reaction will still be >32-fold slower than a competitive $\text{Ad}_{\text{N}}\text{-E}$ route.

In order to make routes (a) and (b) competitive, the present route (a)/route (b) reactivity ratio should increase by 2–3 orders of magnitude. Qualitatively such a change can be achieved by using a more electron-donating α -aryl substituent, a more ionizing solvent, a better leaving group or a weaker nucleophile. The present work gives some information on these points.

The ρ values for a change of the α -aryl group in vinylic solvolysis is -3.4 to -4.6^4 whereas for the $\text{Ad}_{\text{N}}\text{-E}$ route the value is about unity from this work. Consequently, a change of the *p*-MeO of **1a** ($\sigma_{\text{p}} = -0.78$) to a substituent (or substituents) with σ_{p} or $\Sigma\sigma_{\text{p}} \approx -1.5$ should bring the route (a)/route (b) reactivity ratio close to (or even higher than) the desired ratio. We had tried to do so by introducing a 2,4-(MeO)₂ or 2,4,6-(MeO)₃ substituents into **1c**, but the accompanying increase in the reactivity of other sites of the molecule prevented the preparation of the desired vinyl bromides. Compound **2**, which was one of the products of this attempt,⁹ should have the required excessive degree of activation, assuming that an *o*-MeO activates more than an *m*-Br deactivates the $S_{\text{N}}1$ route. However, whereas **2** reacted in 70% MeCN–30% H₂O, cleavage products of the double bond rather than a solvolysis product were generated. Hence this approach failed so far.

A change to a better leaving group than bromine, e.g. OTs or OTf, should increase the $S_{\text{N}}1$ reactivity and affect less the rate-determining nucleophilic addition–elimination rate. The tosylate analog of **1a** is solvolytically 19.1-fold more reactive than **1a** in 70% acetone,¹¹ and a triarylvinyl triflate is almost five orders of magnitude more reactive than the corresponding tosylate.¹² In contrast, the reactivity order of morpholine with $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}(\text{X})=\text{C}(\text{CO}_2\text{Et})_2$ in MeCN for X is OTf (124) > OTs (17) > Cl (1) in the $\text{Ad}_{\text{N}}\text{-E}$ route¹ and since vinyl-Cl and vinyl-Br usually have similar reactivities,^{2,5} a change from Br to OTs will not affect much the relative reactivity of both routes. In contrast, a change to OTf will bring even more than the required increase in the relative reactivity. However, we note that Ad_{N} reaction on crowded vinyl triflates can take place on the sulfur atom with an S–O rather than a C–O bond cleavage.^{1,4}

A change to a more polar solvent should be fruitful, since the *m* value for the $\text{Ad}_{\text{N}}\text{-E}$ route was found here to be appreciably negative, and *m* values are positive for the $S_{\text{N}}1$ route. However, we note that the large reactivity difference persists in an already relatively high ionizing medium and further increase in the ionizing power by addition of water will most likely result in solubility problems.

The change to a poorer nucleophile seems to be the best tool for increasing the route (a)/route (b) reactivity ratio. The rate of route (a) will not be affected by such a change,

Table 3. Yields and analytical data for Fl=(SR)C₆H₄X-*p*

R	X	Yield (%)	M.p. (°C)	Calculated (%)						Found (%)				
				C	H	N	S	Br	Formula	C	H	N	S	Br
<i>p</i> -Tol	NO ₂	71	181–183	76.93	4.54	3.32	7.61	—	C ₂₇ H ₁₉ NO ₂ S	76.70	4.35	2.97	7.99	—
<i>p</i> -Tol	CN	77	195–197	83.76	4.77	3.49	7.99	—	C ₂₈ H ₁₉ NS	84.06	4.55	3.36	7.83	—
<i>p</i> -Tol	Br	65	136–138	71.21	4.21	—	7.04	17.55	C ₂₇ H ₁₉ BrS	71.50	4.08	—	6.98	17.44
<i>p</i> -Tol	H	61	165–166	86.13	5.35	—	8.52	—	C ₂₇ H ₂₀ S	85.89	5.30	—	8.39	—
<i>p</i> -Tol	Me	87	100–101	86.11	5.68	—	8.21	—	C ₂₈ H ₂₂ S	85.97	5.54	—	8.02	—
Me	NO ₂	80	158–159	72.05	4.53	4.20	9.62	—	C ₂₁ H ₁₅ NO ₂ S	—	4.31	3.95	—	—
Me	CN	85	127–128	80.48	4.82	4.47	10.23	—	C ₂₂ H ₁₅ NS	80.30	4.92	4.39	10.02	—
Me	Br	70	162–163	65.40	4.12	—	8.73	21.76	C ₂₁ H ₁₅ BrS	65.64	4.27	—	8.51	21.52
Me	H	90	134–135	83.96	5.37	—	10.67	—	C ₂₁ H ₁₆ S	84.31	5.42	—	10.27	—
Me	Me	70	133–134	83.40	6.00	—	10.60	—	C ₂₂ H ₁₈ S	83.16	5.82	—	10.32	—
Me	OMe	94	139–140	79.21	5.70	—	10.07	—	C ₂₂ H ₁₈ OS	79.43	5.48	—	9.98	—

Table 4. ^1H NMR, UV and mass spectra of the substitution products $\text{Fl}=\text{C}(\text{SR})\text{C}_6\text{H}_4\text{X}-p(\mathbf{4})$

¹ H NMR, δ (ppm)												
R	X	H-1 ^a	H-2 ^b	H-3 ^b	H-4 ^a	H-5 ^c	H-(6+7) ^c	H-8 ^c	H-(2'+6') ^a	H-(3'+5') ^a	X ^d	R ^e
<i>p</i> -Tol	OMe	6.26	6.85	7.21	7.68	7.78	7.38	8.96	7.18	6.92	3.79	2.23, 6.76, 7.15
	Me	6.20	6.83	7.17	7.67	7.77	7.38	8.95	7.15	7.02	2.31	2.22, 6.90, 7.11
	H	6.10	6.80	7.17	7.67	7.76	7.39	8.95	7.21 ^d	7.21 ^d	7.21 ^d	2.22, 6.90, 7.15
	Br	6.18	6.85	7.18	7.66	7.75	7.35	8.93	7.08	7.34	—	2.25, 6.92, 7.12
	CN	6.05	6.83	7.20	7.67	7.76	7.40	8.93	7.31	7.50	—	2.24, 6.91, 7.11
	NO ₂	6.07	6.82	7.20	7.67	7.74	7.41	8.96	7.39	8.09	—	2.23, 6.92, 7.14
Me	OMe	6.16	6.85	7.14	7.66	7.76	7.36	8.72	7.27	7.02	3.89	2.00
	Me	6.11	6.83	7.14	7.67	7.76	7.37	8.70	7.32	7.23	2.48	2.00
	H	6.01	6.80	7.13	7.66	7.75	7.48	8.70	7.37 ^c	7.37 ^c	7.37 ^c	1.98
	Br	6.14	6.87	7.18	7.67	7.76	7.38	8.71	7.27	7.67	—	2.01
	CN	6.00	6.86	7.20	7.69	7.76	7.41	8.72	7.55	7.85	—	2.00
	NO ₂	6.02	6.83	7.19	7.68	7.77	7.40	8.72	7.60	8.41	—	2.00

^a Doublet.

^b Triplet.

^c Multiplet.

^d Singlet.

^e All Me signals at 1.98–2.25 ppm are singlets. For R=*p*-Tol the signals are the centers of protons A and B in an AB quartet.

UV, λ _{max} (nm) (ε)	MS, m/z (relative abundance (%), assignment)
237 (50440), 354 (18140)	406 (100, M), 299 (9, M – An), 283 (79, M – STol), 252 (40, M – STol – OMe)
237 (56000), 352 (22000)	390 (42, M), 299 (14, M – Tol), 267 (40, M – STol), 252 (100, M – STol – Me)
237 (48000), 350 (19500)	376 (100, M), 285 (6, M – Tol), 253 (73, M – STol)
236 (39000), 255 (22200), 263 (21900), 350 (14700)	456, 454 (61, 56, M), 333, 331 (5,4, M – STol), 252 (100, M – STol – Br)
236 (48800), 254 (29800), 263 (29400), 349 (15500)	401 (100, M), 386 (10, M – Me), 310 (5, M – Tol), 299 (27, M – C ₆ H ₄ CN), 278 (39, M – STol), 277 (93, M – H – STol)
195 (50900), 230 (40600), 263 (30600), 334 (16100)	421 (100, M), 406 (8, M – Me), 298 (25, M – STol), 252 (50, M – STol – NO ₂)
197 (60000), 237 (55900), 352 (24100)	330 (100, M), 315 (22, M – Me), 285 (22, M – Me – CH ₂ O), 284 (21, M – Me – OMe), 283 (13, M – SMe), 239 (30, M – C ₇ H ₇)
192 (61700), 238 (51800), 351 (23400)	314 (100, M), 299 (27, M – Me), 284 (46, M – 2Me), 267 (17, M – SMe), 251 (31, M – Me – SMe)
187 (63300), 238 (51700), 350 (23400)	300 (100, M) 285 (51, M – Me), 284 (43, M – H – Me), 253 (22, M – SMe), 252 (45, M – H – SMe)
197 (52800), 237 (51100), 350 (22600)	380, 378 (72, 70, M), 365, 363 (4,4, M – Me), 284 (100, M – Me – Br), 252 (11, M – Br – SMe)
197 (58500), 238 (57900), 351 (20700)	325 (100, M), 310 (67, M – Me), 278 (M – SMe), 252 (12, M – CN – SMe)
197 (54500), 203 (50400), 237 (49100), 264 (35800), 337 (20400)	345 (100, M), 330 (14, M – Me), 299 (25, M – NO ₂), 284 (43, M – NO ₂ – Me), 252 (63, M – NO ₂ – SMe)

^a Doublet.^b Triplet.^c Multiplet.^d Singlet.^e All Me signals at 1.98–2.25 ppm are singlets. For R=*p*-Tol the signals are the centers of protons A and B in an AB quartet.

UV, λ_{max} (nm) (ϵ)	MS, m/z (relative abundance (%), assignment)
237 (50440), 354 (18140)	406 (100, M), 299 (9, M – An), 283 (79, M – STol), 252 (40, M – STol – OMe)
237 (56000), 352 (22000)	390 (42, M), 299 (14, M – Tol), 267 (40, M – STol), 252 (100, M – STol – Me)
237 (48000), 350 (19500)	376 (100, M), 285 (6, M – Tol), 253 (73, M – STol)
236 (39000), 255 (22200), 263 (21900), 350 (14700)	456, 454 (61, 56, M), 333, 331 (5,4, M – STol), 252 (100, M – STol – Br)
236 (48800), 254 (29800), 263 (29400), 349 (15500)	401 (100, M), 386 (10, M – Me), 310 (5, M – Tol), 299 (27, M – C ₆ H ₄ CN), 278 (39, M – STol), 277 (93, M – H – STol)
195 (50900), 230 (40600), 263 (30600), 334 (16100)	421 (100, M), 406 (8, M – Me), 298 (25, M – STol), 252 (50, M – STol – NO ₂)
197 (60000), 237 (55900), 352 (24100)	330 (100, M), 315 (22, M – Me), 285 (22, M – Me – CH ₂ O), 284 (21, M – Me – OMe), 283 (13, M – SMe), 239 (30, M – C ₆ H ₇)
192 (61700), 238 (51800), 351 (23400)	314 (100, M), 299 (27, M – Me), 284 (46, M – 2Me), 267 (17, M – SMe), 251 (31, M – Me – SMe)
187 (63300), 238 (51700), 350 (23400)	300 (100, M) 285 (51, M – Me), 284 (43, M – H – Me), 253 (22, M – SMe), 252 (45, M – H – SMe)
197 (52800), 237 (51100), 350 (22600)	380, 378 (72, 70, M), 365, 363 (4,4, M – Me), 284 (100, M – Me – Br), 252 (11, M – Br – SMe)
197 (58500), 238 (57900), 351 (20700)	325 (100, M), 310 (67, M – Me), 278 (M – SMe), 252 (12, M – CN – SMe)
197 (54500), 203 (50400), 237 (49100), 264 (35800), 337 (20400)	345 (100, M), 330 (14, M – Me), 299 (25, M – NO ₂), 284 (43, M – NO ₂ – Me), 252 (63, M – NO ₂ – SMe)

whereas route (b) will become slower with a poorer nucleophile. There is extensive room for such a change since the thio nucleophiles which favor route (b) are among the most reactive nucleophiles.

In the present work we had shown that *p*-cresolate ion substitutes the bromine of **1a** at 80 °C in DMSO. Since this is not a solvolysis medium, the reaction probably proceeds via route (b). We conclude that the use of such or a weaker nucleophile in a more polar solvent should increase the probability of a competing S_N1 substitution.

EXPERIMENTAL

General. Melting points are uncorrected. NMR spectra were recorded on Bruker WR 200 SY and AMX 400

instruments using CDCl_3 as a solvent. UV spectra were recorded on Kontron Uvikon 860 and Uvikon 930 instruments. Mass spectra were recorded with a Varian MAT 311 instrument.

Materials. 9(α -Bromo- α -arylmethylene)fluorenes (**1**) were obtained from Dr G. Lodder. Commercial *p*-cresol and *p*-toluenethiol (Aldrich) were used after crystallization. Sodium methanethiolate (Merck) and trifluoroethanol (Aldrich) were used without further purification. Spectroscopic-grade acetonitrile (Aldrich) was used.

Solvolysis of 1a in TFE. A solution of **1a** (0.11 g, 0.3 mmol) in trifluoroethanol (7 ml) containing Et_3N

(0.1 ml, 1 mmol) was kept in a sealed ampoule for 70 h at 130 °C. After cooling, it was poured into ice–water (100 ml) and the yellow precipitate formed was filtered and crystallized from light petroleum, giving 9-(α -*p*-methoxyphenyl - α - trifluoroethoxymethylene) fluorene as yellow crystals, m.p. 111–113 °C (85 mg, 75%). ¹H NMR (CDCl₃), δ : 3.94 (3H, s, OMe), 4.13 (2H, q, J =8.4 Hz, CH₂), 6.35 (1H, d, J =7.8 Hz, H-1), 6.91 (1H, t, J =7.3 Hz, H-2), 7.10 (2H, d, J =7.6, An-H), 7.20 (1H, t, J =7.4 Hz, H-3), 7.39 (2H, m), 7.44 (2H, d, J =7.6 Hz, An-H), 7.70 (1H, m, H-8, 7.75–7.78 (1H, m), 8.29–8.34 (1H, m). Mass spectrum (70 eV), m/z (relative abundance (%), assignment): 382(96, M), 271 (100, M – CO₂CH₂CF₃). Analysis: calculated for C₂₃H₁₇F₃O₂, C 72.27, H 4.48, F 14.91; found, C 72.05, H 4.36, F 15.24%.

Substitution of 1a with *p*-cresolate ion. To a solution of *p*-TolONa (131 mg, 1 mmol) in DMSO (8 ml), **1a** (181 mg, 0.5 mmol) was added and the mixture was heated at 80 °C for 4 h, when TLC showed that all **1a** had disappeared. The mixture was poured into water (40 ml), filtered and the solid obtained (60 mg, 32%) was crystallized from CH₂Cl₂, giving 9-(α -*p*-methoxyphenyl- α -*p*-methylphenoxymethylene) fluorene as white crystals, m.p. 215 °C (48 mg, 25%). ¹H NMR (CDCl₃), δ : 2.23 (3H, s, Me), 3.83 (3H, s, MeO), 6.98 (8H, m, Ar-H), 7.22–7.27 (2H, m, Ar-H), 7.34 (1H, t, J =7.3 Hz, Ar-H), 7.52 (2H, d, J =8.7 Hz, Ar-H), 7.76 (2H, m, Ar-H), 8.17 (1H, d, J =7.8 Hz, H-8). Mass spectrum (70 eV), m/z (relative abundance (%), assignment): 390 (65, M), 283 (58, M – OTol), 268 (22, M – OTol – Me), 133 (100, AnCO). Analysis: calculated for C₂₈H₂₂O₂, C 86.13, H 5.68; found, C 86.25, H 5.75%.

Substitutions of compounds 1 with sodium *p*-toluenethiolate and methanethiolate. The following general procedure was used for obtaining the substitution products. To a solution of the bromide (0.7–1.0 g, 0.2–0.3 mmol) in MeOH (5 ml) was added a solution of equimolar amount of *p*-TolSNa in MeOH and the mixture was heated in a sealed tube at 90 °C for 15–20 h. The precipitate formed after cooling was filtered, washed with water (50 ml) and crystallized from EtOH. The faster reaction with MeSNa was performed at room temperature for **1f** and at 40–50 °C for **1d** and **1e** using 1.2–1.3 molar equivalents of MeS[–]. After water–CHCl₃ work-up, the solvent was evaporated and the residue was crystallized from EtOH. Yields, melting points and analytical and spectral data are given in Tables 3 and 4.

Kinetics. A 1.8 ml volume of a 2.10^{–4} M solution of **1** and 1.2 ml of a 0.01 M solution of MeSNa or a 0.004 M solution of *p*-TolSNa, both in 80% MeCN, were mixed in a thermostated 1 cm UV cell and the reaction was followed spectrophotometrically in the range 300–380 nm. Constant isosbestic points (λ_{max} = 319, 328, 327, 325, 326 and 328 nm for X=NO₂, CN, Br, H, Me and MeO, respectively)

persisted during the experiments, indicating the absence of side reactions. The plots of the logarithms of the optical density vs time became curved at higher (75%) reaction percentages. Consequently, although the reactions were followed for up to 4.5 half-lives, initial rate constants were calculated and are given in the tables. Several kinetic runs were repeated and reproducibility of the rate constants was $\pm 1.5\%$.

Reaction of 2. A solution containing **2** (0.1 g, 0.17 mmol) and Et₃N (0.1 ml) in 70% MeCN–30% H₂O (8 ml) was kept in a sealed tube at 130 °C for 24 h. The mixture was poured into water (100 ml), extracted with CHCl₃ (2 $\times$ 10 ml) and the extract was washed with water and dried (CaCl₂). After evaporation of the solvent, TLC showed three main spots. Chromatography on silica gave fluorene (16 mg, 56%) and fluorenone (10 mg, 32%), which were identified by comparison of their ¹H NMR and IR spectra with those of authentic samples.

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