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Vinylic Cations from Solvolysis. 39.[1] Solvolysis of 9-(α-Bromo- and α-(tosyloxy)-*p*-methoxybenzylidene)xanthenes

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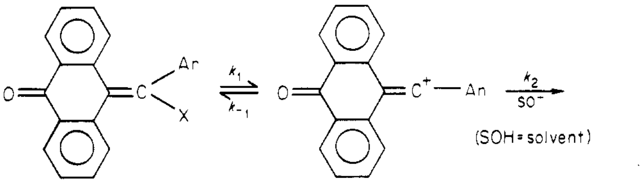
The solvolysis of 9-(α-bromo-*p*-methoxybenzylidene)xanthene (**5**) and its α-tosyloxy analogue **6** was investigated. In 80% EtOH/2,6-lutidine **5** forms the 9-ethoxy derivative **8** and 9-(4-methoxybenzoyl)xanthene (**9**). The titrimetric rate constant k_t decreases during a run, giving a selectivity constant $\alpha' = k_{-1}/k_{SOH} = 96 \pm 14$. In AcOH/NaOAc both the α-acetoxy derivative **10** and **9** are formed, and k_t decreases during a run and becomes steady at ca. 70% reaction. In TFE/2,6-lutidine, $\alpha' = 4220$. The k_{OTs}/k_{Br} ratios ($k(\mathbf{6})/k(\mathbf{5})$) are 0.58 (TFE), 2.1 (AcOH), and 3.8 (80% EtOH). The high selectivity of the derived vinyl cation **11** and the k_{OTs}/k_{Br} values are discussed in terms of steric effects on the approach of the nucleophiles to **11** and the relative steric acceleration of the solvolysis of **5**. The solvolytic behavior is compared with that of 9-(α-bromo-*p*-methoxybenzylidene)anthrone.

The solvolysis of 9-(α-bromo-*p*-methoxybenzylidene)anthrone (**1**), which generates the vinyl cation **3** (eq 1),



1, X = Br
2, X = OTs

3

(1)

plays an important role in the solvolysis of α-arylvinyl derivatives **4**.[2-6] Several characteristic features in the solvolysis of **4** depend on the bulk of the β-substituents

$$RR'C{=}C(X)An$$
4

R and R′. Increase in the bulk of R and/or R′ results in a regular decrease in the tosylate/bromide reactivity ratios (k_{OTs}/k_{Br}) and the Winstein–Grunwald m values and in an increase in the selectivity of the derived cation as measured by the $\alpha = k_{-1}/k_2$ ratio.[2] The maximum steric hindrance was exhibited so far by compounds **1** and **2**, and the various parameters indeed achieve extreme values in their solvolysis. In spite of the high selectivity of the cation **3** (α = 381 for **1** in TFE/2,6-lutidine[4] and 74.4 in AcOH/0.087 M NaOAc),[5] the k_{OTs}/k_{Br} ratios of 0.108 in buffered TFE and 1.2 in buffered AcOH and the m value of 0.28 in aqueous EtOH at 105 °C for **2**[7] are more characteristic for an S_N2 than for an S_N1 reaction. A steric acceleration of the ionization, a steric hindrance to solvation, and a steric hindrance to nucleophilic attack on **3** were invoked as explanations.[2,4,6] We recently used the solvolysis of **1** and other α-aryl analogues as a probe for the operation of the reactivity–selectivity relationship in solvolysis reactions.[5]

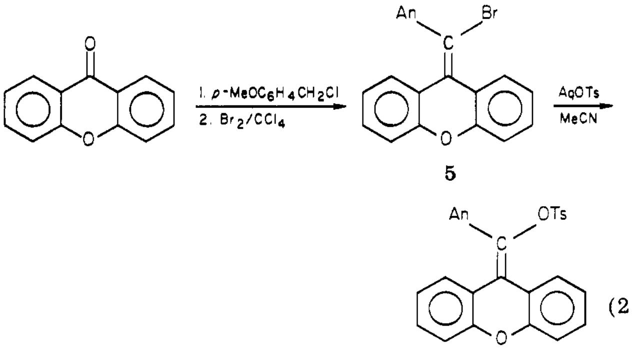
Compounds **1** and **2** differ from the previously studied compounds **4** since the electron-withdrawing carbonyl group should reduce the solvolytic reactivity compared with a sterically similar model compound. Moreover, they are vinylogs of β-bromo-α,β-unsaturated ketones and are therefore capable of undergoing substitution via the competing bimolecular nucleophilic addition–elimination route.[8] The low k_{OTs}/k_{Br} and m values are consistent with such a route, although the extensive common ion rate depression indicates a carbenium ion mechanism. In order to obtain these parameters with a compound that is sterically similar to **1**, but without the β-electron-withdrawing group, we studied the solvolysis of the xanthenylidene derivatives 9-(α-bromo-*p*-methoxybenzylidene)xanthene (**5**) and its α-tosyloxy analogue **6**. Study of these derivatives may also help to delineate the importance of the carbene–carbenium ion hybrid to the structure of the vinyl cation **7**. The only study on a system related to **5** is the

7a 7b

photosolvolysis of the phenyl analogue.[9]

Results

Synthesis. 9-(*p*-Methoxybenzylidene)xanthene was prepared by addition of (*p*-methoxybenzyl)magnesium chloride to xanthone in a modification of Van Campen's method, which reduces the extent of dimerization of the Grignard reagent.[10] Addition of bromine to the alkene proceeded slowly and was accompanied by evolution of HBr and the formation of **5**. Both the slow addition and the elimination of HBr are ascribed to steric crowding of the dibromo derivative. Reaction of **5** with silver tosylate in acetonitrile gave the corresponding tosylate **6** (eq 2).



5

6

(2)

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Table I. Kinetic Data for the Solvolysis of 5 and 6

compd	concn, 10^3 M	solvent/base^a	T, °C	Et_4NBr, 10^3 M	$10^6 k_t^{\circ b}$	k_t°/k_t^{50c}	α', M^{-1}	k_{OTs}/k_{Br}
5	43.5	80% EtOH/0.087 M Lut	105.1		168 ± 13.4	2.2	96 ± 14	
	43.5	80% EtOH/0.087 M Lut	105.1	77.6	35		50	
6	2.0	80% EtOH/0.011 M Lut	105.1		641 ± 27			3.8
5	43.5	AcOH/0.087 M NaOAc	120.3		198^d	4.4		
	43.5	AcOH/0.087 M NaOAc	120.3	77.8	39.6			
	43.5	AcOH/0.087 M NaOAc	120.3	118	40.1			
6	2.0	AcOH/0.004 M NaOAc	120.3		417 ± 8			2.1
5	1.89	TFE/0.0019 M Lut	35		13.2 ± 0.4	3.3	4220 ± 240	
6	3.0	TFE/0.02 M Lut	35		7.67 ± 0.01			0.58

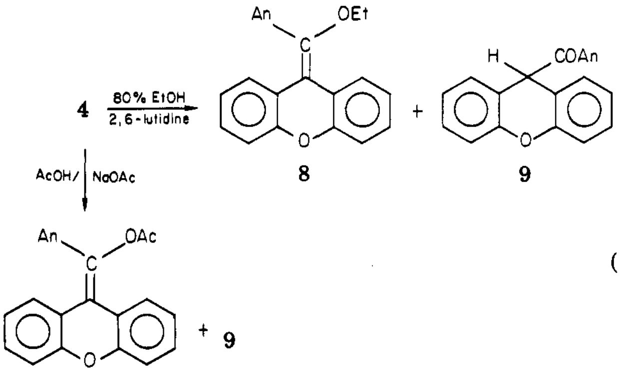
^{a} Lut = 2,6-lutidine. ^{b} k_t° is given when k_t decreases during a run. ^{c} Ratio of k_t° to k_t as half-life. ^{d} From graphical extrapolation of k_t vs. time plot.

Table II. Comparison of the Solvolyses of 1 and 2 with Those of 5 and 6

solvent/base	T, °C	$k_t(5)/k_t(1)$	$k_t(6)/k_t(2)$	$\frac{k_{OTs}/k_{Br}\,[(6)/(5)]}{k_{OTs}/k_{Br}\,[(2)/(1)]}$	$\alpha'(1)/\alpha'(5)$
80% EtOH/2,6-lutidine	105.1	9.33	2.44	5.07	1.64
AcOH/0.087 M NaOAc	120	1.65	0.67	0.41	
TFE/2,6-lutidine	35	1.22	4.5	3.7	0.28 (0.090)^a

^{a} Ratio of $\alpha'(1)$ at 138 °C to $\alpha'(5)$ at 35 °C.

Solvolysis. (a) In 80% EtOH. Solvolysis of **5** in 80% EtOH in the presence of 2 molar equiv of 2,6-lutidine gave the ether α-ethoxy-9-(4-methoxybenzylidene)xanthene (**8**) and the ketone 9-(4-methoxybenzoyl)xanthene (**9**) in a 1:1 ratio (eq 3). The ether was prepared independently by reflux of **4** with Ag_2CO_3 in absolute ethanol. However, attempted preparation of **9** by solvolysis of **5** in 80% acetone/Ag_2CO_3 gave an isomeric ketone with the same molecular peak in its mass spectrum, which may be 11-(*p*-methoxyphenyl)dibenz[*b*,*f*]oxepin-10-one.[11]



(3)

The solvolysis of **5** in 80% EtOH/0.087 M 2,6-lutidine at 105 °C gives a decreasing first-order integrated rate constant (k_t) during a run. The extrapolated initial value k_t°, the mass law constant $\alpha' = k_{-1}/k_{SOH}$, and the fractional decrease of k_t at 1 half-life (k_t°/k_t^{50}) are given in Table I. A single-point rate constant in the presence of 0.078 M Et_4NBr gives k_d = 35.10^{-6} s^{-1}, i.e., k_t°/k_d = 4.81. The corresponding α' value is 50, lower than that obtained from the common ion rate depression. However, correction for normal salt effect[12] will somewhat increase this value. The solvolysis of the vinyl tosylate **6** gives a constant k_t value during a run (Table I).

(b) In AcOH. The acetolysis of **5** in AcOH/0.087 M NaOAc at 120 °C gives a 1:1 mixture of **9** and α-acetoxy-9-(*p*-methoxybenzylidene)xanthene (**10**) (eq 3). The Ag-OAc-promoted acetolysis of **5** gave only **13**.

The k_t value for the acetolysis of **5** in AcOH/0.087 M NaOAc decreases strongly during the kinetic run, k_t°/k_t^{50} = 4.4. However, the rate constant became steady at ca. 70% reaction at a k_t value of 3.9 × 10^{-6} s^{-1}. Reaction in the presence of added 0.078–0.118 M Et_4NBr gave a nondecreasing rate constant of a similar value (Table I). Consequently, the k_t° and the α values could not be obtained from the usual analytical expressions, and the k_t° value was obtained from a graphical extrapolation of a k_t vs. time plot. In contrast, the solvolysis of **6** gave a constant k_t value at 20–54% reaction (Table I).

(c) In 2,2,2-Trifluoroethanol. The solvolysis of **5** in TFE/2,6-lutidine was followed conductometrically at low concentration, and the product was not isolated. The decrease of k_t during a run was again strong. A parallel reaction of **6** gave a steady k_t. The kinetic data are summarized in Table I, together with the tosylate/bromide reactivity ratios $k(6)/k(5)$.

Discussion

The solvolysis of **5** and **6** on the one hand and of **1** and **2** on the other are remarkably similar, in spite of the differences in electron withdrawal by C═O and O. Since charge dispersal by β-aryl groups in the transition state leading to triarylvinyl cations is small,[13] the ortho oxygen of **5** and **6** may exert a net inductive electron withdrawal. However, comparison of the solvolyses of **4**, R = R′ = *o*-anisyl[14] and R = R′ = Ph,[15] indicates a very small rate acceleration by the *o*-MeO groups. Consequently, the xanthenyl oxygen should have a minor polar effect on the solvolysis rate.

The solvolysis rates of the anthronylidene and the xanthenylidene systems are compared in Table II. Except for one case, the xanthenylidene derivatives solvolyze faster. This is true both for the bromides where accurate determination of k_t° in AcOH and TFE is difficult and for the tosylates where this problem is unimportant. The ratios result from differences in inductive effects of C═O and O and from the higher strain in system **1**. In α-

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[11] This compound can be obtained by Ag^+-assisted ionization to **11**, which undergoes 1,2-shift with ring enlargement, followed by capture with water and ketonization.

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arylvinyl systems the strain introduced by the β-substituents affects appreciably the solvolysis rates.[2,16] The lower flexibility of 1 will increase its relative reactivity, counterbalancing the rate-retarding inductive effect. An estimate of the ring-strain accelerating effect is obtained from the solvolysis rate ratio $k(\mathbf{5})/k(\mathbf{4}, \mathrm{R} = \mathrm{R'} = o\text{-anisyl})$ of (2–5) ± 0.1 in AcOH and in 80% EtOH.

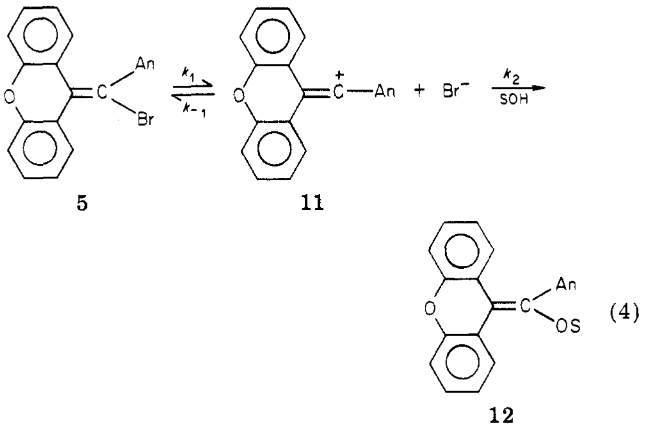
As for the anthronylidene system, the $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios $[k(\mathbf{6})/k(\mathbf{5})]$ of 0.58–3.8 are again much smaller than the values of 10^3–10^4 expected for systems solvolyzing via a free carbenium ion.[17] They are also lower than the ratios of 19.7–28.3 observed for α-anisyl-β,β-disubstituted systems, where the β-substituents are unconnected.[6]

The low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios are due to two effects.[6] The bromide **5** is moderately more reactive than the α-anisyl-β,β-diarylvinyl bromides **4**, R = R′ = Ar, X = Br, but the tosylate **6** is much less reactive than the corresponding tosylates **4**, R = R′ = Ar, X = OTs. Space-filling models indicate a steric acceleration for the solvolysis of **5** (and of **1**) since the Br and the ortho H on the ring cis to it are in a less than van der Waals distance. This is not true for **6** since the tosylate oxygen that is attached to the vinylic system is much smaller than bromine, and the bulky part of the group is remote from the β-substituent. However, X-ray diffraction of **1** and **2**[18] show that the two aromatic rings of the anthronylidene moiety are twisted from the plane of the double bond by 41–44°. The torsion angle of the α-aryl group of **1** is much larger than that of **2**, and the relative acceleration of **1** can be ascribed to this electronic effect. Although we do not have X-ray data for **5** and **6**, we believe that the main geometrical features resemble those for **1** and **2** and the low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios arise from similar reasons.

An alternative explanation that a stabilizing n–π ground-state conjugation, e.g., $\mathrm{Ar_2C^-{-}C(Ar){=}X^+}$ is more important when X = OTs than when X = Br, was previously raised.[19] This interaction, which may be important for **1** and **2** due to the conjugative ability of the carbonyl group, could explain the low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios for the anthronylidene system. However, the observation of low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios for the xanthenylidene system, where such conjugation effect is negligible, excludes this explanation. Indeed, Table II shows that the ratios are higher for the xanthenylidene system in 80% EtOH and TFE buffered by 2,6-lutidine but lower in AcOH/NaOAc. However, the low reactivity of **6** compared with other vinyl tosylates is not explained by the above arguments, and its origin is unclear.

The low $k_{\mathrm{OTs}}/k_{\mathrm{Br}}$ ratios could be due to a different extent of ion-pair return for **5** and **6**. This is excluded since the carbonyl reduction product of **1**, which is a closely structural analogue of **5** and **6**, shows a small or negligible ion-pair return in TFE or in 80% EtOH.[3] Lower extent of ion-pair return is expected for the corresponding tosylate.

Selectivity of the Intermediate Ion. The solvolysis of **5** is accompanied by common ion rate depression[20] within a kinetic run or by added $\mathrm{Et_4NBr}$. This is ascribed to the formation of solvolysis products from the free[20b,c] 9-(p-methoxybenzylidene)xanthenyl ion **11** (eq 4). From the ca. 5-fold decrease in k_t value by added $\mathrm{Et_4NBr}$, we calculate[20b] that ≥80% of the products **12** in 80% EtOH and in AcOH are formed from the free ion. From the rate decrease within a kinetic run in TFE, ≥72% of the products are formed from **11**. In 80% EtOH and TFE these are minimum values since we did not correct for a normal salt effect[12] and only one $\mathrm{Et_4NBr}$ concentration was studied.



The selectivity values α', which measure the competition between the capture of **11** by Br⁻ and the solvent SOH (i.e., $\alpha' = k_{-1}/k_2[\mathrm{SOH}]$), are given in Table I and compared with those of **1** in Table II. The α' value in 80% EtOH is 1.64 times higher for **1**, but the high selectivity of **11** even in this nucleophilic solvent is reflected by the decrease of k_t within a run, a rare phenomenon is nucleophilic solvents. The α' value calculated from the decrease of k_t within a run is ca. 2 times higher than the value obtained in the presence of $\mathrm{Et_4NBr}$. A similar behavior was observed for **1**, where the difference between the two α' values is 2.87. Consequently, the α' values for **1** and **5** in the presence of 0.087 M $\mathrm{Et_4NBr}$ are nearly the same. Differences between the α' values calculated by the two methods probably result from neglect of salt effects on k_t and k_{-1}/k_2 and from possible ion pairing of the added and formed salts.[21]

The high α' value for **5** in TFE at 35 °C is ca. 4-fold and 11-fold higher than α' for **1** at 35 and 138 °C,[4] respectively. A lower selectivity at higher temperature is expected if E_a for the slower reaction with SOH is higher than E_a for the reaction with Br⁻.

The α' value in the solvolysis of **5** in buffered TFE is the highest known in vinylic solvolysis.[2] At a concentration of 1.89×10^{-3} mol L^{-1}, k_t decreases 3.3-fold after 1 half-life. The concentration of **5** was ca. 20 times lower than that for the reaction of **1** and lower than that for all the compounds studied previously. Increase in α' on decreasing the vinyl bromide concentration was observed earlier. Hence, the higher α' value does not indicate that the vinyl cation **11** is more hindered than the ion **3**. Nevertheless, the high α' corroborates the suggestion[2,4] that steric hindrance to an in-plane approach of the nucleophile to the cationoid carbon is a major contributor to the high selectivity. In **11** this effect is due to the location of the 1 and 8 xanthenylidene hydrogens near the trajectory for the cation–nucleophile reaction. Other contributors to the high selectivity are the highly stabilizing α-anisyl group and the low nucleophilicity of TFE.

The high α' value does not fully reflect the high selec-

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tivity of **11** since k_2 is a pseudo-first-order constant.[20a] If the concentration of TFE in the neat solvent (13.9 M) is taken into account, assuming that capture of **11** by either Br^- or TFE is first order in the nucleophile, the dimensionless selectivity α, i.e., the inherent preference ratio for capture of Br^- vs. capture of TFE, will be 58 660.

In contrast with the continuing decrease of k_t for **5** within a run in 80% EtOH and in TFE, the decreasing k_t in AcOH/NaOAc reaches a constant value after 80% reaction. Likewise, addition of Et_4NBr reduces k_t by 5-fold (Table I). The upper limit to the extent of rate depression can be due to (a) a combination of 80% S_N1 route and 20% of a competing non-S_N1 route, (b) 80% product formation from the free cation and 20% from ion pair, and (c) a compensation of rate decrease by common ion rate depression and rate increase due to a normal salt effect.

A competing substitution via nucleophilic addition–elimination[8] is highly unlikely for the electron-rich **5** and **6** with the moderately nucleophilic AcO^-, especially since this route was not observed for the more electrophilic halo olefins **1**[4] and 9-(α-haloanisylidene)fluorene.[15b] An electrophilic addition–elimination route[22] is excluded since proton addition to the α-anisyl-α-halovinyl system is retarded by bulky β-substituents, and the contribution of this route is minor for the reaction of *p*-methoxy-α-bromostyrene[22b] and none for 1,2-dianisyl-2-phenylvinyl bromide.[21]

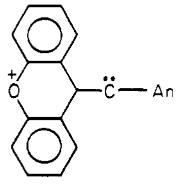
The theory of common ion rate depression predicts an upper limit to the extent of rate depression when part of the products are formed from ion pairs.[20b,c] However, it also suggests that partial or complete product formation from ion pairs occurs from systems where the free ion is less stable than for systems that give products exclusively from the free ion. By all other indications, including the high extent of rate depression in the solvolysis of **5**, ion **11** is more selective and longer lived than most of the α-anisylvinyl cations studied so far.[2a] Since no limit for the rate depression was previously observed, product formation from the ion pair in the solvolysis of **5** is unlikely.

Compensation between a relatively small common ion rate decrease at high reaction percentages and a rate increase due to a salt effect of NaOAc is an unlikely explanation for the constancy of k_t at high reaction percentage, and it was never observed previously. The rate measurement for Br^- release in the presence of a large excess of Et_4NBr is very inaccurate and may be the real source for the observed upper limit in the rate decrease.

Consequently, we did not analyze the rate decrease in AcOH/NaOAc by our procedure, which assumes no limit to the rate depression.[21] We calculated $\alpha = 50$ from the rate decrease at 0.078 M Et_4NBr, but due to the above problem and the lack of knowledge if AcO^- or AcOH is the capturing nucleophile,[23] the meaning of the α value is not clear. The error in the k_t° value, which was observed by graphical extrapolation, as well as the error in the derived k_{OTs}/k_{Br} value is relatively high.

The solvolysis of **6** in the three solvents shows no common ion rate depression, as is mostly the case with other α-anisylvinyl tosylates and mesylates.[19,23] Tosylate ion is much less nucleophilic than Br^- toward vinyl cations, and in combination with its low concentrations in the solvolysis [(1–1.5) × 10^{-3} mol L^{-1} at 50% reaction], ion **11** is captured preferentially by the solvent or its conjugate base rather than by TsO^-.

The solvolysis of **5** and **6** have a bearing on the question of whether the carbene-carbenium ion hybrid **7b** contributes to the structure of the vinyl cation, since hybrid **13**



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is presumably more stable than hybrids **7b** in other vinyl cations. Due to the small to moderate rate acceleration compared with that of other α-anisyl-β,β-diarylvinyl bromides,[2] the steric acceleration discussed above, and the main question of whether the rate data reflect the thermodynamic stability of the ion, no conclusion concerning this question can be achieved.

The formation of both **9** and **10** in the acetolysis of **5** in AcOH/NaOAc finds many precedents in vinylic solvolysis.[4,5,21,24] The ketone **9** is probably generated by a NaOAc-promoted cleavage of **10**.

From the 1:1 ratio of **8** and **9** in 80% EtOH, EtOH is at least 23 times more nucleophilic than water toward **11**. This is a minimum value since vinyl ethers sometimes hydrolyze to the corresponding ketones during the solvolysis.[2a] The derived dimensionless selectivities k_{Br}/k_{H_2O} and k_{Br}/k_{EtOH} are 2130 ± 330 and 2630 ± 405, respectively.

Experimental Section

Melting points were determined with a Fisher melting point apparatus and are uncorrected. NMR spectra were measured with Varian HA-100, T-60, and E-360 instruments, IR spectra with a Perkin-Elmer 337 instrument, and mass spectra with a MAT-311 instrument. Potentiometric titrations were conducted with a Radiometer TTT1 instrument and conductometric measurements with a Pye Conductance Bridge.

Solvents. EtOH (80%) was prepared by mixing redistilled absolute ethanol and conductivity water. AcOH was purified by refluxing glacial AcOH with 1% acetic anhydride for 48 h and distillation. The fraction bp 114 °C was used. The NaOAc/AcOH mixture was obtained by dissolving Na_2CO_3 (Analar) in AcOH. Trifluoroethanol, bp 73–74 °C, was purified according to Rappoport and Houminer.[13]

9-(*p*-Methoxybenzylidene)xanthene. A solution of (*p*-methoxybenzylidene)magnesium chloride, prepared from *p*-methoxybenzyl chloride (24 g, 150 mmol) and Mg (18 g, 75 mmol) in ether (260 mL), was added dropwise during 90 min to a stirred solution of xanthone (15 g, 76 mmol) in dry benzene (50 mL)–ether (100 mL). Reflux and stirring were continued for an additional 2 h. The yellow mixture was poured into a mixture of NH_4Cl (30 g), NH_4OH (7.5 mL), and ice (150 g), extracted with chloroform (50 mL), washed successively with water, aqueous HCl, and aqueous $NaHCO_3$, dried ($CaCl_2$), and evaporated. The NMR revealed a mixture of 1,2-bis(*p*-methoxyphenyl)ethane (27%) and 9-(*p*-methoxybenzylidene)xanthene (73%). Crystallization from ethanol gave 9.5 g (41%) of the latter as pale yellow crystals: mp 107 °C (lit.[25] mp 104–107 °C); UV λ_{max} (EtOH) 247 nm (ϵ 15 500), 287 (6700), 345 (12 000); IR ν_{max} (CS_2) 2840, 1700 (s), 1600 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.68 (3 H, s, MeO), 6.57–7.65 (13 H, m, Ar, =CH); MS, *m/z* 300 (M, B), 286 (M − CH_2, 17), 257 (M − CH_3CO, 25). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.66; H, 5.65. Found: C, 83.98; H, 5.37.

α-Bromo-9-(*p*-methoxybenzylidene)xanthene (5). To 9-(*p*-methoxybenzylidene)xanthene (2 g, 6.7 mmol) in CCl_4 (20 mL) was added bromine (1.06 g, 6.7 mmol) in CCl_4 (10 mL) during 4 h. The solution was washed with dilute aqueous $NaHSO_3$

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solution, water, and dilute $NaHCO_3$ solution, dried ($CaCl_2$), and evaporated. Crystallization from MeOH gave 1.5 g (60%) of yellow crystals of α-bromo-9-(*p*-methoxybenzylidene)xanthene: mp 139–140 °C; UV λ_{max} (EtOH) 320.5 nm (ϵ 12 500), 277 (8800); IR ν_{max} (CS_2) 2840, 1910, 1890, 1850 cm^{-1}; NMR ($CDCl_3$) δ 3.70 (3 H, S, MeO), 6.53–7.15 (12 H, m, Ar); MS, *m/z* 380, 378 (M, 100, 100), 365 (M – Me, 47), 300 (72), 299 (M – Br, 99), 284 (M – Br – MeO, 99), 255 (M – Br – MeO – CH, 99). Anal. Calcd for $C_{21}H_{15}BrO_2$: C, 66.55; H, 3.99; Br, 21.04. Found: C, 66.6; H, 4.00; Br, 20.60.

α-Acetoxy-9-(*p*-methoxybenzylidene)xanthene (10). A mixture of α-bromo-9-(*p*-methoxybenzylidene)xanthene (0.4 g, 1.05 mmol) and AgOAc (175 mg, 1.05 mmol) in AcOH (20 mL) was refluxed for 2 h. The AgBr was filtered, the solution was poured into a mixture of water (25 mL) and CCl_4 (25 mL), and the organic layer was separated, washed with 5% aqueous $NaHCO_3$ solution, and then with water, separated, dried ($CaCl_2$), and evaporated. Crystallization from MeOH gave 200 mg (53%) of white crystals of α-acetoxy-9-(*p*-methoxybenzylidene)xanthene (**10**): mp 150–152 °C; UV λ_{max} (EtOH) 223 nm (ϵ 50 000), 286.5 (11 000), 333 (14 300); IR ν_{max} (CS_2) 1755 (CO_2R), 1600 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2.13 (3 H, s, AcO), 3.82 (3 H, s, MeO), 6.77–7.42 (12 H, m, Ar); MS, *m/z* 358 (M, 13), 316 (23), 315 (M – $COCH_3$, B), 314 (M – H – CH_3CO, 65), 286 (65), 181 (xanthene-H, 35), 135 (AnCO, 58). Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.15; H, 5.36.

α-Ethoxy-9-(*p*-methoxybenzylidene)xanthene (8). A mixture of α-bromo-9-(*p*-methoxybenzylidene)xanthene (0.3 g, 0.76 mmol) and Ag_2CO_3 (326 mg, 1.8 mmol) in absolute ethanol (20 mL) was refluxed fro 62 h in the dark. The mixture was filtered and washed with chloroform (2 × 10 mL), and the solvent was evaporated. Successive crystallizations from methanol and a 1:4 mixture of CH_2Cl_2–petroleum ether (60–80 °C) gave 0.18 g (66%) of yellow needles of **8**: mp 124 °C; UV λ_{max} (EtOH) 233 nm (ϵ 42 000), 289 (10 000), 337 (13 400); IR ν_{max} (KBr) 1605 (C=C, s), 1070, 1025 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.06 (3 H, t, Me), 3.45 (2 H, q, CH_2O), 3.68 (3 H, s, MeO), 6.6–7.33 (12 H, m, Ar); MS, *m/z* 344 (M, 45), 315 (M – Et, B), 287 (M – Et – CO, B), 181 (xanthene-H, 51). Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.33; H, 5.92.

α-(Tosyloxy)-9-(*p*-methoxybenzylidene)xanthene (6). A solution of α-bromo-9-(*p*-methoxybenzylidene)xanthene (0.5 g, 1.31 mmol) in acetonitrile (30 mL) was added to a solution of AgOTs (0.46 g, 1.65 mmol) in acetonitrile (10 mL). The mixture was refluxed for 45 min, the AgBr was filtered, the solvent was evaporated, the solid was washed with chloroform and with water (3 × 100 mL), and dried ($CaCl_2$), and the solvent was evaporated. Crystallization from methanol gave 0.32 g (52%) of yellow crystals of **6**: mp 138–139 °C; UV λ_{max} (EtOH) 223 nm (ϵ 52 000), 285 (10 000), 335 (12 800); IR ν_{max} (CCl_4) 1610 (C=C), 1514, 1454, 1374 (S=O) cm^{-1}; NMR (CCl_4) δ 2.34 (3 H, s, 3.80 (3 H, s, MeO), 6.58–7.33 (16 H, m, Ar); MS, *m/z* 379 (M – Tol, 4), 315 (M – $O_2SC_6H_4Me$, 32), 299 (M – OTs, 64), 286 (47), 284 (35), 255 (32), 181 (xanthene-H, B), 135 (AnCO, B). Anal. Calcd for $C_{28}H_{22}O_5S$: C, 71.47; H, 4.71; S, 6.81. Found: C, 71.68; H, 4.66; S, 6.62.

9-(*p*-Methoxybenzoyl)xanthene (9). An ampule containing α-bromo-9-(*p*-methoxybenzylidene)xanthene (0.1 g, 0.25 mmol) in AcOH (6 mL) containing NaOAc (87 mmol) was kept for 36 h at 120 °C. The solvent was evaporated, and the remainder was extracted with CCl_4, dried ($CaCl_2$), and evaporated. The brown oil was separated on a silica TLC plate to two compounds that were identified by their spectral properties as **10** and 9-(*p*-methoxybenzoyl)xanthene (**9**): IR ν_{max} (KBr) 1655 (C=O, s), 1460 (s), 1265 (s), 760 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.8 (3 H, s, MeO), 5.6 (1 H, s, CHCO), 6.7–7.9 (12 H, m, Ar); MS *m/z* 316 (M, 2), 197 (32), 196 (42), 181 (M – AnCO, 97), 168 (22), 152 (30), 135 (AnCO, B).

11-(*p*-Methoxyphenyl)dibenz[*b*,*f*]oxepin-10-one. A mixture of α-bromo-9-(*p*-methoxybenzylidene)xanthene (0.4 g, 1.05 mmol) and Ag_2CO_3 (0.45 g, 1.6 mmol) in 70% acetone (60 mL) was refluxed for 1 week. The mixture was filtered from the silver salts and added to a mixture of CCl_4 (50 mL) and water (30 mL). The organic layer was separated, dried ($CaCl_2$), and evaporated. Crystallization from CH_2Cl_2–petroleum ether (60–80 °C) (3:5) gave 0.2 g (60%) of white needles: mp 132 °C; UV λ_{max} (EtOH) 285 nm (ϵ 16 800, sh), 297 (17 100); IR ν_{max} (KBr) 1665 (C=O), 1600, 985, 505 cm^{-1}; NMR ($CDCl_3$) δ 3.6 (3 H, s, MeO), 6.35 (1 H, s, CHCO), 6.6–7.7 (12 H, m, Ar); MS, *m/z* 316 (M, 6), 198 (48), 197 (M – AnC, B), 181 (M – AnCO, 32), 135 (AnCO, 60).

Kinetics. Except for reactions in TFE, the sealed ampules technique was used.

(a) In 80% EtOH. Due to the low solubility of **5** in aqueous EtOH, it was weighed separately into ampules containing 80% EtOH/2,6-lutidine. The ampules were kept at the reaction temperature. The Br^- was titrated with 0.02 M $AgNO_3$. The vinyl tosylate **6** was dissolved in absolubte EtOH–2,6-lutidine, water was added to give 80% EtOH, and the mixture was divided into ampules. The conductance of each ampule at the appropriate time was measured at 25 °C with a Pye conductance bridge.

(b) In AcOH. The preparation of the solution of **5** in AcOH/NaOAc and the potentiometric titration were similar to the work in 80% EtOH. The vinyl tosylate **6** is easily soluble in AcOH/NaOAc, and a stock solution was prepared. At the appropriate time the ampule was opened, the AcOH was evaporated, and the remainder was washed with CH_2Cl_2. The reaction was followed by anhydrous titration of the NaOAc with a solution of $HClO_4$ in AcOH, using crystal violet as an indicator.

(c) In TFE. By use of low concentrations of **5** and **6**, the reaction was followed continuously in a conductance cell at 25 °C. The estimated error is ±1%. The estimated errors in the other methods are 5–8% for each kinetic point.

Calculation of k_t and α'. The rate constants for the first-order solvolysis of **6** were calculated by the KINDAT program.[26] The α' value is based on a steady-state treatment of eq 4, which after integration gives eq 5, where $a = [RX]_0$ and $x = [Br]_t$. A plot

$$t/\ln\,[a/(a-x)] = 1/k_1 + (\alpha'/k_1)[(a-x)/\ln(a/(a-x))] \qquad (5)$$

of $t/\ln\,[a/(a-x)]$ vs. $[(a-x)/\ln\,(a/(a-x))]$ was linear with a slope of α'/k_1 and an intercept of $1/k_1$. The best values were calculated by a program developed by Kaspi.[7]

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Registry No. **5**, 87712-58-1; **6**, 87712-59-2; **8**, 87712-60-5; **9**, 87712-61-6; **10**, 87712-62-7; 9-(*p*-methoxybenzylidene)xanthene, 2961-56-0; 11-(*p*-methoxyphenyl)dibenz[*b*,*f*]oxepin-10-one, 87712-63-8.

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