

aqueous EtOH" is misleading since "TFE-EtOH" should be reserved for reactions in binary mixtures of the two alcohols.

- (34) The method of Raber, Harris, and co-workers¹⁷ utilizes a statistical analysis of the slope, the intercept, and their uncertainties. Hence, it appears superior in certain cases to the more convenient "two-points" method. However, there is an arbitrary criterion which accompanies the statistical analysis. In our opinion, a parallel arbitrary criterion together with a quantitative use of the log ($k_{\text{EtOH}}/k_{\text{TFE}}$) values of -5 and 1.8 will make the

two treatments equivalent.

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 (36) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1506.
 (37) Gilman, H., Blatt, A. H., Eds. "Organic Syntheses", Collect. Vol. I; Wiley: New York, 1941; p 146.
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Vinyl Cations from Solvolysis. 29.^{1,2} Solvolysis of 9-(α -Bromoarylidene)anthrones as a Probe to the Reactivity-Selectivity Relationship in Solvolysis Reactions

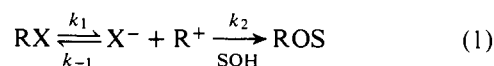
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Abstract: The solvolyses of 9-(α -bromoarylidene)anthrones **5a** (Ar = An), **5b** (Ar = Tol), **5c** (Ar = Ph), and **5d** (Ar = *o*-An) in 1:1 AcOH-Ac₂O/NaOAc and in TFE/2,6-lutidine and of **5a** in buffered AcOH and 80% EtOH were investigated. An extensive common ion rate depression by the formed or added Br⁻ ion was observed. Selectivity constants $\alpha = k_{\text{Br}^-}/k_{\text{AcO}^-}$ and $\alpha' = k_{\text{Br}^-}/k_{\text{TFE}}$ or $k_{\text{Br}^-}/k_{80\% \text{EtOH}}$ for competitive capture of the derived cations **14** by Br⁻ vs. AcO⁻ or the solvent were calculated. The α values in 1:1 AcOH-Ac₂O, the α' values in TFE, and the reactivities (k_t^0 values) are structure dependent and follow the order **5a** > **5d** > **5b**. The results for **5c** are not sufficiently accurate for reliable selectivity determination. The nature of the capturing nucleophile in AcOH-containing media is discussed and evidence for product formation nearly exclusively from a solvolytically generated *free* vinyl cation in AcOH, AcOH-Ac₂O, and TFE is given. Linear or nearly linear reactivity-selectivity relationships of log k_t^0 vs. log α or log α' for **5a**, **5b**, and **5d** were obtained, but the selectivity differences are moderate in 1:1 AcOH-Ac₂O and small in TFE. This behavior is discussed in relation to Ritchie's constant selectivity rule for stable cations and the linear reactivity-selectivity observed for less selective ions. It is suggested that the different selectivity relationships represent different regions of an overall nonlinear reactivity-selectivity plots for carbonium ion reactions. The merits and disadvantages of measuring selectivities by common ion rate depression are discussed.

A widely used relationship in mechanistic organic chemistry is the reactivity-selectivity relationship,³ according to which, in a family of closely related reactions, increased reactivity of a reactant or an intermediate is associated with a lower selectivity. Many cases of this relationship were reviewed,³ but serious questions concerning its validity were recently raised.^{4,5} An area where the relationship was observed is in solvolytic reactions involving carbonium ion intermediates.^{3a,6} Since the solvolytically generated cations are highly reactive and formed mostly in steady-state concentrations, direct kinetic measurements of their reactivities and selectivities are usually unavailable. Instead, the relative reactivities of a series of carbonium ions R⁺ are inferred from the solvolysis rates of their precursors, e.g., the halides RX. Hammond's postulate⁷ is being used in assuming that the faster the solvolysis of RX the more stable and less reactive is the formed carbonium ion. The relative selectivities of the ions were determined in two ways. First, competition of two nucleophiles for R⁺ gives two capture products and the selectivity ratio is obtained from their ratio by assuming that the capture rates are proportional to the concentrations of the nucleophiles. Applying this method for the competitions of N₃⁻ and H₂O^{6d,e} or for mixtures of two nucleophilic solvents, especially aqueous alcohols,^{6f-n} gave linear reactivity-selectivity relationships.

The second method is a kinetic one based on the phenomenon of common ion rate depression.^{6a,8} When products are formed from the *free* cations R⁺ (eq 1), capture by the solvent



SOH (k_2) competes with the recombination reaction of R⁺ and X⁻ (k_{-1}). From the decrease of the first-order solvolysis rate

constant by the X⁻ formed during the reaction or added externally, or by measuring the incorporation of labeled X⁻, the competition ratios k_X/k_{SOH} can be evaluated. A reactivity-selectivity relationship was observed by this method for the solvolysis of substituted benzhydryl halides.^{6a,c}

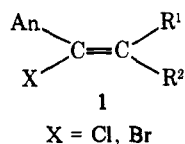
A contrasting behavior was discovered recently by Ritchie.^{5,9} A study of the combination reaction of anions with stable organic cations revealed a large difference in the relative reactivities of the cations but constant selectivities toward a large series of nucleophiles. A similar relationship holds also for reactions of nucleophiles with activated aromatic,¹⁰ carbonyl,¹¹ vinyllic,¹² and sulfonyl¹³ substrates.

A satisfactory explanation for this behavior is not available,¹⁴ and it raises the question: how could the contrasting "reactivity-selectivity" and "constant selectivity" relationships for reactions of organic cations mutually coexist? One explanation is that a reactivity-selectivity relationship holds for unstable cations but it reaches a plateau at higher selectivity for the more stable cations.¹⁵ Another explanation notes that a selectivity which is based on the product distribution reflects a weighted average of the selectivities of the product-forming ion pairs and free ions rather than the selectivity of a single species.^{5,16} Indeed, reactivity-selectivity relationships were used in the study of ion pairs formed in solvolysis.^{6f,g,i-o,17}

For evaluating this suggestion¹⁸ and for comparison of the selectivities of the solvolysis intermediates and the stable cations,^{5,9} the solvolysis reaction should fulfill several prerequisites. First, it should be shown that the cationoid species involved in the selectivity measurements is a *free* carbonium ion. Second, the extents of ion pair and external ion returns^{8b,c} should be known so that the ionization rate constant would serve as a measure of the stability and the reactivity of R⁺. Third, a ki-

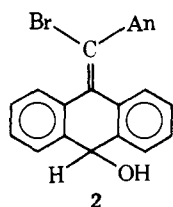
netic measurement of the selectivity will avoid the assumption of a correlation between the product ratios and [nucleophile] which is not necessarily true if the solvent is one of the nucleophiles studied.^{61,19} Fourth, very similar compounds should be studied. Since steric effects may affect either selectivity relationship,^{9c} a constant steric environment around the reaction center is desirable.

We have previously shown that the solvolysis of many α -anisylvinyl halides (**1**, An = *p*-methoxyphenyl) proceeds with



common ion rate depression in solvents such as buffered AcOH or Ac₂O–AcOH,^{1,20,21} 2,2,2-trifluoroethanol (TFE), or aqueous TFE.^{20,22,23} We calculated selectivity constants $\alpha = k_{\text{X}^-}/k_{\text{SO}^-}$ or $\alpha' = k_{\text{X}^-}/k_{\text{SOH}}$ for competition between X⁻ and the solvent SOH or its conjugate base SO⁻ for solvolysis of **1**. Some of these selectivity constants were higher than those for saturated compounds which solvolyzed much more rapidly.^{6a,8,20} The selectivities of compounds **1** increase gradually on increasing the bulk of R¹ and R².^{20,21e} Since this behavior is due to different steric environments it should not be used for probing the generality of the reactivity–selectivity principle. However, the high selectivities, the nearly exclusive product formation from the free ion in some systems, and the convenient reactivity range suggest that solvolysis of appropriate vinylic systems can be used to probe the selectivity rule applicable for solvolytically generated free ions.

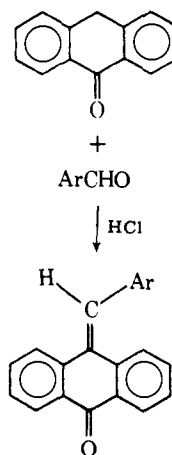
The highest selectivity observed in vinylic solvolysis was for 9-(α -bromoanisylidene)anthrone,^{20,21h,24} where hindered nucleophilic approach to the vacant orbital by adjacent hydrogens increases the selectivity of the cation. The products are nearly exclusively derived from the free ion and aryl-substituted analogues should therefore comply with the first prerequisite above. The fractions of ion-pair return were previously evaluated for two vinyl bromides from the concurrent solvolysis and *cis*–*trans* isomerization.^{21f,25} Recently, the k_{α}/k_t probe was applied for the optically active anthranol (**2**).^{1,23} In



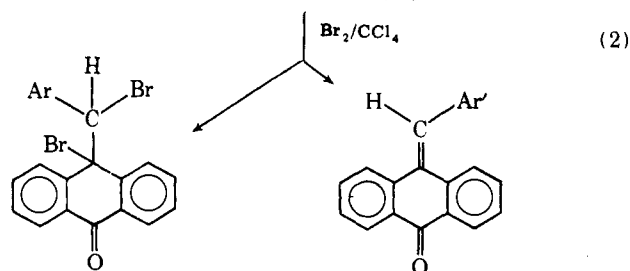
TFE²³ and in 80% EtOH¹ $k_{\alpha}/k_t \sim 1$ and ion-pair return with racemization is negligible, fulfilling the second prerequisite above for a system related to the anthronylidene system. Consequently, for probing the selectivity behavior of sterically similar, solvolytically generated free cations we solvolyzed several 9-(α -bromoarylidene)anthrones.

Results

Synthesis. The 9-(α -bromoarylidene)anthrones **5** were prepared by a modification of the method of Julian and Magnani²⁶ which involves acid-catalyzed condensation of anthrone with a substituted benzaldehyde to form 9-arylidenanthrone **3**, bromine addition to the double bond of **3** to form the dibromide **4**, and dehydrobromination to **5** with potassium *tert*-butoxide (eq 2). Except for a base-promoted debromination of the dibromides **4** which accompanies the dehydrobromination, preparation of compounds **5a**–**c** presented no problem. The structure of **5a** was also corroborated by X-ray analysis.²⁷ However, when at least one activating substituent was present at an ortho position of the aryl group,

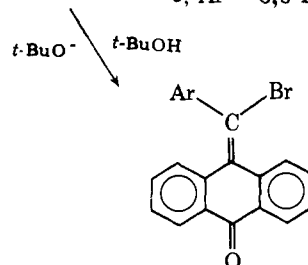


- 3a**, Ar = An
b, Ar = Tol
c, Ar = Ph
d, Ar = *o*-An
e, Ar = 2,4-(OMe)₂C₆H₃
f, Ar = 2,4,6-(OMe)₃C₆H₂
g, Ar = 2,4,6-Me₃C₆H₂



- 4a**, Ar = An
b, Ar = Tol
c, Ar = Ph
d, Ar = *o*-An

- 6a**, Ar' = 5-Br-2-MeOC₆H₃
b, Ar' = 5-Br-2,4-(MeO)₂C₆H₂
c, Ar' = 3-Br-2,4,6-(MeO)₃C₆H₂
d, Ar' = 3-Br-2,4,6-Me₃C₆H₂
e, Ar' = 3,5-Br₂-2,4,6-(MeO)₃C₆H₂



- 5a**, Ar = An
b, Ar = Tol
c, Ar = Ph
d, Ar = *o*-An

ring bromination either competed with addition of bromine to the double bond or was the exclusive reaction. Bromination of 9-(*o*-methoxybenzylidene)anthrone **3d** at room temperature in chloroform gave a product which was inert to refluxing AgOAc in AcOH for 48 h. This was identified as the 5-bromo derivative **6a** by ozonolysis to 5-bromo-2-methoxybenzaldehyde and by the NMR spectrum. The hydrogens ortho to the methoxy group in **3a**, **3d**, and **5a** are at a higher field than the other aromatic protons. The higher field proton of **6a** is a doublet ($J = 9$ Hz) centered at δ 6.79 and it is ascribed to H-5 of **6a**. The absence of meta coupling indicated that position 5 was occupied by the bromine.

The NMR of the crude reaction mixture indicated that addition of bromine to the double bond accompanies the formation of **6a**. On reducing the temperature to 0 °C and con-

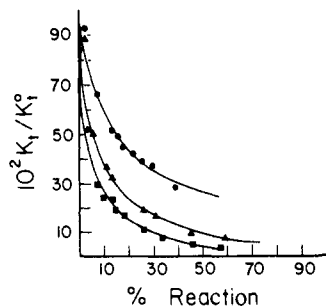


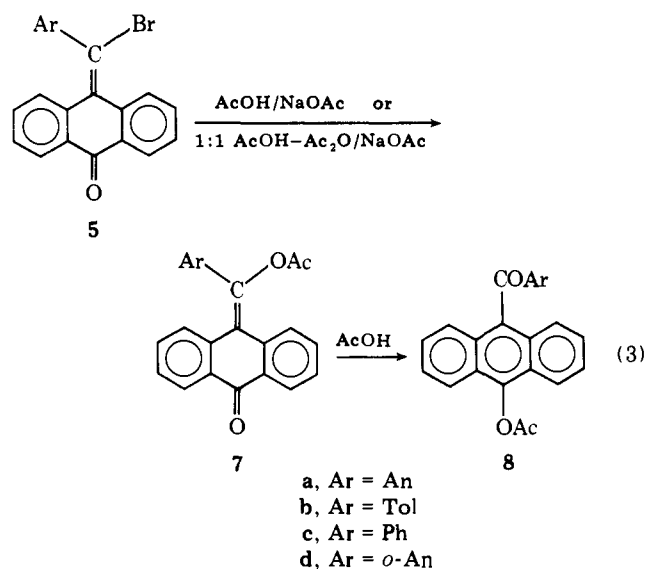
Figure 1. Relative decrease of k_t with the progress of the reaction for the solvolyses of **5a** (■), **5b** (●), and **5d** (▲) in 1:1 AcOH–Ac₂O/NaOAc at 138 °C.

ducting the reaction in CCl₄ the dibromide **4d** was obtained exclusively. Dehydrobromination gave **5d**.

Exclusive ring bromination took place with more activated 9-arylideneanthrones **3**. The 2,4-dimethoxy and the 2,4,6-trimethoxy derivatives **3e** and **3f** gave the 3-bromo or the 5-bromo products **6c** and **6b**, which were isolated and easily identified by the NMR of the aryl group. Formation of the dibromo derivative **6c** from **3f** was also indicated by NMR. Likewise bromination of 9-mesitylideneanthrone **3g** gave the 3-bromo derivative **6d**, which was identified by NMR. Lowering the temperature, changing the solvent, and use of pyridinium bromide perbromide as the brominating agent did not change the course of these reactions. Consequently, only the solvolysis of **5a–d** was investigated.

Solvolysis in AcOH and in 1:1 AcOH–Ac₂O. Some solvolysis experiments were conducted in pure AcOH buffered by NaOAc. However, the solubility of **5**, Ar = Tol, Ph, in AcOH is low. Previous study showed that the rate constant in AcOH decreases somewhat by addition of acetic anhydride but the selectivity of the ion increases^{21g} and since the solubility of compounds **5** is higher in 1:1 AcOH–Ac₂O this binary solvent mixture, buffered by NaOAc, was used.

The observed solvolysis products of **5a–d** at 140 °C are the rearranged 9-acetoxy-10-arylanthracenes **8a–d** (eq 3). These



are probably derived from the unrearranged vinylic acetates **7a–d**, since it was previously shown that **7a** rearranges rapidly to **8a** in AcOH/NaOAc under the reaction conditions,²⁸ but no evidence for the presence of compounds **7** during the solvolysis was observed.

The first-order integrated titrimetric rate constants k_t decreased strongly with the progress of the reaction. Figure 1 shows the relative decrease of k_t , i.e., k_t/k_t^0 when k_t^0 is k_t

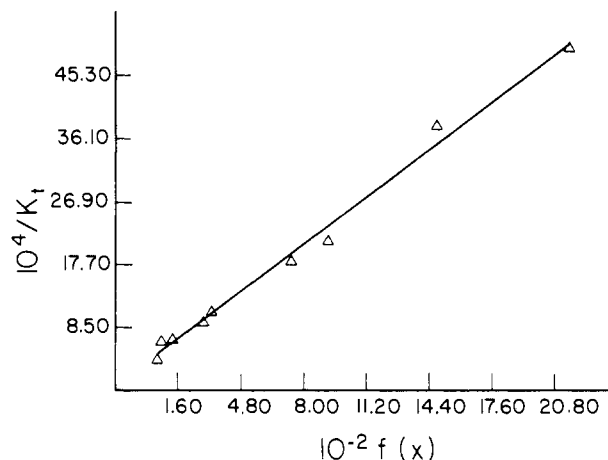


Figure 2. A $1/k_t$ vs. $f(x)$ plot (eq 5) for the solvolysis of **5d** in 1:1 AcOH–Ac₂O at 138 °C.

extrapolated to zero reaction time, as a function of the progress of the reaction for **5a**, **5b**, and **5d**. The rate decrease follows the order **5a** > **5d** > **5b**. The rate decrease was treated in two ways: first, by assuming that AcOH is the nucleophile capturing R⁺ (SOH of eq 1) and that the NaOAc serves only as a “normal” salt in the ionization step and as a neutralizing salt, eq 4 where $\alpha' = k_{-1}/k_2 = k_{Br^-}/k_{AcOH}$ is obtained from eq 1. The k_1 ($=k_t^0$) and the α' values were calculated from the intercept and the slope of a $1/k_t$ against $f'(x)$ plot (eq 4) by using program NOA.^{22b} Second, by assuming a competition of AcO⁻ and Br⁻ for R⁺, rate equation 5, where $\alpha = k_{Br^-}/k_{AcO^-}$, $n = [AcO^-]_0/[RBr]_0$, is obtained.^{21f}

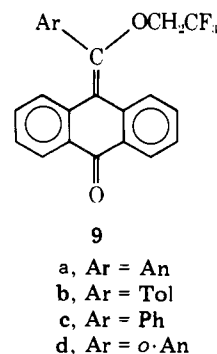
$$1/k_t = 1/k_1 + (\alpha'/k_1)[(a-x)/\ln(a/(a-x))] \\ = 1/k_1 + (\alpha'/k_1)f'(x) \quad (4)$$

$$1/k_t = 1/k_1 + [\alpha/k_1(1-n)] [n \ln(na/(na-x)) / (\ln(a/(a-x)) - 1)] \\ = 1/k_1 + (\alpha/k_1)f(x) \quad (5)$$

A plot of $1/k_t$ against $f(x)$ (cf. eq 5) was linear as shown in Figure 2 for compound **5d**, and α and k_1^0 were computed by computer program SHA1^{21f} from the slope and the intercept. Table I gives the derived kinetic data calculated by the two models.

The reaction of **5c** at 138 °C was very slow and 7% reaction was obtained after 3 weeks. A strong rate decrease was observed for the first 3% reaction, but, since this can be due to experimental error, the α and α' values contain a very large error.

Solvolysis in TFE/2,6-Lutidine. Solvolysis of **5a–d** in TFE buffered by 0.08 mol of 2,6-lutidine gave the trifluoroethyl ethers **9a–d**. The k_t values decreased strongly during the kinetic



run and the k_t^0 and α' values were calculated from eq 4 by assuming that TFE is the capturing nucleophile. The data are given in Table II and a plot of k_t/k_t^0 vs. % reaction for **5a**, **5b**, and **5d** is shown in Figure 3. The decrease of the k_t/k_t^0 values follows the order **5a** > **5d** > **5b** but the differences are smaller

Table I. Solvolysis of Compounds **5** in AcOH-Ac₂O/NaOAc^a

no.	compd	<i>t</i> , °C	% Ac ₂ O ^b	<i>n</i> ^c	calcd by eq 5			calcd by eq 4		
					10 ³ <i>k</i> ₁ ⁰ , s ⁻¹	<i>α</i>	<i>r</i> ^d	10 ³ <i>k</i> ₁ ⁰ , s ⁻¹	<i>α</i> ' ^e , M ⁻¹	<i>r</i> ^d
1	5a	138	50	9	1.36 ± 0.31 ^e	106 ± 26 ^e	0.998	16.9 ± 4.4	21 150 ± 6260	0.996
2		160	50	10	3.90 ± 4.27	58 ± 65	0.994	-5.3 ± 0.7	1524 ± 94	0.984
3		138	90	8	0.52 ± 0.08	91 ± 17	0.995	1.0 ± 0.02	2960 ± 180	0.993
4		120.3 ^f	0	8	0.12 ± 0.03 ^g	32 (75) ^g				
5		120.3 ^f	0	6	0.0072 ± 0.001	24 ^h				
6	5b	138	50	10	(1.82 ± 0.11)10 ⁻³	21 ± 3	0.976	(1.94 ± 0.01)10 ⁻³	328 ± 24	0.981
7		140 ⁱ	0	10	(1.89 ± 0.21)10 ⁻³	8.8 ± 1.4	0.988	(2.16 ± 0.02)10 ⁻³	156 ± 9	0.990
8		150	50	7	(2.88 ± 0.01)10 ⁻³	9.8 ± 0.4	0.995	(2.92 ± 0.001)10 ⁻³	137 ± 5	0.996
9		150 ^f	50	7	(2.59 ± 0.01)10 ⁻³	6.5 ± 0.6	0.975	(2.88 ± 0.01)10 ⁻³	257 ± 19	0.987
10		150 ^j	50	5				(1.69 ± 0.01)10 ⁻³	380 ± 22	0.995
11	5c	138 ^k	50	7	(1.72 ± 0.04)10 ⁻⁴	(184 ± 58)	0.836	(1.77 ± 0.003)10 ⁻⁴	2440 ± 710	0.836
12	5d	138	50	9	0.029 ± 0.008	63 ± 19	0.995	0.0435 ± 0.0015	1482 ± 119	0.992
13		150	50	7	0.25 ± 0.04	79 ± 24	0.969	0.36 ± 0.06	1720 ± 200	0.976

^a [**5**] = 0.04 M; [NaOAc] = 0.08 M unless otherwise stated. ^b % Ac₂O (v/v) in the AcOH-Ac₂O solvent. ^c Number of points used for the correlations. ^d Correlation coefficient of the linear plot. ^e Reaction followed to 89% reaction but only points up to 58% reaction were used in the correlation. High deviations in both *k*₁⁰ and *α* are shown by points at higher reaction percentages. ^f [**5**] = 0.044 M; [NaOAc] = 0.088 M. ^g An extrapolation of a *k*₁ vs. % reaction plot was used for calculation of *k*₁⁰ in this case. The *α* value was calculated from this value and from eq 5. The value in parentheses was obtained by Br⁻ ion exchange in the presence of added bromide ion (see text). ^h In the presence of 0.087 M Et₄NBr. The value was not corrected for a normal salt effect. ⁱ [NaOAc] = 0.04 M. ^j Reaction in the absence of NaOAc. ^k Reaction measured up to 7% reaction. A large rate increase was shown in the first reaction percentages.

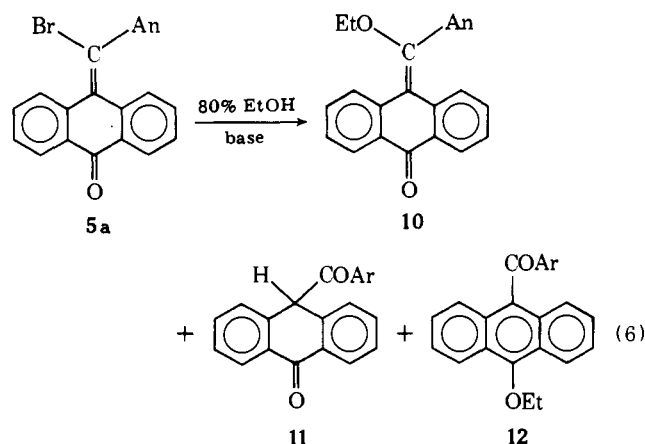
Table II. Solvolysis of Compounds **5** in 80% EtOH and in TFE

compd ^a	solvent	base ^b	concn, M	<i>n</i> ^c	<i>t</i> , °C	10 ⁵ <i>k</i> ₁ ⁰ , s ⁻¹	<i>α</i> ' ^d , M ⁻¹	<i>r</i> ^d
5a	80% EtOH	NaOAc	0.087	6	105.1	35 ^e		
5a	80% EtOH	lutidine	0.087	6	105.1	18.0 ± 1.42	158 ± 21	0.994
5a	80% EtOH	lutidine	0.087	6	105.1	3.1 ^f	55	
5a	TFE	lutidine	0.08	22	138	244 ± 22	381 ± 56	0.970
5b	TFE	lutidine	0.08	7	138	1.98 ± 0.01	218 ± 3	0.993
5c	TFE	lutidine	0.08	12	138	0.092 ± 0.000 06	(429 ± 51) ^g	0.942
5d	TFE	lutidine	0.08	7	138	16.9 ± 0.03	293 ± 10	0.997

^a [**5**] = 0.0435 M in 80% EtOH and 0.04 M in TFE. ^b Lutidine = 2,6-lutidine. ^c Number of points used in the linear regression. ^d Correlation coefficient of the linear regression. ^e *k*₁⁰/*k*₁^{50% reaction} = 1.4; *α*' was not calculated (see text). ^f In the presence of 0.087 M Et₄NBr. ^g Based on points at low reaction percentages.

than in 1:1 AcOH-Ac₂O. The fit to eq 4 is demonstrated in Figure 4. The solvolysis of **5c** was very slow and *k*₁ decreased at the beginning of the reaction more strongly than expected from the decrease at longer reaction times. This is reflected in the low correlation coefficient of eq 4 and the *α*' value for **5c** is therefore not very meaningful.

Solvolysis in 80% EtOH. Solvolysis of **5a** in 80% EtOH buffered by 0.087 mol of 2,6-lutidine for 22 h at 105 °C showed (by NMR) the formation of 68% of the vinyl ether **10**, which was isolated. Additional signals were ascribed to the ketone **11** (*δ* 5.98, 18%) and to the rearranged ether **12** (*δ* 1.37 (t, Me), 4.33 (q, CH₂), 14%) (eq 6) in analogy with the formation of



a rearranged acetate in AcOH.²⁸ Compounds **11** and **12** were not isolated.

In the presence of 0.087 M NaOAc the NMR showed after 8.5 h that the rearranged acetate **8a** (45%), the ether **10** (40%), **11** (8%), and **12** (7%) were formed. The *k*₁ values decreased with the progress of the reaction and *k*₁⁰ and *α*' (Table II) were calculated by eq 4. On addition of 0.087 mol of Et₄NBr, *k*₁ decreased to 19% of the initial value and it remained constant during the run. The rate constant in the presence of NaOAc was 1.95 times higher than in the presence of 2,6-lutidine. The rate decrease during the run was moderate compared with that in the presence of 2,6-lutidine. A plot according to eq 4 was nonlinear since eq 4 does not reflect the capture by the AcO⁻. The *k*₁⁰ value was obtained from extrapolation of a plot of *k*₁ vs. % reaction.

Discussion

Solvolysis in AcOH and AcOH-Ac₂O. Identity of the Capturing Nucleophile. In vinylic solvolysis in acidic solvents a buffering base is essential in order to avoid substitution via electrophilic addition-elimination.²⁹ However, the use of NaOAc as the buffering base in AcOH and in AcOH-Ac₂O raises the possibility that, in spite of its lower concentration, the stronger nucleophile AcO⁻ rather than the neutral AcOH is the main or the exclusive nucleophile capturing R⁺. A basic question in the selectivity study is whether to assume exclusive capture by AcO⁻ and to calculate *α*, or exclusive capture by AcOH and to calculate *α*', or whether both nucleophiles capture R⁺ concurrently.

Comparison of the lines based on eq 4 and 5 is of little help in this respect since the correlation coefficients are rather similar (Table I) and the plots are similar in appearance to Figure 2, although the deviation of the points from the line of

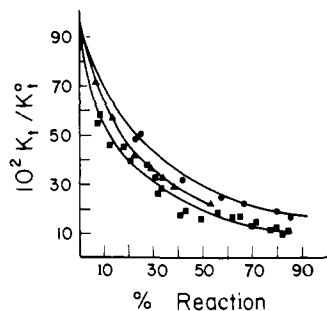


Figure 3. Relative decrease of k_t with the progress of the reaction for the solvolysis of **5a** (■), **5b** (●), and **5d** (▲) in TFE/2,6-lutidine at 138 °C.

eq 4 is slightly higher. However, the k_t^0 values calculated by eq 4 (e.g., 1.69×10^{-2} for **5a** and 4.35×10^{-5} for **5d**) are higher than those calculated by eq 5. This difference may indicate capture by AcO^- for the following reason. For exclusive capture by AcO^- the extent of rate depression increases with time since $[\text{Br}^-]$ increases and $[\text{AcO}^-]$ decreases. This results in the linearity of $1/k_t$ vs. $f(x)$ (eq 5) with an intercept of $1/k_t^0$. If the NOA program which is based on eq 4 and assumes a constant nucleophile concentration is applied to the same data, a higher deviation from linearity at higher reaction percentages will be observed. At low reaction percentages the $[\text{AcO}^-]$ term changes slightly and the selectivities calculated by both equations will be close. Consequently, the slope and k_t^0 according to eq 4 will be higher, as observed.

If general salt effects are neglected, the α value should be independent of $[\text{AcO}^-]$. In contrast, the α' value should increase on decreasing $[\text{AcO}^-]$ since the consequent lower k_t will be ascribed to increased return by Br^- . For capture by AcOH an increase in $[\text{AcO}^-]$ should not affect α' but α should increase since the expected extent of rate decrease is lower than that based on eq 5. Table I shows that at a lower initial AcO^- concentration the α values for **5b** are smaller and the α' values are higher. The larger and more regular change in the α' values and the higher k_t^0 value in the absence of added salt support capture by AcO^- . The reason for the lower α at higher $[\text{AcO}^-]$ is not clear, although an incomplete dissociation of both the NaOAc and the formed NaBr should affect appreciably the capture rates of R^+ by both AcO^- and Br^- . The small increase in k_t^0 values on increasing the $[\text{NaOAc}]$ is due to a normal salt effect.

An alternative probe for identifying the capturing nucleophile comes from rearrangement studies. The extent of degenerate β -anisyl rearrangement in the $[\beta\text{-}^{14}\text{C}]$ trianisylvinyl cation **13** formed by deamination of the corresponding triazene is 76.2% in AcOH but only 33.6% in the presence of 0.243 M NaOAc .³⁰ This indicates capture of the unrearranged ion by AcO^- and from the appropriate reaction scheme a $k_{\text{AcO}^-}/k_{\text{AcOH}}$ ratio of 366 is obtained for capture of the "hot" trianisylvinyl cation.

In our studies the initial $[\text{AcOH}]/[\text{AcO}^-]$ ratios are 220 in AcOH and 108–217 in 1:1 $\text{AcOH}\text{-Ac}_2\text{O}$. Consequently, even if a $k_{\text{AcO}^-}/k_{\text{AcOH}}$ value of 366 is used, a major part of the product is due to capture by AcO^- . Since the solvolytically generated ions **14** are "colder" and sterically more hindered than the ion **13** from the deamination, a higher $k_{\text{AcO}^-}/k_{\text{AcOH}}$

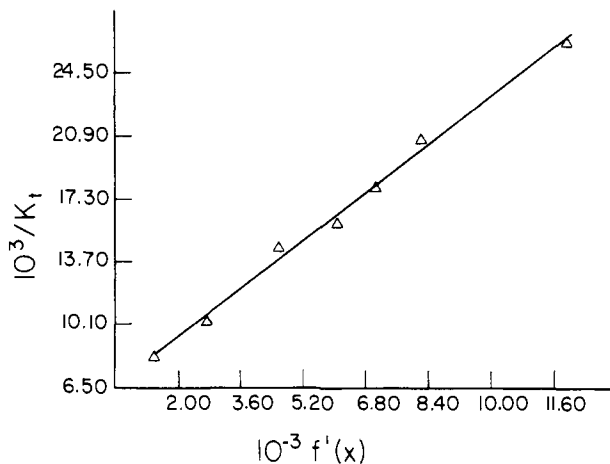
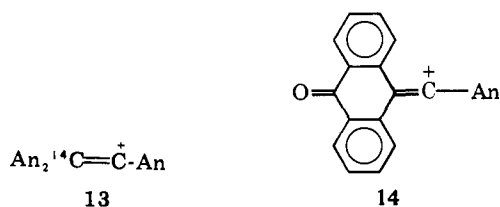


Figure 4. A $1/k_t$ vs. $f'(x)$ plot (eq 4) for the solvolysis of **5d** in TFE/2,6-lutidine at 138 °C.

is expected.³¹ All these results make it likely that the nucleophile capturing **14** is the acetate ion. The following discussion is based on this assumption, although the main conclusions are independent of this assumption.

Evidence for Product Formation from the Free Ion. A main prerequisite for using system **5** as a reactivity–selectivity probe is evidence for product formation nearly or completely so from the free cation **14**. The lowest k_t values measured during the kinetic runs in 1:1 $\text{AcOH}\text{-Ac}_2\text{O}$ were 4, 7, and 28% of k_t^0 for **5a**, **5d**, and **5b**, respectively. The k_t value for **5a** in AcOH in the presence of added Br^- is ca. 4% of the k_t^0 . By using Winstein's relationship^{8b,c}

$$\% \text{ of products from free ions} = 100(1 - k_d/k_t^0) \quad (7)$$

where k_d is the depressed rate constant in the presence of the added salt; ≥ 96 , ≥ 93 , and $\geq 72\%$ of the products are formed from the free ion in the solvolysis of **5a** (both in AcOH and in 1:1 $\text{AcOH}\text{-Ac}_2\text{O}$), **5d**, and **5b**, respectively. These are minimum values since higher $[\text{Br}^-]$ was not applied. However, it is clear that product formation is almost exclusive from the free ion since the lines calculated by eq 4 and 5 which assume no limit to the rate depression fit the experimental points. If product formation from ion pairs is appreciable, a leveling off of the rate decrease at high reaction percentages is expected, as observed for the solvolysis of 2,4-(MeO)₂ $\text{C}_6\text{H}_3\text{-CH}_2\text{CH}_2\text{OTs}$.^{8b} The prerequisite is therefore fulfilled at least for **5a**, **5b**, and **5d**. Owing to the smaller extent of reaction studied for **5c** the possibility of involvement of ion pairs cannot be excluded.

Reactivity–Selectivity Relationship in 1:1 $\text{AcOH}\text{-Ac}_2\text{O}$. Inspection of Table I and of Figure 1 shows that the increase in k_t^0 is accompanied by an increase in either the α or the α' values. Consequently, even if the $k_{\text{AcO}^-}/k_{\text{AcOH}}$ ratios differ for the different cations **14**, a qualitative reactivity–selectivity relationship still holds. The comparison involves only a small number of substrates owing to our failure to prepare more reactive substrates and to the large reactivity span which does not enable the study of at least 2 half-lives of the slow substrates under conditions used for the other substrates. The results for **5c** should not be compared with the other substrates. If steric effects are to be completely excluded, only the solvolyses of **5a** and **5b** should be compared.

A relative reactivity measure is the Hammett ρ^+ value of -6.0 for these two substrates when σ^+ values are used.³² This very high value indicates an extensive charge delocalization in the transition state. The selectivity change is much smaller as shown by the relationship $\log k_t^0 = -11.8 + 4.4 \log \alpha$, which is shown in Figure 5. The point for **5d** shows a 1.40 times higher selectivity than expected from the line, probably due to the

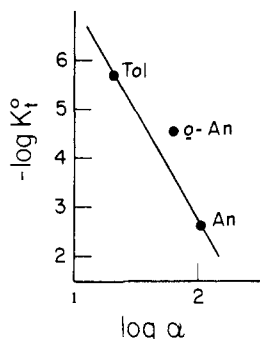
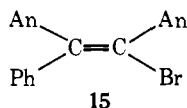


Figure 5. A $\log k_t^0$ vs. $\log \alpha$ plot for the solvolysis of compounds **5** in 1:1 AcOH-Ac₂O/NaOAc at 138 °C.

steric effect of the *o*-methoxy substituent. The effect is smaller than that usually shown by β substituents^{20,21} since the aryl group and the vacant orbital in the ion **14d** are in perpendicular planes and steric shielding for an in-plane approach of Br⁻ and AcO⁻ nucleophiles to this orbital is small.

Effect of Solvent Composition. Comparison of runs 1, 3, and 4 for **5a** and 6 and 7 for **5b** show that the α value increases and the k_t^0 value decreases on addition of 50% Ac₂O to the AcOH. The relatively high error in the α values makes it difficult to decide whether the observed decrease in α for **5a** in 90% Ac₂O-10% AcOH is a genuine effect. The two changes reflect a different response of the ionization and dissociation steps to the effect of the solvent. Hydrogen bonding to the leaving group assists the ionization step and enhances it in the AcOH-rich media, although the higher dielectric constant of Ac₂O ($\epsilon(\text{Ac}_2\text{O}) = 20$;³³ $\epsilon(\text{AcOH}) = 6.2$ ³³) counterbalances this effect and reduces the difference between the k_t^0 values. On the other hand, the free ion is more stable at the higher dielectric Ac₂O-rich media and the selectivity increases correspondingly.

This behavior finds precedent in the solvolysis of *threo*-3-anisyl-2-butyl brosylate,³⁴ where the product in pure AcOH was obtained from ion pairs, whereas on addition of Ac₂O the ionization rate decreased and the fraction of product formed from the free ion increased. Likewise, the ionization rate constant for (*E*)-1,2-dianisyl-2-phenylvinyl bromide (**15**)



decreased by ca. 50% and α increased ca. twofold on changing the solvent from AcOH to 1:1 AcOH-Ac₂O.^{21g}

On addition of Ac₂O to the AcOH k_t for the solvolysis of *threo*-3-anisyl-2-butyl brosylate first increases and then decreases owing to the involvement of ion pairs.³⁴ The monotonous decrease of k_t^0 in our system on increasing the percentage of Ac₂O suggests that the extents of ion-pair return in AcOH and in AcOH-Ac₂O do not differ much, as found for compound **15**.^{21g} We believe that the extent of ion-pair return is smaller for compound **5** and that the adherence to eq 5 excludes products formation from ion pairs.

Solvolysis and Reactivity-Selectivity Relationship in TFE.

2,2,2-Trifluoroethanol is both higher dielectric (ϵ 26.14)³⁵ and better ionizing ($Y = 1.045$)³⁶ than 1:1 AcOH-Ac₂O ($Y = 2.47$).^{21g} Consequently, a longer lifetime and higher selectivity are expected for the ion **14**. High selectivities were previously observed in the solvolyses of Me₂C=C(An)Br^{22b} and triarylvinyl bromides^{22a} in TFE. Since $pK_a(2,6\text{-lutidinium}) < pK_a(\text{TFE})$, the nucleophiles competing for R⁺ are Br⁻ and the TFE solvent. The α' values are therefore the appropriate selectivity constants and their magnitude is higher than in 1:1 AcOH-Ac₂O since the competition is between an anion and a neutral nucleophile. The low nucleophilicity should increase

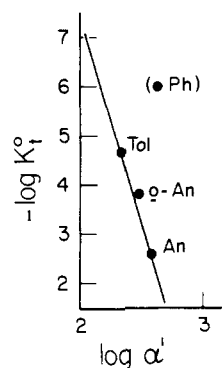


Figure 6. A $\log k_t^0$ vs. $\log \alpha'$ plot for the solvolysis of compounds **5** in TFE/2,6-lutidine at 138 °C.

the values but its good anion solvating ability reduces simultaneously the nucleophilicity of the Br⁻ ion and the α' values.

A plot of $\log k_t^0$ at 138° vs. σ^+ values for **5a-c** is linear with a ρ^+ value of -4.54 . This value indicates again the high polarity of the transition state for the vinylic solvolysis in TFE.

A reactivity-selectivity plot of $\log k_t^0$ vs. $\log \alpha'$ for compounds **5a**, **5b**, and **5d** is linear (Figure 6) according to the equation

$$\log k_t^0 = -25.5 + 8.12 \log \alpha' \quad (8)$$

The point for **5c** when Ar = Ph shows a severe deviation from this plot. The calculated α' value from eq 8 is 145, whereas the observed value is 429. This is not surprising since the few points at relatively early reaction percentages for **5c** gave a very severe scatter of the points when eq 4 was applied (cf. the value of r in Table II). The rough trend is a strong decrease of k_t at 7-15% reaction (1.5-8 days) and a much lower decrease at 15-31% reaction (8-18 days). An obvious high error associated with measurements of low reaction percentages for very long reaction times may be the reason for this behavior. However, since compound **5c** is the least reactive of those studied, product formation from both the free ion and an ion pair should be considered. In this case eq 4 is not applicable at the whole range and the approximately constant k_t value after long reaction times is due to product formation from ion pairs only. This possibility is unlikely for two reasons. First, trifluoroethanolysis of triphenylvinyl bromide gave products mainly from the free ion.^{22a} Although the carbonyl group of **5c** destabilizes **14c** compared with the triphenylvinyl cation, this effect is more than counterbalanced by the higher selectivity due to steric effects of the β substituents, as observed with the α -anisyl analogues.^{20,21} Second, in the case of ion pair return the α' value will be higher than 429; i.e., the selectivity of **14c** will be higher than that of any other ion **14**. Since even in the extreme case of behavior according to Ritchie's equation^{5,9} all the ions **14** should show a similar selectivity, and since Figure 6 suggests a reactivity-selectivity relationship for the other compounds **5**, we ascribe the deviation of **5c** from Figure 6 to an experimental error.

The analysis of the rate decrease for **5a**, **5d**, and **5b** shows that ≥ 90 , ≥ 75 , and $\geq 84\%$ of the products are formed from the free vinyl cations **14**, and the linearity of plots like Figure 4 suggests that all the products are formed from the free cation. Reactions $\geq 90\%$ reaction or in the presence of large excess of added Br⁻ were not followed owing to their slowness. However, a study of **2**, the reduced analogue of **5a**, in the presence of large excess of Bu₄NBr showed a 99-fold decrease in k_t , i.e., $\geq 99\%$ of the products are formed from the free ion. The similar solvolysis rates of **2** and **5a** and the similar steric environments at the vicinity of the derived cations justify the

assumption that products are formed nearly exclusively from the free ion **14a** and probably also from **14b** and **14d**. Consequently, the α' values are the appropriate measures for comparison with Ritchie's N_+ values if the titrimetric rate constants k_t^0 are either identical with the ionization rate constants k_{ion} or proportional to them. If ion pairs are involved and the extent of ion-pair return is correlated with the stability of the free ion, the $k_{\text{ion}}-\alpha'$ plot will have a different shape than that of Figure 6.

The qualitative conclusion of a reactivity-selectivity relationship will still be valid but the slope (s) of the reactivity-selectivity plot, which measures the "deviation" from Ritchie's rule,^{5,9} will be different. The mutual fulfillment of eq 9 and 10 gives the dependency of the selectivity on the σ^+ of the substituent (eq 11). Ritchie's correlation will be obtained when

$$\log k_t^0 = s \log \alpha' + \text{constant} \quad (9)$$

$$\log k_t^0 = \sigma^+ \rho^+ + \text{constant} \quad (10)$$

$$\log \alpha' = (\rho^+/s) \sigma^+ + \text{constant} \quad (11)$$

the ρ^+/s term will approach zero, either when ρ^+ is very low or when s is very high. In the present case where $\rho^+/s = -0.56$ it is highly unlikely that the k_t^0/k_{ion} ratios for the different compounds will be so different that the ρ^+/s ratio will approach zero. A reactivity-selectivity relationship based on k_{ion} is therefore also expected.

Fortunately we have recently acquired data on the extent of ion-pair return in a closely related system in TFE. The ionization of the optically active **2** was followed both by titrimetry and by polarimetry and the k_{α}/k_t^0 value was found to be ca. unity.²³ Ion-pair return with racemization is therefore negligible and $k_t^0 = k_{\text{ion}}$. It is highly likely that the same conclusion also holds for the reaction of the analogous **5a** and that, if ion-pair return occurs with the other compounds studied, its extent is low.

The Reactivity-Selectivity Relationship and the Constant Selectivity Relationship for Carbonium Ion Reactions. The goal of the present investigation was to determine the selectivity rule for solvolytically generated free ions. The common ion rate depression observed in the solvolysis of the vinylic derivatives **5** served as a probe for this purpose and discussions of the merits and difficulties of both the system and the method are necessary before further discussion of the results.

The formation of products almost exclusively from the free cation and the extensive common ion rate depression are novel features of the vinylic solvolysis of α -arylvinylic derivatives²⁰⁻²² and an advantage in this respect. A steric explanation for these phenomena was previously given²⁰⁻²² and it will be elaborated for these systems, including compounds **5**, in a forthcoming publication.³⁸ The disadvantage of our vinylic system includes the difficulty of preparing the appropriate precursors, and in general the possible involvement of competing routes which lead to the same products,^{20,29} the difficulty in evaluating the extent of ion-pair return by the k_{α}/k_t probe except in specific cases, and the question of the capturing nucleophile in a buffered system.

The main advantages of the application of the common ion rate depression tool are three. (a) It is a kinetic method analogous to that applied by Ritchie^{5,9} for the study of stable cations, thus avoiding the assumptions involved in the selectivity measurements by product distribution.^{6d-o} (b) It measures the selectivity of the free cation and not an average selectivity of several cationoid species. (c) It enables the study of nucleophiles such as Cl^- or Br^- which were not studied with the stable cations since the products of the $\text{R}^+ + \text{Nu}^-$ reaction are solvolytically reactive.

However, there are several disadvantages of using this method. First, the necessity to follow the reaction to completion

under the same conditions makes it very difficult to study substrates of wide range of solvolytic reactivity. Second, it is limited to comparison of only two specific nucleophiles—the leaving group and the solvent or its conjugate base. Third, it is possible that the capture by the solvent is a general-base-catalyzed process but this is not easily evaluated by the method. Fourth, in buffered solutions, incomplete dissociation and ion pairing of both the buffering salt and the salt produced in the reaction result in a concentration dependence of the α values^{20,21f,g} and their comparison is permitted only under identical conditions. Fifth, in both eq 4 and 5 α , α' , and k_t^0 (k_1) are obtained from the same plot and they are correlated since the slopes are α/k_1 and α'/k_1 , respectively. This may lead to an artificial reactivity-selectivity relationship if the reactivities are not very much different. Finally, when the common ion rate depression is extensive, the error in the α and α' values is relatively high. This is reflected in the errors of Tables I and II. We refrain from a detailed discussion of the last four problems, which will be discussed elsewhere.^{38,39}

Some of these complications can be overcome by investigating the common ion rate depression via incorporation of a labeled leaving group. This method was investigated for several benzhydryl derivatives^{6c} and is discussed further below.

In spite of these difficulties we want to emphasize that the α and α' values are at present the only selectivity values for solvolytically generated free cations which can be compared with Ritchie's N_+ values. Tables I and II and Figures 1 and 3 clearly show a reactivity-selectivity relationship for the ions **14** in both 1:1 AcOH-Ac₂O and TFE. In order to ascertain this behavior the incorporation of radioactive bromide into the unreacted **5a** and **5b** during their solvolysis in AcOH/NaOAc was studied.³⁹ A reactivity-selectivity relationship similar to that found here was again observed. There are now several systems for which common ion rate depression or incorporation of a labeled leaving group leads to an apparent reactivity-selectivity relationship. The solvolysis of 1-anisyl-2,2-diphenylvinyl iodide in 70% DMF gives α' values of 30–50, whereas α' for triphenylvinyl iodide is 0.⁴⁰ The α' values for the corresponding tosylates in 70% acetone are 9 and 0, respectively.^{21d} In both cases common ion rate depression was not observed for the α -phenyl derivatives and product formation from ion pairs cannot be excluded. Several α' values were determined by common ion rate depression^{6a} and by ³⁶Cl⁻ incorporation^{6c} for the solvolysis of benzhydryl chlorides **16** in



16

aqueous acetone. Product formation in this case is, at least to a large extent, via the free cation. An appreciable change in the selectivity as a function of the substituent was observed. For example, in 85% acetone α' increases 10.6-fold from **16**, $\text{Ar} = p\text{-O}_2\text{NC}_6\text{H}_4$, $\text{Ar}' = \text{An}$ to $\text{Ar} = \text{Ar}' = \text{An}$.^{6c} The corresponding change in the solvolysis rate constants is 2650-fold. The selectivity change from $\text{Ar} = \text{An}$, $\text{Ar}' = \text{Tol}$ to $\text{Ar} = \text{Ar}' = \text{An}$ is only 2.5-fold, whereas the solvolysis rate constant changes 35-fold. In a previous work^{22a} we noted that the ratio $\alpha'(\text{An}_2\text{C}=\text{C}(\text{Br})\text{An})/\alpha'(\text{Ph}_2\text{C}=\text{C}(\text{Br})\text{Ph})$ in TFE is only 1.7, although the solvolysis rates of the two compounds differ by several orders of magnitude. This ratio, as well as the evidence from common ion rate depression which shows product formation from the free cations, resembles the selectivity change observed for compounds **5** in TFE.

Consequently, in TFE the difference in the selectivity constants α' for ions with a similar steric bulk but with a different α substituent is rather small. The differences ($\Delta \log \alpha'$) are $\log \alpha'(\text{14a}) - \log \alpha'(\text{14b}) = 0.19$; $\log \alpha'(\text{An}_2\text{C}=\text{C}^+\text{An}) - \log \alpha'(\text{Ph}_2\text{C}=\text{C}^+\text{Ph}) = 0.23$. The difference in $\log \alpha$ (**14a**) – $\log \alpha$ (**14b**) in AcOH/NaOAc is 0.70 and the highest $\Delta \log \alpha'$

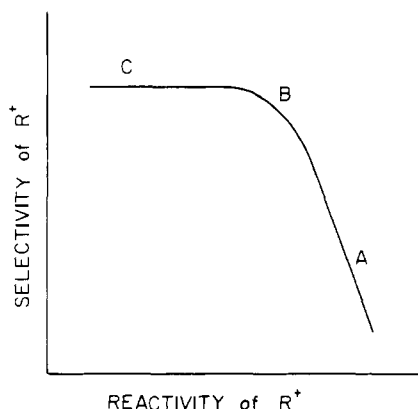


Figure 7. A schematic reactivity-selectivity plot for the reactions of carbonium ions R^+ : (A) linear reactivity-selectivity region; (B) transition region; (C) constant selectivity region.

value is $\log \alpha' (4\text{-PhC}_6\text{H}_4\text{C}^+\text{HPh}) - \log \alpha' (4\text{-O}_2\text{NC}_6\text{H}_4\text{-C}^+\text{HPh}) = 1.07$ in 70% acetone.^{6c}

Ritchie's "constant selectivity" rule^{5,9} is that for a pair of nucleophiles, Nu_1 and Nu_2 , the $\log(k_{\text{Nu}_1}/k_{\text{Nu}_2})$ ratio is constant. When $\text{Nu}_2 = \text{H}_2\text{O}$, the ratio is defined as the N_+ value. N_+ values are not available for the pairs of nucleophiles Cl^- , H_2O in aqueous acetone, Br^- , TFE in TFE, and Br^- , AcO^- in AcOH, so that the absolute value of $\log \alpha$ and $\log \alpha'$ cannot be compared with the corresponding differences in the N_+ values of the two nucleophiles. However, according to the constant selectivity rule the $\Delta \log \alpha$ or $\Delta \log \alpha'$ values should be close to zero. The present results indicate that the rule does not hold for the solvolytically generated triarylvinylic, benzhydryl, and **14** ions. However, the deviations from the rule for vinylic ions with similar steric bulk are small in TFE. Higher deviations are found for **14** in AcOH/NaOAc or for $\text{ArAr}'\text{-CH}^+$ in aqueous acetone.

These results should be considered together with the linear reactivity-selectivity plots obtained for the pairs of nucleophiles N_3^- , H_2O ^{6d,e} or EtOH, H_2O ^{6f-m,o} for solvolytically less reactive systems on the one hand, and the constant selectivity found for stable cations^{5,9} on the other. Although it is possible that some or even most of the substrates on the linear reactivity-selectivity plots give products from ion pairs, it is clear that structure-dependent and structure-independent selectivities are found for different types of carbonium ions. We believe that the answer to this contradiction lies in a gradual change in the selectivity on changing the reactivity of the cation. As for other linear free energy relationships, the linearity does not apply for the whole structural range. The reactivities and the selectivities are linearly related for a restricted structural change but on extending the range a nonlinear relationship is obtained.¹⁵ This is demonstrated schematically in Figure 7. For very reactive ions (formed slowly from the precursors RX) the selectivity is low, but it increases linearly with the increased stability (lower reactivity) of R^+ . Region A is therefore the reactivity-selectivity region, which was observed previously.^{6d-m,o}

The reasons for the linearity can be different for different pairs of nucleophiles. For two neutral nucleophiles, such as EtOH and H_2O , it could result from the operation of the Hammond postulate. For a competition between an anionic nucleophile (e.g., N_3^- , Br^-) and a neutral one (e.g., H_2O , AcOH) it is likely that the reaction with the former is diffusion controlled and the linearity is an outcome of the expected reactivity-selectivity relationship in the reaction with the neutral nucleophile. This possibility was discussed recently in detail.^{15,41} For very stable ions which can be isolated, the selectivity is structure independent and region C is the constant-selectivity region where Ritchie's relationship applies.^{5,9} An

explanation for this behavior in terms of the reactivity-selectivity principle was attempted.¹⁴ Region B is a transition region where a relatively large reactivity change is associated with a small selectivity change. This represents the behavior of our vinyl cations in TFE. It is interesting that the most stable ion on the linear reactivity-selectivity plot for N_3^- and H_2O is the Ph_3C^+ ion.^{5c} However, the $k_{\text{N}_3^-}/k_{\text{H}_2\text{O}}$ value of 1000 used for this ion is in error since the water concentration in 80% acetone was not taken into account. If this is taken into account, $k_{\text{N}_3^-}/k_{\text{H}_2\text{O}} = 11\,100$ and curvature in the plot is observed.

Two other situations were not included in Figure 7. They involve the possible existence of another region of constant selectivity beyond region A when the reactivities of both nucleophiles are diffusion controlled, i.e., $\log(k_{\text{Nu}_1}/k_{\text{Nu}_2})$ is 0. Another situation involves "inversed" or "negative" selectivities. These were observed recently for reactions of adamantyl derivatives in mixed solvents^{6j,n,19} and ascribed to the involvement of ion pairs. The reason for inverted selectivities for reactions of two anions, i.e., $k_{\text{Nu}_1^-} > k_{\text{Nu}_2^-}$ for one substrate and $k_{\text{Nu}_2^-} > k_{\text{Nu}_1^-}$ for another substrate,^{6b,42} is not clear.⁴³

Solvent Effects on the k_t^0 and the α Values. Table II enables a comparison of the k_t^0 and the selectivity values of **5a** in TFE and in 80% EtOH, whereas comparison with Table I enables an indirect comparison with the values in AcOH. The k_t^0 value in TFE at 138 °C is 13.5 times higher than in 80% EtOH at 105.1 °C. The activation energy is unknown but by using the values for related systems it is found that the reactivities are comparable. This is not surprising since the Grunwald-Winstein m value for the solvolysis of 9-(α -tosyloxyanisylidene)anthrone, the tosylate analogue of **5a**, is 0.28 at 105 °C in aqueous EtOH,⁴⁴ so that change in the ionizing power by one Y unit, from 80 to 60% EtOH, increases k_t only 2.2-fold. The behavior is expected to be similar for **5a**. More surprising is the relatively small difference between the α values since the α value in TFE is only 2.5 times higher than in 80% EtOH. TFE is much less nucleophilic than 80% EtOH³⁷ and the lifetime of the ion should be longer in TFE than in 80% EtOH. Consequently, k_{-1} of eq 1 should be larger for 80% EtOH. However, the solvation of the bromide ion by the electrophilic solvent is probably higher in TFE than in 80% EtOH and this effect will reduce k_{-1} in TFE compared to the value in EtOH. The two effects are apparently nearly balanced. It should be noted that the difference in the α' values is much smaller than for other α -anisylvinyl systems. This is another example for decrease in the selectivity with an increase in the reactivity. For example, common ion rate depression was not observed for 1-anisyl-2,2-diphenylvinyl bromide⁴⁵ and its extent was very low for the 1,2-dianisyl-2-phenylvinyl bromides^{21g} in aqueous ethanol, whereas the extent of common ion rate depression in TFE for trianisylvinyl bromide is relatively high.⁴⁶

Experimental Section

Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded with Varian T-60, EM-360, and HA-100 instruments and the data are given in δ units downfield from tetramethylsilane. UV spectra were recorded with a Varian Techtron 635 instrument, IR spectra with a Perkin-Elmer 337 instrument, and mass spectra with a Varian MAT 311 instrument.

Solvents and Materials. Ethanol was purified according to Lund and Bjerrum.⁴⁷ EtOH (80%) was prepared with conductivity water. Dry acetic acid (containing $\leq 1\text{-}2\%$ acetic anhydride) was prepared according to Rappoport and Apeloig.⁴⁸ Acetic anhydride (BDH) was distilled twice and the fraction boiling at 139 °C was used. 2,2,2-Trifluoroethanol was purified according to Rappoport and Kaspi^{22b} and the fraction boiling at 73-74 °C was used. 2,6-Lutidine was distilled from pure KOH. Tetrabutylammonium bromide (Eastman), mp 107-108 °C, was crystallized from ethyl acetate. The preparation of 9-(α -bromo-*p*-methoxybenzylidene)anthrone (**5a**), mp 145-146 °C, was described previously.²⁸

9-(*p*-Methylbenzylidene)anthrone (3b). *p*-Tolualdehyde (25 g, 0.128

mol) and anthrone (25 g, 0.13 mol) were fused together at 150 °C and hydrochloric acid was bubbled through the melt for 2 h, during which time the temperature was decreased to 120 °C. Further cooling to 60 °C and addition of ethanol (10 mL) gave 32.4 g (85%) of crystals. Recrystallization from ethanol gave yellowish needles of 9-(*p*-methylbenzylidene)anthrone: mp 147–148 °C (lit.⁴⁹ 152 °C); λ_{\max} (EtOH) 237 nm (ϵ 42 000), 300 (11 700), 382 (10 800); ν_{\max} (KBr) 1650 (s, C=O), 1600 cm⁻¹ (s); δ (CDCl₃) 2.25 (3 H, s, Me), 7.00–8.00 (13 H, m containing a singlet at 7 ppm, Ar + :CH); *m/e* 296 (m, 100%), 286 (92%), 252 (M – HCO – Me, 54%).

Anal. Calcd for C₂₂H₁₆O: C, 89.18; H, 5.40. Found: C, 89.20; H, 5.16.

9-Bromo-9-(α -bromo-*p*-methylbenzyl)anthrone (4b). To a solution of 9-(*p*-methylbenzylidene)anthrone (**3b**, 15 g, 50 mmol) in carbon tetrachloride (1000 mL), bromine (8.1 g, 50 mmol) in carbon tetrachloride (100 mL) was added at 0 °C with stirring during 24 h. The mixture was washed with sodium thiosulfate and then with water, and the solvent was dried (MgSO₄) and evaporated. Addition of acetone (10 mL) gave 20.5 g (90%) of pale yellow crystals of 9-bromo-9-(α -bromo-*p*-methylbenzyl)anthrone: mp 150–151 °C; λ_{\max} (EtOH) no maxima at 225–400 nm; ν_{\max} (KBr) 1660 (vs, C=O), 1600 cm⁻¹ (s); δ (CCl₄) 2.25 (3 H, s, Me), 5.60 (1 H, s, CH), 6.58 (4 H, center of AA'BB' q, *J* = 10 Hz, Tol), 7.22–8.48 (8 H, m, Ar).

Anal. Calcd for C₂₂H₁₆Br₂O: C, 57.89; H, 3.51; Br, 35.08. Found: C, 57.48; H, 3.32; Br, 35.57.

9-(α -Bromo-*p*-methylbenzylidene)anthrone (5b). **A.** 9-Bromo-9-(α -bromo-*p*-methylbenzyl)anthrone (**4b**, 13.7 g, 0.03 mol) in *tert*-butyl alcohol (250 mL) containing potassium *tert*-butoxide (3.92 g, 0.035 mol) was stirred for 48 h at 30 °C. NMR showed the presence of 40% of the dehydrobromination product together with 60% of 9-(*p*-methylbenzylidene)anthrone. The mixture was separated on a silica column using benzene as the eluent. The first, green-yellow, fraction is the dehydrobromination product **5b** and the second yellow fraction is **3b**.

Crystallization from ethanol gave crystals of 9-(α -bromo-*p*-methylbenzylidene)anthrone: mp 167–169 °C; λ_{\max} (EtOH) 238 nm (ϵ 46 600), 283 (18 100), 356 (10 400); ν_{\max} (KBr) 1665 (vs, C=O), 1600 cm⁻¹ (s); δ (CCl₄) 2.33 (3 H, s, Me), 6.77–8.41 (12 H, m containing a singlet at 7 ppm, Ar); *m/e* 376, 374 (M, 22, 22%), 361, 359 (M – Me, 0.2, 0.2%), 295 (M – Br, 100%), 280 (M – Me – Br, 20%), 252 (M – Me – Br – CO, 34%).

Anal. Calcd for C₂₂H₁₅BrO: C, 70.40; H, 4.00; Br, 21.33. Found: C, 70.42; H, 4.08; Br, 20.78.

B. A 1:1 mixture of **3b** and **5b** was obtained by using the same concentrations of the reactants in THF for 24 h at room temperature.

C. Dehydrobromination of **4b** with DBN was conducted with the same concentrations and under the same conditions as described in method **B** for **4d**. The yield of **5b** was 50%.

9-(*o*-Methoxybenzylidene)anthrone (3d). 2-Methoxybenzaldehyde (25 g, 0.18 mol) and anthrone (25 g, 0.13 mol) were fused at 150 °C with stirring. Hydrochloric acid was bubbled for 30 min through the mixture during which the temperature decreased to 120 °C. After the mixture was cooled to 60 °C, ethanol (10 mL) was added. Yellow needles (32 g, 80%) were precipitated. Recrystallization from ethanol gave yellow crystals of *o*-methoxybenzylidenanthrone: mp 146–147 °C (lit.⁴⁹ 153 °C); λ_{\max} (EtOH) 239 nm (ϵ 36 000), 275 sh (13 200), 385 (9300); ν_{\max} (KBr) 1650 cm⁻¹ (s, C=C); δ (CDCl₃) 3.86 (3 H, s, MeO), 6.6–8.4 (13 H, m, Ar + :CH); *m/e* 312 (M, 100%), 297 (M – Me, 12%), 281 (M – MeO, 30%), 268 (M – CHO – Me, 16%), 252 (M – CHO – MeO, 21%), 239 (43%), 206 (MH – C₆H₄OMe, 86%), 178 (MH – C₆H₄OMe – CO, 27%), 121 (MeOC₆H₄CH₂, 65%).

Anal. Calcd for C₂₂H₁₆O₂: C, 84.59; H, 5.16. Found: C, 84.76; H, 5.11.

9-Bromo-9-(α -bromo-*o*-methoxybenzyl)anthrone (4d). A solution of 9-(*o*-methoxybenzylidene)anthrone (**3d**, 15.6 g, 0.05 mol) in carbon tetrachloride (1000 mL) was cooled to 0 °C and bromine (8 g, 0.05 mol) in carbon tetrachloride (1000 mL) was added during 2 h at 0 °C with vigorous stirring. Stirring was continued for an additional 48 h and the reaction mixture was washed successively with aqueous sodium bisulfite and aqueous sodium bicarbonate mixtures and water, dried (MgSO₄), and evaporated at room temperature. On addition of acetone (5 mL) a white, amorphous solid was precipitated. Dissolution in tetrahydrofuran and addition of water up to turbidity precipitated 21 g (90%) of monoclinic, white crystals of 9-bromo-9-

(α -bromo-*o*-methoxybenzyl)anthrone: mp 154 °C; λ_{\max} (EtOH) 230 nm sh (ϵ 20 000), 265 sh (13 000), 285 sh (11 000); ν_{\max} 1665 cm⁻¹ (vs, C=O); δ (CDCl₃) 3.38 (3 H, s, MeO), 6.20–7.13 (5 H, m, *o*-An + :CH), 7.41–8.58 (8 H, m, Ar); *m/e* 474, 472, 470 (M, 0.2, 0.4, 0.2%), 393, 391 (M – Br, 5.3, 5.3%), 312 (M – Br₂, 100%), 296 (M – Br – HBr – Me, 17.5%), 280 (M – Br₂ – MeOH, 38%), 238 (54%), 206 (99%).

Anal. Calcd for C₂₂H₁₆Br₂O₂: C, 56.05; H, 3.18; Br, 33.97. Found: C, 55.88; H, 3.42; Br, 34.26.

9-(α -Bromo-*o*-methoxybenzylidene)anthrone (5d). **A.** To a suspension of the dibromide **4d** (11.8 g, 0.025 mol) in dry *tert*-butyl alcohol (250 mL), a solution of potassium *tert*-butoxide (3 g, 0.03 mol) in *tert*-butyl alcohol (50 mL) was added at room temperature under nitrogen. After the mixture was stirred for 48 h the solvent was evaporated and the remainder was poured into water and extracted several times with ether (100 mL). The organic phase was washed with water and dried (MgSO₄) and the solvent was evaporated. The mixture which was separated on a silica column using benzene as the eluent gave a 1:2 ratio of **5d** to **3d**: λ_{\max} (EtOH) 230 nm (ϵ 34 600), 285 (15 300), 353 (7900); ν_{\max} (KBr) 1670 cm⁻¹ (C=O); δ (CDCl₃) 3.51 (3 H, s, MeO), 6.68–8.55 (12 H, m, Ar); *m/e* 392, 390 (M, 26, 26%), 311 (M – Br, 34%), 298 (M – Br – CH, 78%).

Anal. Calcd for C₂₂H₁₅BrO₂: C, 67.52; H, 3.87; Br, 20.43. Found: C, 67.66; H, 3.97; Br, 20.50.

B. To a solution of **4d** (9.5 g, 0.021 mol) in dry THF (100 mL) a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 2.6 g, 0.021 mol) in THF (25 mL) was added slowly under nitrogen and the mixture was stirred for 24 h. The precipitate of DBN·HCl was filtered, the solvent was evaporated, and the workup was continued as in method **A** above. The yield of **4d** was 4 g (49%).

9-Bromo-9-(α -bromobenzyl)anthrone (4c). To a solution of 9-benzylidenanthrone [*m/e* 282 (M, 87%), 281 (M – H, 100%), 265 (M – OH, 15%), 253 (30%), 252 (51%), 204 (64%), 180 (57%), 152 (49%)] (14.1 g, 0.05 mol) in carbon tetrachloride (1000 mL) at 0 °C, a solution of bromine (8 g, 0.05 mol) in carbon tetrachloride (100 mL) was added with stirring during 48 h. The solution was washed with sodium thiosulfate and water and dried (CaCl₂) and the solvent was evaporated. On addition of acetone (10 mL) a pale yellow powder of 9-bromo-9-(α -bromobenzyl)anthrone, 20 g (90%), mp 128 °C (lit.⁵⁰ 148 °C), was precipitated: λ_{\max} (EtOH) no maxima in the UV or the visible region; ν_{\max} (KBr) 1675 (vs, C=O), 1600 cm⁻¹ (s); δ (CDCl₃) 5.68 (1 H, s, CH), 6.42–8.48 (13 H, m, Ar); *m/e* 444, 442, 440 (M, 0.1, 0.2, 0.1%), 363, 361 (M – Br, 0.9, 0.9%), 282 (M – Br₂, 100%), 253 (51%), 240 (38%).

Anal. Calcd for C₂₁H₁₄Br₂O: C, 57.0; H, 3.17; Br, 36.2. Found: C, 57.14; H, 3.16; Br, 36.54.

9-(α -Bromobenzylidene)anthrone (5c). To a solution of the dibromide **4c** (11 g, 0.025 mol) in dry tetrahydrofuran (100 mL), potassium *tert*-butoxide (3.36 g, 0.03 mol) in tetrahydrofuran (20 mL) was added slowly under nitrogen at 0 °C with stirring. The stirring continued for 24 h. The solvent was evaporated, and the remainder extracted with ether, washed with water, and chromatographed over silica using benzene as the eluent, giving 5.4 g (60%) of 9-(α -bromobenzylidene)anthrone, mp 147 °C, after crystallization from methanol: λ_{\max} (EtOH) 228 nm (ϵ 38 000), 285 (15 600), 354 (8700); ν_{\max} (KBr) 1670 (vs, C=O), 1600 cm⁻¹ (s); δ (CDCl₃) 6.86–8.50 (Ar); *m/e* 362, 360 (M, 25, 25%), 281 (M – Br, 100%), 252 (M – HBr – CO, 30%), 250 (M – HBr – H₂CO, 30%), 208 (34%), 180 (38%).

Anal. Calcd for C₂₁H₁₃BrO: C, 69.81; H, 3.60; Br, 22.16. Found: C, 69.88; H, 3.80; Br, 22.12.

9-(2',4',6'-Trimethoxybenzylidene)anthrone (3f). 2,4,6-Trimethoxybenzaldehyde (5 g, 0.025 mol) and anthrone (6 g, 0.031 mol) were fused at 150 °C, then cooled to 120 °C and dry gaseous hydrochloric acid was bubbled through the mixture for 20 min. Polymerization was extensive at longer reaction times. On addition of acetone (10 mL), anthrone and bianthrone precipitated and were filtered. On standing, 7.5 g (80%) of yellow powder was obtained. Crystallization from ether-petroleum ether (60–80 °C) gave pure 9-(2',4',6'-trimethoxybenzylidene)anthrone: mp 169–170 °C; δ (CDCl₃) 3.50 (6 H, 2 s, 2,6-MeO), 3.81 (3 H, s, 4-MeO), 6.06 (2 H, s, 3,5-H), 7.25–8.33 (9 H, m, Ar).

Anal. Calcd for C₂₄H₂₀O₄: C, 77.42; H, 5.38. Found: C, 77.71; H, 5.09.

9-(3'-Bromo-2',4',6'-trimethoxybenzylidene)anthrone (6c). To a solution of **3f** (1 g) in chloroform (100 mL), bromine (0.5 mL) in chloroform (50 mL) was added either at room temperature or at –70

°C. The same reaction was also conducted in carbon tetrachloride with irradiation for 2 h. Hydrogen bromide was evolved in all cases. The organic solution was washed with sodium bisulfite, dried, and concentrated. Addition of methanol precipitated 1.21 g (100%) of yellow crystals of 9-(3'-bromo-2',4',6'-trimethoxybenzylidene)anthrone: mp 182–183 °C; δ (CDCl₃) 3.40 (3 H, s, MeO), 3.86 (3 H, s, MeO), 3.96 (3 H, s, MeO), 6.31 (1 H, s, C₆H(OMe)₃Br), 7.33–8.46 (9 H, m, anthronylidene protons + :CH).

Anal. Calcd for C₂₄H₁₉BrO₄: C, 63.86; H, 4.42; Br, 17.73. Found: C, 63.77; H, 4.35; Br, 17.47.

9-(2',4'-Dimethoxybenzylidene)anthrone (3e). 2,4-Dimethoxybenzaldehyde (6.6 g, 0.04 mol) was fused together with anthrone (6 g, 0.031 mol) at 150 °C. Dry gaseous hydrogen chloride was bubbled through the melt during 90 min and the temperature gradually decreased to 120 °C. The mixture was cooled to 60 °C and crystals were precipitated on addition of ethanol (10 mL). Crystallization from acetic acid or 2-propanol gave 8.5 g (80%) of orange needles of 9-(2',4'-dimethoxybenzylidene)anthrone: mp 151 °C; λ_{\max} (EtOH) 242 nm (ϵ 44 000), 275 sh (12 000), 404 (11 800); ν_{\max} (KBr) 1660 (s, C=O), 1605 (s), 1460 (s), 1290 (s), 1210 cm⁻¹ (s); δ (CDCl₃) 3.70 (3 H, s, MeO), 3.81 (3 H, s, MeO), 5.95–8.23 (12 H, m, Ar).

Anal. Calcd for C₂₃H₁₈O₃: C, 80.70; H, 5.26. Found: C, 81.03; H, 5.48.

9-(5'-Bromo-2',4'-dimethoxybenzylidene)anthrone (6b). A. To a solution of 9-(2',4'-dimethoxybenzylidene)anthrone (3.4 g, 0.01 mol) in carbon tetrachloride (70 mL), bromine (1.6 g, 0.01 mol) in carbon tetrachloride (700 mL) was added dropwise at 0 °C with stirring. The stirring was continued for 24 h, during which hydrogen bromide was evolved. The brown-green solution was washed with sodium bisulfite, sodium bicarbonate, and water and dried (CaCl₂) and the solvent was evaporated. Addition of acetone (10 mL) to the remaining oil gave yellow powder which on recrystallization from 1:1 ethanol–2-propanol gave 3.3 g (80%) of yellow needles of 9-(5'-bromo-2',4'-dimethoxybenzylidene)anthrone: mp 185–187 °C; λ_{\max} (EtOH) 241 nm (ϵ 49 000), 280 sh (15 200), 397 (12 000); ν_{\max} (KBr) 1660 (vs, C=O), 1600 cm⁻¹ (vs, C=C); δ (CCl₄) 3.88 (3 H, s, MeO), 3.95 (3 H, s, MeO), 6.45 (1 H, s, H-3'), 7.27–8.30 (10 H, m, Ar + :CH); *m/e* 422, 420 (M, 100, 100%), 343 (69%), 326 (M – Br – Me, 39%), 312 (M – HBr – CO, 40%), 283 (M – HBr – CO – H, 38%), 239 (31%), 227 (40%), 206 (82%), 178 (30%).

Anal. Calcd for C₂₃H₁₇BrO₃: C, 65.56; H, 4.04; Br, 19.00. Found: C, 65.62; H, 4.32; Br, 18.62.

B. To a solution of **3e** (0.34 g, 0.001 mol) in CS₂ (200 mL), bromine (0.16 g, 0.001 mol) in CS₂ (20 mL) was added slowly and the mixture was stirred at –100 °C overnight. The black precipitate which was formed was filtered and washed with acetone. Its NMR was consistent with that of **6b** obtained by method A above.

C. When the bromination of **3e** was conducted with the same reagent concentrations at –70 °C in chloroform for 4 h, **6b** was obtained and identified by NMR. Longer reaction times gave further reaction: **3e** (1.71 g, 0.05 mol) was dissolved in chloroform (200 mL). The mixture was cooled to –70 °C and bromine (0.8 g, 0.05 mol) in chloroform (50 mL) was added slowly. The mixture was kept for 24 h at –70 °C and an additional 4 h at 0 °C and washed with sodium thiosulfate solution and then with water, and the organic layer was separated, dried (CaCl₂), and evaporated. Addition of acetone (5 mL) to the resulting oil precipitated 2 g (34%) of a white solid; δ (CDCl₃) 3.43 (3 H, s, MeO), 3.76 (3 H, s, MeO), 6.03, 6.20, 6.36 (3 × 1 H, 3 s, H- α ,3',6'), 7.26–8.50 (8 H, m, Ar). The presence of the three one-hydrogen singlets was ascribed to the formation of the 5', α , β -tribromo derivative.

The tribromide obtained above (0.58 g, 0.001 mol) was reacted with potassium *tert*-butoxide (0.22 g, 0.002 mol) in *tert*-butyl alcohol (200 mL) for 24 h at room temperature. After workup the NMR of the mixture showed several signals for methoxy groups and single hydrogens which were consistent with the presence of 45% of the unreacted tribromide and 45% of the debromination product **6b**.

D. To a stirred solution of **3e** (0.34 g, 0.001 mol) in acetic acid (100 mL), pyridinium perbromide (0.32 g, 0.001 mol) was added. A black solid precipitated immediately. Its NMR was consistent with a 2:1 mixture of **6b** (which was isolated by crystallization from methanol) and the 5', α , β -tribromo derivative.

9-(5'-Bromo-2'-methoxybenzylidene)anthrone (6a). To a stirred solution of 9-(*o*-methoxybenzylidene)anthrone (7.8 g, 0.025 mol) in chloroform (200 mL), bromine (4 g, 0.025 mol) in chloroform (50 mL) was added during 10 min. The stirring was continued for 24 h,

during which hydrogen bromide evolution was observed. After successive washing with aqueous sodium bisulfate solution, aqueous sodium bicarbonate solution, and water, the organic phase was dried (MgSO₄), the solvent was evaporated, and acetone (20 mL) was added to the remaining oil. The crude product (7 g) was dissolved with stirring in a saturated ethanolic solution of potassium hydroxide (100 mL) at room temperature. Yellow needles (5 g, 51%) of 9-(5'-bromo-2'-methoxybenzylidene)anthrone were obtained. Crystallization from ethanol gave a pure sample: mp 159 °C; λ_{\max} (EtOH) 237 nm (ϵ 42 000), 282 (14 000), 375 (10 600); ν_{\max} (KBr) 1655 (s, C=O), 1605 cm⁻¹ (s); δ (CDCl₃) 3.79 (3 H, s, MeO), 6.78 (1 H, d, *J* = 8.5 Hz, H-3?), 7.18–8.32 (11 H, m, Ar + :CH); *m/e* 392, 390 (M, 11, 11%), 311 (M – Br, 3%), 208 (anthraquinone, 90%), 180 (fluorenone, 100%).

Anal. Calcd for C₂₂H₁₅BrO₂: C, 67.52; H, 3.83; Br, 20.48. Found: C, 67.83; H, 3.84; Br, 19.88.

Ozonolysis of 9-(5'-Bromo-2'-methoxybenzylidene)anthrone. Ozonolysis of 0.5 g (1.28 mmol) of **6a** in methylene chloride (50 mL) was conducted for 3 h at –70 °C. The solvent was evaporated and a solution of potassium iodide (0.6 g, 3.6 mmol) in acetic acid (10 mL) was added. After the mixture was stirred for 3 h at room temperature 10% aqueous sodium thiosulfate solution (20 mL) and ether (50 mL) were added. The organic phase was separated, washed successively with 10% aqueous sodium thiosulfate, 5% aqueous sodium bicarbonate, and water, dried (MgSO₄), and evaporated. The product was crystallized from ethanol. The first fraction which separated at room temperature consisted of 9,10-anthraquinone (0.2 g, 80%), mp 290 °C, which was identified by analysis, UV, IR, NMR, and mass spectra. On cooling to –70 °C white crystals (0.2 g, 75%) of 5-bromo-2-methoxybenzaldehyde, mp 117 °C (lit.⁵¹ 116.4 °C), were separated: λ_{\max} (EtOH) 221 nm (ϵ 25 000), 252 (11 200), 332 (3800); ν_{\max} (KBr) 1680 (vs, C=O), 1595 cm⁻¹ (s, C=C); δ (CCl₄) 3.83 (3 H, s, MeO), 6.76 (1 H, d, *J* = 9 Hz, H-3), 7.47 (1 H, d of d, *J*₃₄ = 9, *J*₄₆ = 2 Hz, H-4), 7.78 (1 H, d, *J* = 2 Hz, H-6), 10.23 (1 H, s, CHO); *m/e* 216, 214 (M, 100, 100%), 201, 199 (M – Me, 18, 18%), 198, 196 (M – H₂O, 36, 36%), 187, 185 (M – CHO, 15, 15%), 172, 170 (M – Me – CHO, 40%), 135 (M – Br, 10%).

9-Mesitylidenanthrone (3g). A mixture of mesitylaldehyde (4 g, 0.027 mol) and anthrone (6 g, 0.031 mol) was fused at 150 °C and hydrochloric acid was bubbled through the mixture for 2 h at 150–120 °C. The mixture was cooled to 60 °C and ethanol (10 mL) was added. Unreacted anthrone and bianthrone precipitated first, followed by mesitylidenanthrone (4 g, 46%). Crystallization from benzene-petroleum ether gave yellow-brown crystals: mp 200 °C with sublimation; δ (CCl₄) 2.03 (6 H, 2 s, 2 Me), 2.28 (3 H, s, Me), 6.81 (2 H, broad s, H-3, H-5), 7.05–8.31 (9 H, m, Ar + :CH).

Anal. Calcd for C₂₄H₂₀O: C, 88.89; H, 6.17. Found: C, 88.54; H, 5.79.

Bromination of Mesitylidenanthrone. Mesitylidenanthrone (70 mg) was dissolved in carbon tetrachloride (0.5 mL) and 1 drop of bromine was added. Hydrogen bromide was evolved and a precipitate was formed. The solution was decanted and NMR of the soluble fraction showed three methyl singlets at δ 1.96, 2.28, and 2.43 in a 1:1:1 ratio and a 1 H singlet at δ 6.83. The product is tentatively 3-bromo-mesitylidenanthrone (**6d**).

The remaining oil was washed with a minimum amount of acetone and dissolved in CDCl₃. NMR showed a 6 H singlet (2,6-Me) at 2.20 ppm, a 3 H singlet at 2.70 ppm (4-Me), and no signal in the 6.8-ppm region. The product is tentatively 3,5-dibromomesitylidenanthrone (**6e**). The product and the reaction were not investigated further.

9-Acetoxy-10-(*p*-methylbenzoyl)anthracene (8b). A mixture of 9-(α -bromo-*p*-methylbenzylidene)anthrone (**5b**, 0.5 g, 1.33 mmol), silver acetate (0.22 g, 1.33 mol), and sodium acetate (106 mg, 1.33 mmol) in 1:1 AcOH–Ac₂O (20 mL) was kept in a sealed ampule for 48 h at 140 °C. The mixture was filtered and on addition of water (50 mL) a solid was precipitated. This was filtered and extracted with methylene chloride (30 mL). The organic phase was washed with water, dried (MgSO₄), and evaporated and the remainder was separated on a TLC silica plate using 10% acetone–90% petroleum ether (60–80 °C). Two crystallizations of the main fraction from ethanol with active carbon gave 140 mg (30%) of yellow needles of **8b**: mp 163–164 °C; λ_{\max} 254 nm (ϵ 87 500), 336 (2200), 352 (5200), 371 (8700), 391 (8700); ν_{\max} (KBr) 1765 (s, AcO), 1660 (vs, C=O), 1600 cm⁻¹ (s, C=C); δ (CDCl₃) 2.46 (3 H, s, Me), 2.70 (3 H, s, Me), 7.20–8.16 (12 H, m, Ar); *m/e* 354 (M, 8%), 312 (M – CH₂CO, 100%), 311 (M – Ac, 20%) 295 (M – AcO, 7%), 221 (M – CH₂CO

– Tol, 25%), 193 (M – Ac – CO – Tol, 8%), 165 (fluorenyl⁺, 8%), 119 (TolCO⁺, 15%), 91 (Tol⁺, 10%).

Anal. Calcd for C₂₄H₁₈O₃: C, 81.36; H, 5.08. Found: C, 81.31; H, 5.05.

9-Acetoxy-10-benzoylanthracene (8c). A mixture of 9-(α -bromo-benzylidene)anthrone (**5c**, 0.5 g, 1.38 mmol), silver acetate (0.23 g, 1.38 mmol), and sodium acetate (0.11 g, 1.38 mmol) in acetic acid (10 mL) was kept in a sealed ampule at 140 °C for 120 h. After the mixture was cooled and filtered, water (50 mL) was added and the organic precipitate was filtered, extracted with benzene (40 mL), washed successively with water, aqueous sodium bicarbonate solution, and water, dried (MgSO₄), and evaporated. The NMR showed the formation of 25% of **8c**. The material was separated on a TLC silica plate with benzene and the **8c** fraction was recrystallized from ethanol in the presence of activated carbon, giving 0.1 g (23%) of yellow needles of **8c**: mp 193 °C; λ_{\max} (EtOH) 246 nm (ϵ 47 500), 336 (3900), 352 (6700), 370 (9900), 391 (9200); ν_{\max} (KBr) 1765 (vs, Ac), 1660 (vs, C=O), 1595 cm⁻¹ (m, C=C); δ (CDCl₃) 2.70 (3 H, s, Ac), 7.30–8.16 (13 H, m, Ar); *m/e* 340 (M, 8%), 298 (M – CH₂CO, 100%), 297 (M – Ac, 11%), 281 (M – AcO, 3%), 221 (M – CH₂CO – Ph, 48%), 193 (M – CH₂CO – CO – Ph, 11%), 165 (fluorenyl⁺, 10%), 105 (PhCO⁺, 13%), 77 (Ph⁺, 13%).

Anal. Calcd for C₂₃H₁₆O₃: C, 81.17; H, 4.70. Found: C, 81.11; H, 4.82.

9-Acetoxy-10-(*o*-methoxybenzoyl)anthracene (8d). A mixture of 9-(α -bromo-*o*-methoxybenzylidene)anthrone (**5d**, 0.5 g, 1.28 mmol), silver acetate (0.21 g, 28 mmol), and sodium acetate (0.1 g, 1.28 mmol) in a 1:1 mixture of acetic acid and acetic anhydride (30 mL) was kept in a sealed ampule at 140 °C for 48 h. The mixture was cooled to room temperature and filtered. Water (50 mL) was added to the filtrate, the organic precipitate was filtered, extracted with benzene, washed successively with water, aqueous sodium bicarbonate solution, and water and dried (MgSO₄), and the solvent was evaporated. The crude product was separated on a TLC silica plate using 15% acetone–85% petroleum ether (60–80 °C). Crystallization from ethanol gave 0.19 g (40%) of yellow needles of **8d**: mp 176 °C; λ_{\max} (EtOH) 256 nm (ϵ 106 000), 325 sh (5600), 335 (6000), 354 (6800), 372 (9400), 393 (9000); ν_{\max} (KBr) 1770 (s, AcO), 1650 (s, C=O), 1600 cm⁻¹ (s, C=C); δ (CDCl₃) 2.60 (3 H, s, AcO), 3.36 (3 H, s, MeO), 6.80–8.03 (12 H, m, Ar); *m/e* 370 (M, 12%), 328 (M – CH₂CO, 100%), 327 (M – Ac, 9%), 311 (M – AcO, 9%), 221 (M – CH₂CO – *o*-An, 16%), 194 (M – *o*-AnCO, 50%), 193 (M – *o*-An – 2CO, 11%), 165 (fluorenyl⁺, 12%), 135 (*o*-AnCO⁺, 70%), 107 (*o*-An⁺, 15%).

Anal. Calcd for C₂₄H₁₈O₄: C, 77.84; H, 4.88. Found: C, 77.02; H, 4.92.

9-(*p*-Methoxy- α -trifluoroethoxybenzylidene)anthrone (9a). A solution of 9-(α -bromoanisylidene)anthrone (**5a**, 0.2 g, 0.51 mmol) in trifluoroethanol (10 mL) containing 2,6-lutidine (0.18 g, 1.02 mmol) was kept in a sealed ampule at 140 °C for 72 h. The solvent was evaporated and the oil was separated on a TLC silica plate using 10% acetone–90% petroleum ether (60–80 °C) as the solvent. The fraction with the highest *R_f* which was obtained as a yellow oil (140 mg, 70%) which we failed to crystallize is the trifluoroethyl ether **9a**: λ_{\max} (EtOH) 240 nm (ϵ 40 000), 290 (17 600), 372 (14 000); ν_{\max} (KBr) 1660 (s, C=O), 1600 cm⁻¹ (s, C=C); δ (CCl₄) 3.75 (2 H, q, *J* = 8 Hz, CH₂), 3.78 (3 H, s, MeO), 6.70–8.46 (12 H, m, Ar); *m/e* 410 (M, 63%), 237 (M – CF₃CH₂, 7%), 312 (M – CF₃CHO, 15%), 311 (M – CF₃CH₂O, 7%), 299 (M – CF₃CH₂ – CO, 100%), 284 (M – CF₃CHO – CO, 12%), 268 (16%), 255 (12%), 239 (15%), 164 (8%), 135 (AnCO⁺, 14%), 107 (An, 3%), 77 (Ph, 6%).

Anal. Calcd for C₂₄H₁₇F₃O₃: C, 70.24; H, 4.15. Found: C, 70.42; H, 4.44.

Reaction of 5a with Silver Carbonate in TFE. A mixture of **5a** (0.5 g, 1.28 mmol) and silver carbonate (0.18 g, 0.64 mmol) in TFE (20 mL) was kept in a sealed ampule at 140 °C for 96 h. The red reaction mixture was filtered, the solvent was evaporated, and the remainder was chromatographed over silica using benzene as the eluent. Two products were isolated: (a) anthraquinone (0.18 g, 70%), which was identified by its melting point and NMR spectrum, and (b) a colorless oil identified as 2,2,2-trifluoroethyl *p*-methoxybenzoate [ν_{\max} (neat) 1735 (vs, C=O), 1610 cm⁻¹ (vs, C=O)]; δ (CDCl₃) 3.91 (3 H, s, MeO), 4.75 (2 H, q, *J* = 8.5 Hz, CH₂), 7.03, 8.12 (4 H, centers of the two halves of AA'BB' q, An)].

Anal. Calcd for C₁₀H₉F₃O₃: C, 51.28; H, 3.84; F, 24.35. Found: C, 51.31; H, 3.81; F, 24.70.

9-(*p*-Methyl- α -trifluoroethoxybenzylidene)anthrone (9b). A sealed ampule containing 9-(α -bromo-*p*-methylbenzylidene)anthrone (**5b**, 0.2 g, 0.53 mmol) and 2,6-lutidine (0.19 g, 1.06 mmol) in TFE (10 mL) was kept at 140 °C for 120 h. The solvent was evaporated and the remainder was separated on a TLC silica plate using benzene as the eluent. The first fraction (120 mg, 60%) was unreacted **5b**. The second fraction (60 mg, 29%), a yellow oil which we were unable to crystallize, was identified as the ether **9b** by its spectral properties: λ_{\max} (EtOH) 236 nm (ϵ 41 700), 288 (19 900), 373 (11 000); ν_{\max} (KBr) 1670 (vs, C=O), 1600 cm⁻¹ (s, C=C); δ (CCl₄) 2.13 (3 H, s, Me), 3.56 (2 H, q, *J* = 8 Hz, CH₂), 6.60–8.16 (12 H, m, Ar); *m/e* 394 (M, 63%), 314 (40%), 311 (M – CF₃CH₂, 20%), 299 (23%), 296 (M – CF₃CHO, 22%), 295 (M – CF₃CH₂O, 39%), 283 (M – CF₃CH₂ – CO, 100%), 268 (M – CF₃CHO – CO, 36%), 252 (M – CF₃CH₂O – Me – CO, 23%), 239 (27%), 164 (15%), 126 (13%), 119 (TolCO⁺, 48%), 91 (C₇H₇⁺, 26%), 77 (Ph, 3%).

9-(*o*-Methoxy- α -trifluoroethoxybenzylidene)anthrone (9d). An ampule containing 9-(α -bromo-*o*-methoxybenzylidene)anthrone (**5d**, 0.2 g, 0.51 mmol) and 2,6-lutidine (0.18 g, 1.02 mmol) in TFE (10 mL) was kept at 140 °C for 96 h. The solvent was evaporated, the crude product was separated on a TLC silica plate using benzene as the eluent, and the first two fractions containing the unreacted **5d** and the trifluoroethyl ether **9d** were further separated on a silica plate using toluene as the eluent. Crystallization from methanol gave 83 mg (40%) of yellow crystals of **9d**: mp 158–159 °C; λ_{\max} (EtOH) 231 nm (ϵ 41 000), 287 (20 700), 363 (9800); ν_{\max} (KBr) 1670 (vs, C=O), 1600 (vs, C=C); δ (CCl₄) 3.53 (3 H, s, MeO), 3.76 (2 H, q, *J* = 8 Hz, CH₂), 6.73–8.43 (12 H, m, Ar); *m/e* 410 (M, 100%), 342 (MH – CF₃, 51%), 327 (M – CF₃CH₂, 33%), 312 (M – CF₃CHO, 7%), 311 (M – CF₃CH₂O, 5%), 299 (M – CF₃CH₂ – CO, 60%), 281 (15%), 255 (19%), 239 (17%), 208 (M – An – CF₃CH₂C, 60%), 193 (27%), 180 (45%), 164 (10%), 152 (32%), 135 (*o*-AnCO⁺, 13%), 91 (C₇H₇⁺, 7%), 77 (Ph, 10%).

Anal. Calcd for C₂₄H₁₇F₃O₃: C, 70.24; H, 4.15. Found: C, 70.03; H, 4.19.

9-(α -Ethoxyanisylidene)anthrone (10). A mixture of 9-(α -bromoanisylidene)anthrone (**5a**, 785 mg, 0.002 mol) and silver carbonate (552 mg, 0.002 mol) in absolute ethanol (30 mL) was refluxed in the dark for 24 h. The mixture was filtered, the silver bromide precipitate was washed with warm chloroform, the solvent was evaporated, and the remaining oil was crystallized from ethanol. Yellow crystals of **10** (610 mg, 85%), mp 124–125 °C, were obtained: λ_{\max} (EtOH) 236 nm (ϵ 47 600), 286 (19 300); ν_{\max} (CS₂) 3050–2920 (m, C–H), 2830 (m, OMe), 1658 (vs, C=O), 1335 (s), 1300 (s), 1255 cm⁻¹ (vs); δ (CDCl₃) 1.12 (3 H, t, *J* = 6.8 Hz, Me), 3.57 (2 H, q, *J* = 6.8 Hz, CH₂), 3.73 (3 H, s, MeO), 6.65–8.50 (12 H, m, Ar); *m/e* 356 (M, 88%), 328 (M – CO, 14%), 299 (M – CO – Et, 100%), 268 (M – CO – Et – OMe, 12%), 255 (12%), 208 (67%), 180 (fluorenone, 50%), 152 (41%), 135 (AnCO, 81%), 77 (Ph, 16%).

Anal. Calcd for C₂₄H₂₀O₃: C, 80.88; H, 5.66. Found: C, 80.70; H, 5.52.

Kinetic Procedure. The sealed ampule technique was used. The formation of the bromide ion was followed titrimetrically or potentiometrically using a Radiometer TTTic titrator. The treatment of the data was described earlier.^{21f,22g}

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Scope and Mechanism of the Reaction of Olefins with Anhydrides and Zinc Chloride to Give β,γ -Unsaturated Ketones

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Abstract: The synthesis of β,γ -unsaturated ketones from carboxylic acid anhydrides, zinc chloride, and a variety of cyclic and acyclic olefins is found to be effective only for simple anhydrides and olefins. The conversions of 1-methylcyclohexene (**3**) to 6-acetyl-1-methylcyclohexene (**4**) and of methylenecyclohexane (**9**) to 1-cyclohexenylacetone (**10**) are illustrative of the 22 cases included. The observation of a product isotope effect in the absence of a corresponding kinetic isotope effect in the series methylenecyclohexane, methylenecyclohexane-2,2- d_2 (**9-d₂**), and methylenecyclohexane-2,2,6,6- d_4 (**9-d₄**) is compelling evidence for a reaction intermediate. Substituent effects are taken to support a carbocationic species and the regioselectivity of the reaction is consistent with intramolecular proton transfer in that intermediate. The value of the series **9**, **9-d₂**, and **9-d₄** for distinguishing concerted and stepwise mechanisms for formal ene reactions is noted.

An intriguing aspect of the Friedel-Crafts acylation of olefins is the frequent, and sometimes exclusive, formation of β,γ -unsaturated ketonic products.¹ In fact, it often is found that the accompanying, and generally more stable, α,β -unsaturated ketones are produced by isomerization of the initially formed unconjugated isomer. Mechanistic postulates for the

reaction have ranged from early suggestions of a carbonium ion intermediate²⁻⁴ (**1**) to a more recent emphasis on a concerted process⁵ (**2**).

The acylation of an olefin is conveniently carried out by reaction in acetic anhydride with zinc chloride catalyst. A seminal discovery was the report of Deno and Chafetz that the