

- plot for 2-(4-nitrophenoxy)tetrahydropyran covered 7 pK units and was linear.
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## Vinylic Cations from Solvolysis. 26.<sup>1</sup> Solvolysis of 9-( $\alpha$ -Chlorovinyl)anthracene and Selectivity of the Derived Ion

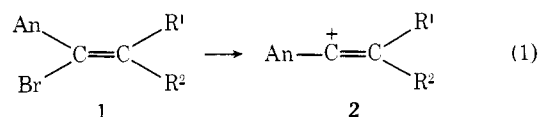
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**Abstract:** The solvolysis of 9-( $\alpha$ -chlorovinyl)anthracene (**3**) in 80% EtOH, 90% acetone, and AcOH gives both solvolysis and elimination products. The Winstein–Grunwald  $m$  value is 0.77 in 80% EtOH at 120 °C and  $k(\text{AcOH})/k(\text{AcOD}) = 0.91$  in the buffered acids. The reaction shows a common ion rate depression and the observed selectivity (mass loss) constants decrease with an increase in solvent nucleophilicity:  $\alpha(\text{AcOH}) > \alpha(90\% \text{ Me}_2\text{CO}) > \alpha(80\% \text{ EtOH})$ . The products are formed mainly from the free  $\alpha$ -(9-anthryl)vinyl cation **20**. The  $\alpha$  value for the solvolysis of 9-( $\alpha$ -chloroethyl)anthracene (**4**) is only slightly higher than that for **3**, while  $k(\mathbf{4})/k(\mathbf{3}) = 6.9 \times 10^4$  in 90% acetone. The effect of the  $\alpha$ -9-anthryl group as an activating group for both the  $S_N1$  and the  $Ad_E$ -E routes and the role of steric effects on these reactions and on the  $S_N1$  vs. E1 routes of  $\alpha$ -arylvinyl cations are discussed. Complications in evaluating  $\alpha$  for **20** due to the uncertainty in the nature of the capturing nucleophiles and to the E1 reaction are revealed, the importance of the bulk of the  $\alpha$ -aryl group in determining the selectivity of  $\beta,\beta$ -unsubstituted vinyl ions is discussed, and the selectivities of the structurally related vinylic (**20**) and trigonal (**25**)  $\alpha$ -(9-anthryl)-substituted ions are compared.

An unusual feature of the solvolysis of several  $\alpha$ -arylvinyl systems is the appearance of common ion rate depression.<sup>3-6</sup> In terms of the Ingold–Winstein solvolysis scheme,<sup>7</sup> the products in these cases are formed, at least in part, from a "free" vinyl cation intermediate.<sup>7b,c</sup> Such external ion return<sup>7b</sup> and selectivity are usually associated with a long lifetime of the intermediate,<sup>7</sup> and its appearance for the allegedly high-energy,<sup>8</sup> and hence short-lived, vinyl cations seems surprising. The selectivity of  $\alpha$ -anisylvinyl cations was ascribed by us partially to the charge-stabilizing effect of the  $\alpha$ -anisyl group, but mainly to steric effects arising from the geometry of the diagonal vinyl cation.<sup>3-6</sup> The vacant orbital in trigonal cations is in a plane perpendicular to the plane of the substituents, and reaction with the leaving group or with the solvent is from the least hindered direction. In contrast, the vacant orbital of a vinyl cation is in the plane of the substituents, and both the solvent and a capturing nucleophile approach the ion from the most hindered direction. Consequently, increase in the bulk of the vinylic substituents will increase the steric hindrance to capture of the ion by a nucleophile, resulting in increased lifetime and selectivity of the ion.

This explanation was borne out in previous studies on the solvolysis of  $\alpha$ -anisyl  $\beta,\beta$ -disubstituted vinyl bromides **1** (eq 1). The selectivities, as measured by the competitive capture of the ion **2** by  $\text{Br}^-$  vs. capture by the solvent in 2,2,2-trifluoroethanol, or by  $\text{AcO}^-$  in AcOH, increase regularly with an increase in the bulk of  $R^1$  and  $R^2$  in the order  $R^1, R^2 = \text{H} < R^1, R^2 = \text{Me} < R^1, R^2 = \text{Ar} < R^1R^2C = \text{anthronylidene}$ .<sup>6</sup>



A test of this "steric hypothesis" by changing the bulk of the  $\alpha$  substituent was not yet performed. Since the  $\beta,\beta$ -unsubstituted system **1**,  $R^1 = R^2 = \text{H}$ , shows no selectivity either in aqueous ethanol or in AcOH,<sup>4</sup> an obvious experiment will be a search for selectivity in the solvolysis of  $\beta,\beta$ -unsubstituted systems where the  $\alpha$ -aryl group is bulkier than anisyl. Ortho substitution increases the bulk of the  $\alpha$ -aryl substituents. However, the few ortho- $\alpha$ -aryl substituted  $\beta,\beta$ -unsubstituted systems studied so far were investigated mainly<sup>9</sup> in the highly nucleophilic aqueous ethanol, or occasionally at very low concentrations of the leaving group in AcOH,<sup>9</sup> i.e., under conditions which are unfavorable for the observation of selectivity.

A closely related problem concerns the reactivity–selectivity relationship. There is presently an apparent controversy between the operation of the reactivity–selectivity principle (higher reactivity of the species results in lower selectivity)<sup>10</sup> for several solvolysis reactions and the "constant selectivity" rule observed by Ritchie for capture of stable carbocations by nucleophiles.<sup>11</sup> In addition, we found that some of our slowly formed vinyl cations **2** show higher selectivity even than that of the rapidly formed benzhydryl cation.<sup>12</sup> In order to delineate the effects responsible for this deviation from the two "selec-

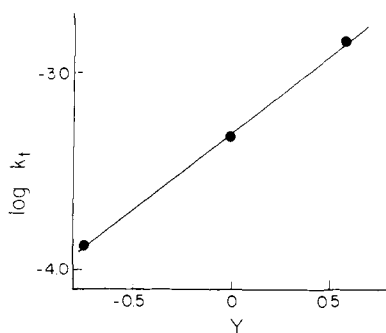
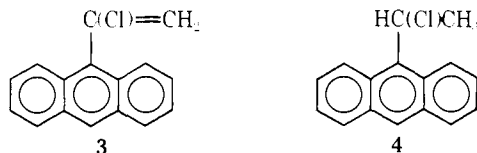


Figure 1. An  $mY$  plot in 70–90% EtOH for the solvolysis of **3**.

tivity rules" mentioned above, structurally more related vinylic and saturated systems should be compared.

For these reasons we selected 9-( $\alpha$ -chlorovinyl)anthracene (**3**) for solvolysis study. The  $\alpha$ -anthryl group is much bulkier than the  $\alpha$ -anisyl group, and the presence of the structurally related  $\beta$ -anthronylidene group in a vinylic system leads to high selectivity.<sup>13</sup> Judged by the limited data for the solvolysis of relevant saturated systems, an  $\alpha$ -anthryl group is also a better positive charge stabilizer than an  $\alpha$ -anisyl group.<sup>14</sup> Most important, the solvolysis of the saturated analogue, 9-( $\alpha$ -chloroethyl)anthracene (**4**), was shown by Berliner and Shieh to give common ion rate depression in aqueous acetone.<sup>14b</sup> Hence, the selectivities of **3** and **4**, as close structurally as possible for



a saturated and an unsaturated halide, can be compared.

Other characteristics of the vinylic solvolysis of  $\alpha$ -anisylvinyl systems respond in a similar way to the increased bulk of the  $\beta$  substituent. For example, the sensitivity to a change of the solvent as measured by the Winstein–Grunwald  $m$  value<sup>15</sup> decreases with the increased bulk of the  $\beta$  substituent,<sup>6,13b</sup> probably as a result of steric hindrance to solvation. Likewise, the relative extent of elimination compared with solvent capture for **2** increases on increasing the bulk of  $R^2$  when  $R^1 = H$ ,<sup>3c,4,16–18</sup> presumably owing to the formation of the less hindered acetylenic product. A study of a bulky  $\alpha$ -aryl group can test again the importance of steric effects in these phenomena.

## Results

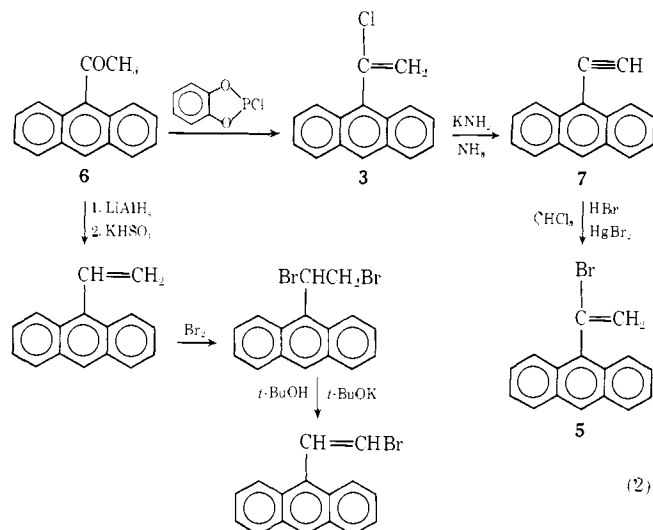
**Synthesis.** 9-( $\alpha$ -Chlorovinyl)anthracene (**3**) was prepared from the reaction of 9-acetylanthracene (**6**) with catechyl phosphorus trichloride.<sup>19</sup> 9-( $\alpha$ -Bromovinyl)anthracene (**5**) was prepared by mercuric bromide catalyzed addition of hydrobromic acid to 9-ethynylantracene (**7**) in chloroform. The acetylene **7** was obtained, in turn, from the dehydrochlorination of **3** with sodamide in liquid ammonia. Bromination of 9-vinylantracene gave 9-( $\alpha,\beta$ -dibromoethyl)anthracene, but dehydrobromination with potassium *tert*-butoxide in *tert*-butyl alcohol did not give **5**, but the isomeric 9-( $\beta$ -bromovinyl)anthracene (eq 2).

**Solvolysis in Aqueous Ethanol.** Solvolysis of **3** in 70, 80, and 90% (v/v) aqueous ethanol buffered by 2,6-lutidine gave first-order titrimetric rate constants  $k_1$  (Table I). Since a possible decrease of the rate constants at high reaction percentages was indicated by the data at 80% ethanol, a run in the presence of three times molar excess of tetraethylammonium chloride was followed by NMR. The buildup of the signals of the methyl group of 9-acetylanthracene (**6**) and of the methyl

Table I. Solvolysis of 9-( $\alpha$ -Chlorovinyl)anthracene in Aqueous Ethanol at 120 °C

| % EtOH (v/v) in EtOH–H <sub>2</sub> O | $10^2[RCl]$ , M | $10^2[2,6\text{-lutidine}]$ , M | $10^4k_1$ , s <sup>-1</sup> |
|---------------------------------------|-----------------|---------------------------------|-----------------------------|
| 70                                    | 3.0             | 6.8                             | 14.4 ± 0.2                  |
| 80                                    | 3.9             | 8.7                             | 3.85 ± 0.05                 |
| 80                                    | 3.5             | 6.8                             | 4.68 ± 0.07                 |
| 80                                    | 3.5             | 7.2                             | 3.49 ± 0.17 <sup>a</sup>    |
| 90                                    | 3.4             | 7.3                             | 1.33 ± 0.02                 |

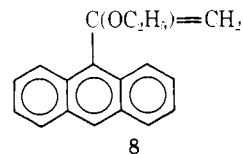
<sup>a</sup> In the presence of 0.104 M Et<sub>4</sub>NCl.



and the methylene protons of 9-( $\alpha$ -ethoxyvinyl)anthracene (**8**) was compared with the decrease of the intensity of the signals of the vinylic protons of **3**. A somewhat lower rate constant than in the absence of the added chloride ion was obtained, suggesting that some common ion rate depression took place.

A good linear dependence of  $\log k_1$  for the solvolysis in 70, 80, and 90% EtOH on the ionization power parameter  $Y$ <sup>15</sup> was obtained. The slope of this relationship is  $m = 0.77$  at 120 °C (Figure 1), and by assuming that  $m_1/m_2 = T_2/T_1$ ,<sup>20</sup> extrapolation gave  $m = 1.01$  at 25 °C.

The reaction products are 9-acetylanthracene (**6**), 9-ethynylantracene (**7**), and 9-( $\alpha$ -ethoxyvinyl)anthracene (**8**),



which were isolated from the reaction mixture by TLC. The product distribution was estimated from the NMR of the crude reaction mixture, using the signals at  $\delta$  2.73 (Me of **6**), 3.88 (HC $\equiv$  of **7**) 4.3, 4.7 (=CH<sub>2</sub> of **8**), 4.03 (CH<sub>2</sub> of **8**), and 1.3 (Me of **8**). Overlap of the acetylene signal with part of the methylene quartet of **8** appreciably reduced the accuracy in the determination of **7** since its amount was obtained from the difference of the calculated and observed integrations of the CH<sub>2</sub> region of **8**. The product distribution at 28–84% reaction is 21 ± 3% of **6**, 19 ± 2% of **7**, and 60 ± 2% of **8**. A slight increase in the percentage of **6** during the reaction at the expense of **7** and **8** is within the experimental error.

**Solvolysis in AcOH.** Solvolysis of **3** in AcOH buffered by NaOAc gave integrated rate constants  $k_1$  [from  $(2.3/t) \log (a/(a-x))$ ] which decreased progressively with the progress of the reaction. For example,  $k_1$  at ca. 70% reaction is ca. one-quarter of the initial value ( $k_1^0$ ). This rate decrease is demonstrated in Figure 2. Assuming that the rate decrease is

Table II. Acetolysis of 9-( $\alpha$ -Chlorovinyl)anthracene

| run | solvent | base                 | [RCl],<br>10 <sup>2</sup> M | [base],<br>10 <sup>2</sup> M | T, °C | n <sup>a</sup> | 10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup> | capture by OAc <sup>-</sup> ,<br>$\alpha'$ | r <sup>d</sup> | 10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup> | capture by AcOH <sup>c</sup> ,<br>$\alpha$ | r <sup>d</sup> |
|-----|---------|----------------------|-----------------------------|------------------------------|-------|----------------|--|--|----------------|--|--|----------------|
| 1   | AcOH    | NaOAc                | 3.96                        | 8.40                         | 120   | 8              | 7.2 ± 1.2 <sup>e</sup>                           | 10.0 ± 2                                   | 0.994 24       | 9.1 ± 1.9  | 213 ± 61                                   | 0.982 04       |
| 2   | AcOH    | NaOAc                | 3.90                        | 4.36                         | 120   | 6 <sup>f</sup> | 6.8 ± 0.3  | 8.9 ± 0.9                                  | 0.992 67       | 7.4 ± 0.6  | 144 ± 22                                   | 0.990 20       |
| 3   | AcOH    | NaOAc                | 3.64                        | 8.65                         | 140   | 8              | 4.2 ± 0.3 <sup>g</sup>                           | 3.6 ± 0.4                                  | 0.996 01       | 12.6 ± 6.9                                       | 693 ± 420                                  | 0.988 34       |
| 4   | AcOH    | NaOAc                | 3.81                        | 8.50                         | 140   | 6              | 73 ± 6 <sup>h</sup>                              | 10 ± 2                                     | 0.979 83       | 87 ± 20  | 188 ± 67                                   | 0.970 78       |
| 5   | AcOH    | NaOAc                | 3.81                        | 8.50                         | 140   | 5 <sup>i</sup> | 95 ± 4   | 15 ± 2                                     | 0.993 01       | 151 ± 44   | 385 ± 139                                  | 0.992 87       |
| 6   | AcOH    | Bu <sub>4</sub> NOAc | 3.81                        | 8.60                         | 120   | 7              | 55 ± 7 <sup>i</sup>                              | 6 ± 1.5                                    | 0.958 74       | 56 ± 8   | 97 ± 30                                    | 0.939 56       |
| 7   | AcOH    | Bu <sub>4</sub> NOAc | 3.81                        | 8.60                         | 120   | 5 <sup>j</sup> | 71 ± 5   | 9.4 ± 1.7                                  | 0.983 84       | 85 ± 23  | 182 ± 74                                   | 0.972 50       |
| 8   | AcOD    | Bu <sub>4</sub> NOAc | 3.90                        | 8.60                         | 120   | 6              | 20.7 ± 3.5 <sup>k</sup>                          | 10.8 ± 2.4                                 | 0.994 18       | 23 ± 12  | 174 ± 122                                  | 0.931 38       |
| 9   | AcOD    | Bu <sub>4</sub> NOAc | 3.90                        | 8.60                         | 120   | 5              | 22.7 ± 3.6 <sup>l</sup>                          | 11.5 ± 3.9                                 | 0.955 54       | 27 ± 14  | 218 ± 158                                  | 0.934 30       |

<sup>a</sup> Number of points in the run. <sup>b</sup> Calculated by eq 3. <sup>c</sup> Correlation coefficient of the linear regression of eq 3 or 4. <sup>d</sup> At 7% reaction,  $k_1 = 5.54 \times 10^{-5} \text{ s}^{-1}$ . <sup>e</sup> Points at >70% reaction were excluded from the calculation. <sup>f</sup>  $k_1 = 4.5 \times 10^{-5} \text{ s}^{-1}$  at 6.7% reaction. <sup>g</sup>  $k_1 = 4.5 \times 10^{-4} \text{ s}^{-1}$  at 19.2% reaction. <sup>h</sup>  $k_1 = 4.33 \times 10^{-4} \text{ s}^{-1}$  at 7.5% reaction. <sup>i</sup> Points below 12% reaction (which showed large deviation) were excluded from the calculation. <sup>j</sup> Points below 14.4% reaction. <sup>k</sup>  $k_1 = 13.0 \times 10^{-5} \text{ s}^{-1}$  at 14.3% reaction. <sup>l</sup>  $k_1 = 13.0 \times 10^{-5} \text{ s}^{-1}$  at 14.4% reaction.

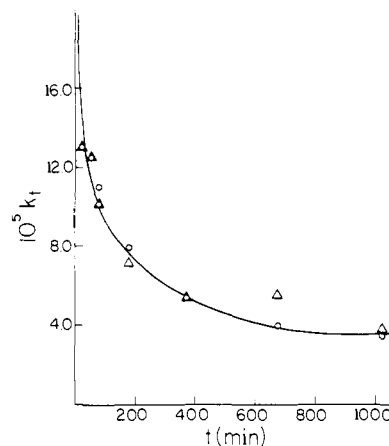


Figure 2. Decrease of the integrated rate constant for the reaction of **3** with time: O, 0.039 M RCl, 0.086 M Bu<sub>4</sub>NOAc in AcOD; Δ, 0.038 M RCl, 0.086 M Bu<sub>4</sub>NOAc in AcOH.

due to common ion rate depression by the liberated halide ion, rate equations 3 and 4 were applied in order to calculate the  $k_1^0$  value and the selectivity constants.<sup>5</sup> These are the integrated rate equations which are based on a simple solvolysis scheme (Scheme I) which assumes the presence of only one intermediate—the free carbonium ion R<sup>+</sup>. In eq 3 and 4,  $a$  is the initial concentration of **3**,  $x$  is the [Cl<sup>-</sup>] at the time  $t$ , and  $n$  is [OAc<sup>-</sup>]<sub>0</sub>/[RCl]<sub>0</sub>. Equation 3 is based on the assumption of a competitive capture of R<sup>+</sup> by chloride ion ( $k_{-1}$ ) and by the solvent ( $k_2$ ; SOH = AcOH) with a selectivity constant  $\alpha = k_{-1}/k_2$ , while eq 4 assumes that the capturing nucleophile is the acetate ion ( $k_2'$ ; SO<sup>-</sup> = AcO<sup>-</sup>) and the selectivity constant is  $\alpha' = k_{-1}/k_2'$ . The best  $k_1$  and  $\alpha$  (or  $\alpha'$ ) values were searched by using our earlier computer programs SHAI and NOA,<sup>3f,5</sup> which plot the experimental  $1/k_1$  values vs.  $f(x)$  or  $f'(x)$ , and the data are given in Table II. An example of the computer-calculated lines is shown in Figure 3. Corrections for salt effects caused by the change from NaOAc or Bu<sub>4</sub>NOAc to NaCl and Bu<sub>4</sub>NCl were not introduced. The errors involved in such calculations are discussed below and elsewhere.<sup>5</sup> In the calculations we usually omitted points at ≤6.5% reaction owing to the large experimental error and points over 50–55% reaction which deviate from the straight lines obtained according to the two equations as discussed previously.<sup>5</sup> Table II suggests that the fit to eq 4 is better than the fit to eq 3.

$$1/k_1 = 1/k_1 + (\alpha/k_1)[(a-x)/(\ln a/(a-x))] = 1/k_1 + (\alpha/k_1)f(x) \quad (3)$$

where

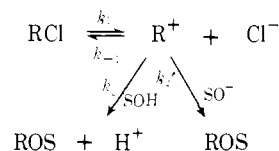
$$f(x) = (a-x)/[(\ln a/(a-x))]$$

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

where

$$f'(x) = (1-n)[(n \ln (na/(na-x)))/\ln (a/(a-x)) - 1]$$

The reaction was also conducted in AcOD and the possible errors in the extrapolated  $k_1^0$  and the  $\alpha'$  values were minimized by applying the same reaction times and conditions for a parallel reaction with AcOH.<sup>21</sup> The solvent isotope effect at the Scheme I



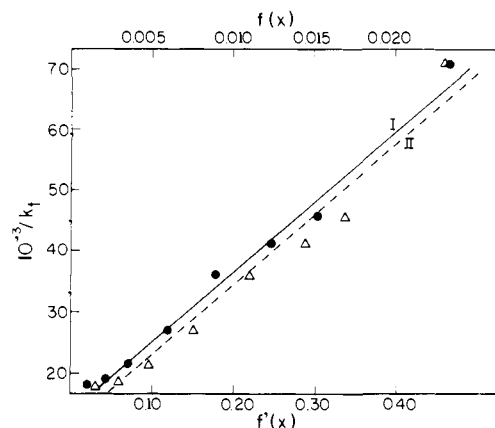


Figure 3. Plot of  $1/k_1$  vs.  $f'(x)$  (eq 4, solid line (I), O, lower scale) and vs.  $f(x)$  (eq 3, broken line (II), ▲, upper scale) for the acetolysis of 0.0396 M of **3** with 0.084 M of NaOAc in AcOH (run 1, Table II). The lines are the best lines drawn by the computer.

same substrate and base concentrations  $k_1^0(\text{AcOH})/k_1^0(\text{AcOD})$  is  $0.91 \pm 0.15$  at  $120^\circ\text{C}$ . The similarity of the rates in the two solvents is demonstrated in Figure 2 and also in Figure 4 which demonstrates the fit with eq 4 for both solvents.

The extent of common ion rate depression was also evaluated from an experiment in the presence of external chloride ion concentration ( $[\text{Et}_4\text{NCl}] = 0.134 \text{ M}$ ) three times higher than the RCl concentration (0.0428 M) in the presence of  $\text{Bu}_4\text{NOAc}$  (0.0885 M). Under these conditions the rate constant decreased much less during the reaction, from  $2.05 \times 10^{-5}$  at 22.5% reaction to  $1.55 \times 10^{-5}$  at 74% reaction. Extrapolation to zero reaction time gave a value of  $k_1^0 = (2.20 \pm 0.1) \times 10^{-5}$ . Since titration is very inaccurate in the presence of large amounts of external  $\text{Cl}^-$ , the reaction was followed by NMR: the intensities of the vinylic signals of **3** at  $\delta$  5.58 and 6.17 were compared with those of the acetate **9** at  $\delta$  5.25 and 5.80 and the methyl signal of **9** ( $\delta$  2.0) was compared with that of the ketone **6** ( $\delta$  2.78). The percentage of products obtained from the free carbonium ion is given under these conditions by eq 5, and the  $\alpha'$  value by eq 6,<sup>22</sup> where  $k_d$  is the depressed rate constant by the added chloride ion, and  $k_1^0$  is the undepressed rate constant. When a  $k_1^0$  value of  $(20 \pm 4) \times 10^{-5} \text{ s}^{-1}$  is taken from the experiment with  $\text{Bu}_4\text{NOAc}$  as a buffer, we find from eq 5 that  $\geq 89\%$  of the solvolysis products are obtained from the free vinyl cation, and from eq 6 that  $\alpha' = 6$ .

$$100(k_1^0 - k_d)/k_1^0 = \% \text{ of product formed from free ions} \quad (5)$$

$$k_1^0/k_d = 1 + \alpha'[\text{Cl}^-]/[\text{OAc}^-] \quad (6)$$

Two different NaOAc concentrations were studied. As expected for competition between  $\text{Cl}^-$  and  $\text{OAc}^-$  (eq 4) the decrease of  $k_1$  was larger at the lower  $[\text{OAc}^-]$  concentration, but not as large as expected from the difference of the  $[\text{OAc}^-]$  concentrations.

The importance of salt association was evaluated from reaction in the presence of  $\text{Bu}_4\text{NOAc}$ . The kinetic behavior was the same as with NaOAc, but both the  $k_1^0$  value and the  $\alpha'$  value were higher than those in the presence of sodium acetate.

From the extrapolated  $k_1^0$  values at 120 and  $140^\circ\text{C}$   $\Delta H^\ddagger = 40 \pm 1 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -5 \pm 3 \text{ eu}$ . These errors do not include the large error introduced by the extrapolation which leads to the  $k_1^0$  values.

The acetolysis products are 9-acetylanthracene (**6**), 9-ethynylantracene (**7**) and 9-( $\alpha$ -acetoxyvinyl)anthracene (**9**). The

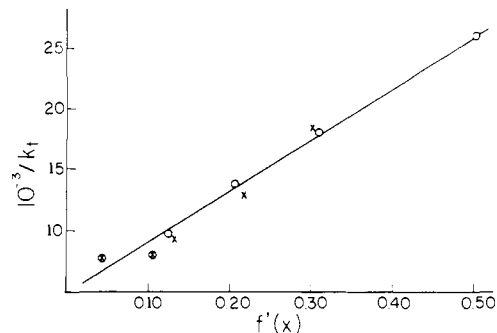
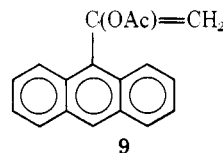


Figure 4. A plot of  $1/k_1$  vs.  $f'(x)$  (eq 4) for the data of Figure 2: O, points for AcOH; X, points for AcOD. The line is the best line for the AcOH data. The first two points are common to AcOH and AcOD.

Table III. Acetolysis Products of **3** at  $120^\circ\text{C}^a$

| time, min | with 0.084 M NaOAc |                             | with 0.086 M $\text{Bu}_4\text{NOAc}$ |                             |
|-----------|--------------------|-----------------------------|---------------------------------------|-----------------------------|
|           | % RCOMe            | % RC-(OCOMe): $\text{CH}_2$ | % RC-CH                               | % RC-(OCOMe): $\text{CH}_2$ |
| 22        |                    | 100                         |                                       |                             |
| 50        |                    | 100                         | 50                                    | 50                          |
| 75        |                    |                             | 50                                    | 50                          |
| 180       |                    | 100                         | 17                                    | 83                          |
| 370       |                    |                             | 14                                    | 86                          |
| 412       | 9                  |                             | 91                                    |                             |
| 675       | 11                 |                             | 89                                    | 100                         |
| 930       | 20                 |                             | 80                                    |                             |
| 1740      | 35                 |                             | 65                                    |                             |
| 2500      | 70                 |                             | 30                                    |                             |

<sup>a</sup> R = 9-anthryl; [RCl] = 0.04 M.



product distribution (Table III) was determined from the integration of the appropriate NMR signals of the crude reaction mixture. Compounds **6** and **9** were isolated from the reaction mixtures or from the reaction of **3** with  $\text{AgOAc}$ . In the presence of NaOAc, only the vinyl acetate **9** is obtained at short reaction times, although the presence of **7** was occasionally recorded. Hydrolysis of **9** takes place with the progress of the reaction and 9-acetylanthracene is formed. In the faster reaction in the presence of tetrabutylammonium acetate both **7** and **9** are formed in nearly equal amounts at short reaction times, but the relative amount of the acetylene decreases and finally no acetylene is observed, while relatively a greater amount of vinyl acetate was formed at longer reaction time. 9-Acetylanthracene was not observed up to reaction time of 675 min (89% reaction).

The loss of **7** at longer reaction times prompted a study of the reaction of 9-ethynylantracene with acetic acid buffered by  $\text{Bu}_4\text{NOAc}$ . When 0.055 M of **7** was reacted in AcOH/0.092 M  $\text{Bu}_4\text{NOAc}$  at  $120^\circ\text{C}$ , **9** was obtained in 80% yield, and the rate constant ( $k_{\text{add}}$ ) at 25–79% reaction is  $(2.16 \pm 0.19) \times 10^{-4} \text{ s}^{-1}$ .

A preliminary solvolysis experiment was conducted with 9-( $\alpha$ -bromovinyl)anthracene (**5**) at  $83^\circ\text{C}$ . A two-point run at 18 and 36% reaction gave  $k_1 = 5.6 \times 10^{-6} \text{ s}^{-1}$ . Extrapolation of the  $k_1^0$  value for **3** to  $83^\circ\text{C}$  gave  $k_1 = 2.6 \times 10^{-7} \text{ s}^{-1}$ , leading to a  $k_B/k_{\text{Cl}}$  ratio of 21.5. This value should be regarded only as a rough estimate since  $k_1^0$  for **5** should be higher than the  $k_1$  value obtained at higher percentages of reaction. On the other hand, the activation energy for **3** seems rather high and

**Table IV.** Solvolysis of 9-( $\alpha$ -Chlorovinyl)anthracene in 90% Acetone (v/v) at 140 °C

| [RCI],<br>10 <sup>2</sup> M | [2,6-lutidine],<br>10 <sup>2</sup> M | 10 <sup>5</sup> k <sub>1</sub> <sup>0</sup> , s <sup>-1</sup> | $\alpha$ | n <sup>a</sup> | r <sup>b</sup> |
|-----------------------------|--------------------------------------|---|----------|----------------|----------------|
| 3.80                        | 9.00                                 | 3.87 ± 0.14   | 55 ± 7   | 5              | 0.9890         |
| 3.32                        | 8.05                                 | 4.67 ± 0.28   | 58 ± 13  | 5              | 0.96019        |
| 3.58                        | 9.00                                 | 3.49 ± 0.18   | 44 ± 11  | 5              | 0.94784        |

<sup>a</sup> Number of points used for the calculation. <sup>b</sup> Correlation coefficient of the regression according to eq 3.

probably introduces a compensating effect on the  $k_{Br}/k_{Cl}$  ratio.

**Solvolysis in 90% Acetone (v/v).** Solvolysis of **3** in 90% acetone buffered by 2,6-lutidine also showed a decrease of  $k_t$  with the progress of the reaction. For example, at 75% reaction  $k_1/k_1^0 = 0.47$ . The  $k_1^0$  and the  $\alpha$  values were calculated by eq 3 and the results are given in Table IV. Correction for the volume change of the solvent at 140 °C was introduced.

The solvolysis rate was also followed by NMR in the presence of an excess (0.11 M) of added Bu<sub>4</sub>NCl. The  $k_1$  value of  $(3.6 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$  is only 9% of the average  $k_1^0$  value ( $4.01 \times 10^{-5} \text{ s}^{-1}$ ) in the absence of added chloride ion. Consequently, by eq 5,  $\geq 91\%$  of the products are formed from free vinyl cations. The  $\alpha$  value which was calculated from eq 7 is 100.

$$k_1^0/k_d = 1 + \alpha[\text{Cl}^-] \quad (7)$$

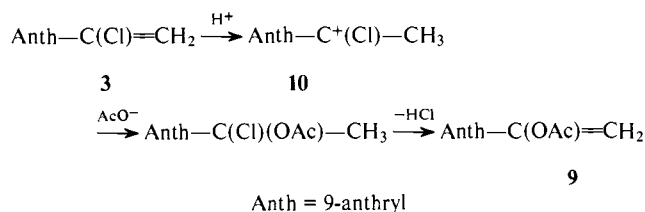
The solvolysis products are 9-acetylanthracene (**6**) and 9-ethynylanthracene (**7**) and their ratio remains nearly constant during the reaction. A detailed six-point run with 0.041 M of **3** and 0.09 M of 2,6-lutidine gave an average product distribution at 16–54% reaction of  $20.7 \pm 1.8\%$  of **6** and  $79.3 \pm 1.8\%$  of **7**.

## Discussion

**Exclusion of Non-S<sub>N</sub>1 Routes.** The multitude of mechanistic routes for substitution at a vinylic carbon<sup>23</sup> requires that non-S<sub>N</sub>1 routes such as nucleophilic<sup>23,24</sup> and electrophilic<sup>4,25</sup> addition–elimination routes should be excluded for each new system investigated.

In our system a nucleophilic addition–elimination route in basic aqueous EtOH or in 90% acetone is unlikely both on structural grounds and by analogy with systems studied previously. In 80% EtOH it is also excluded by the higher  $k_1$  at lower base concentrations, by the relatively high Winstein–Grunwald  $m$  value of 0.77 at 120 °C, and by the  $\alpha$ -anthryl/

## Scheme II



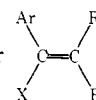
$\alpha$ -anisyl reactivity ratio discussed below. It is discarded in 90% acetone owing to the appearance of common ion rate depression.

**S<sub>N</sub>1 vs. Ad<sub>E</sub>-E Routes.** The possibility that compound **3** solvolyzes by electrophilic addition–elimination (Ad<sub>E</sub>-E route)<sup>4,25</sup> in AcOH (Scheme II) should be considered. The  $\alpha$ -anthryl group stabilizes the carbocationic transition states for both the S<sub>N</sub>1 and the rate-determining electrophilic addition, but since the ground state is identical, it is difficult to predict a priori which of the routes is more activated. There is a delicate balance between the two routes for diverse vinylic systems as shown in Table V where the solvent isotope effect is applied as the main tool for distinguishing between them. The  $k_{\text{AcOH}}/k_{\text{AcOD}}$  values are  $1.0 \pm 0.2$  for S<sub>N</sub>1 reactions<sup>4,26</sup> and the values of 1.05 for the acetolyses of 1-adamantyl tosylate<sup>26</sup> and trianisylvinyl *p*-bromobenzenesulfonate<sup>3d</sup> are typical. For rate-determining electrophilic addition (e.g., **3** → **10** in Scheme II),  $k_{\text{AcOH}}/k_{\text{AcOD}} > 1$  and the value of 3.4 for the addition of AcOH to *p*-methoxystyrene<sup>3d</sup> is typical. Table V demonstrates that a change in the leaving group (systems 1, 2, and 3), the  $\beta$  substituent (systems 1 and 8 vs. systems 2 and 7), or the carboxylic acid solvent (systems 4 and 5 vs. systems 6, 9, and 10) results in a change in the relative importance of the two routes. Compound **3** seems especially vulnerable to the Ad<sub>E</sub>-E route since the presence of two  $\beta$  hydrogens results in reduced steric hindrance to the Ad<sub>E</sub>-E route, and the increased importance of the Ad<sub>E</sub>-E route for poorer leaving groups<sup>4</sup> makes chlorine the leaving group for which the two mechanisms intersect for  $\alpha$ -chloro-*p*-methoxystyrene (**11**).<sup>4</sup> It is therefore gratifying to find that **3** solvolyzes via S<sub>N</sub>1, as judged by the solvent isotope effect of 0.91. This is supported by the appearance of common ion rate depression and by two additional criteria which were discussed previously:<sup>4,5a</sup> the  $k_{Br}/k_{Cl}$  and the  $k_{80\% \text{ EtOH}}/k_{\text{AcOH}}$  ratios. The ratios (Table V) are  $< 1$  for compound **11** where the Ad<sub>E</sub>-E route contributes appreciably, and are  $> 1$  for compound **12** which solvolyzes via S<sub>N</sub>1. The ratios for **3** are  $> 1$  and together with the  $(k_{\text{aq EtOH}}/k_{\text{AcOH}})_Y$  of 0.76 they exclude the Ad<sub>E</sub>-E route. Hence, the solvolyses of **3** and **11** demonstrate that the  $\alpha$ -aryl

**Table V.** Effect of Structural and Medium Parameters on the Competition between the Ad<sub>E</sub>-E and the S<sub>N</sub>1 Routes for in Carboxylic Acids

| no. | Ar                | R <sup>1</sup>   | R <sup>2</sup> | X   | solvent              | $k_{\text{RCOOH}}/k_{\text{RCOOD}}$ | $k_{80\% \text{ EtOH}}/k_{\text{AcOH}}$ | $k_{Br}/k_{Cl}$ | mechanism                                | ref |
|-----|-------------------|------------------|----------------|-----|----------------------|-------------------------------------|---|-----------------|--|-----|
| 1   | An                | H                | H              | Br  | AcOH                 | 1.45                                |   |                 | S <sub>N</sub> 1 + (Ad <sub>E</sub> -E?) | 4   |
| 2   | An                | H                | H              | Cl  | AcOH                 | 1.94                                | 0.13                                    | 0.46            | S <sub>N</sub> 1 + (Ad <sub>E</sub> -E)  | 4   |
| 3   | An                | H                | H              | OAc | AcOH                 | 3.45                                |   |                 | Ad <sub>E</sub> -E                       | 4   |
| 4   | An                | Me               | Me             | Br  | AcOH                 | 0.85                                |   |                 | S <sub>N</sub> 1                         | 3g  |
| 5   | An                | Me               | Me             | OTs | CF <sub>3</sub> COOH | 1.07                                |   |                 | S <sub>N</sub> 1                         | a   |
| 6   | An                | An               | An             | OTs | AcOH                 | 1.05                                |   |                 | S <sub>N</sub> 1                         | 3d  |
| 7   | An                | An               | Ph             | Cl  | AcOH                 | 1.10                                | 1.3                                     | 24              | S <sub>N</sub> 1                         | 5a  |
| 8   | An                | An               | Ph             | Br  | AcOH                 | 1.11                                | b                                       |                 | S <sub>N</sub> 1                         | 5a  |
| 9   | Tol <sup>c</sup>  | Tol <sup>c</sup> | Ph             | Br  | AcOH                 | 0.96                                |   |                 | S <sub>N</sub> 1                         | d   |
| 10  | Tol <sup>c</sup>  | Tol <sup>c</sup> | Ph             | Br  | CF <sub>3</sub> COOH | 3.4                                 |   |                 | Ad <sub>E</sub> -E                       | d   |
| 11  | Anth <sup>e</sup> | H                | H              | Cl  | AcOH                 | 0.91                                | 11 <sup>f</sup>                         | 21.5            | S <sub>N</sub> 1                         | g   |

<sup>a</sup> Z. Rappoport and J. Kaspi, *Tetrahedron Lett.*, 3813 (1971). <sup>b</sup>  $(k_{80\% \text{ EtOH}}/k_{\text{RCOOH}})_Y = 0.46$ . <sup>c</sup> Tol = *p*-tolyl. <sup>d</sup> C. C. Lee, A. J. Paine, and C. F. Ko, *Can. J. Chem.*, **55**, 2310 (1977). <sup>e</sup> Anth = 9-anthryl. <sup>f</sup> By using the *mY* plot  $(k_{\text{aq EtOH}}/k_{\text{AcOH}})_Y = -1.64 = 0.76$ . <sup>g</sup> This work.

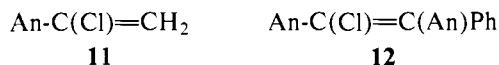


**Table VI.** Relative Reactivities of Saturated and Vinylic Compounds

| saturated RX | vinylic RX | solvent                | T, °C | $k_{\text{sald-RX}}/k_{\text{vinylic-RX}}$ | ref |
|--------------|------------|------------------------|-------|--|-----|
| <b>13</b>    | <b>14</b>  | 50% MeOH               | 130   | $1.1 \times 10^6$                          | a   |
| <b>15</b>    | <b>16</b>  | 80% EtOH               | 25    | $2 \times 10^{10}$                         | b   |
| <b>17</b>    | <b>18</b>  | EtOH                   | 36.5  | $1.4 \times 10^6$                          | c   |
| <b>4</b>     | <b>3</b>   | 90% Me <sub>2</sub> CO | 140   | $6.9 \times 10^4$                          | d   |

<sup>a</sup> Reference 27. <sup>b</sup> Estimated by Rappoport and Gal (ref 20) by comparing  $k_1$  for **15** (V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, **90**, 418 (1968)) with the extrapolated  $k_1$  for **16** (ref 16). <sup>c</sup> Estimated by Yates and Périé (ref 9) from their data for **18**, by assuming the same  $k_{\text{OTs}}/k_{\text{Br}}$  ratio in 100 and 80% EtOH and a  $k_{\text{Br}}/k_{\text{Cl}}$  ratio of 60, and by extrapolation from 80 to 100% EtOH with  $m = 0.62$ . The data for **17** are from ref 29. <sup>d</sup> The  $k_1$  value for **4** is based on the data of Berliner and Shieh (N. Shieh, Ph.D. Thesis, Bryn Mawr College, 1957) and an  $E_a$  value of 16.6 kcal/mol as calculated by us from the best  $k_1^0$  values of Table VII.

group can also change the relative importance of the S<sub>N</sub>1 and the Ad<sub>E</sub>-E routes. The reasons for this are discussed below.

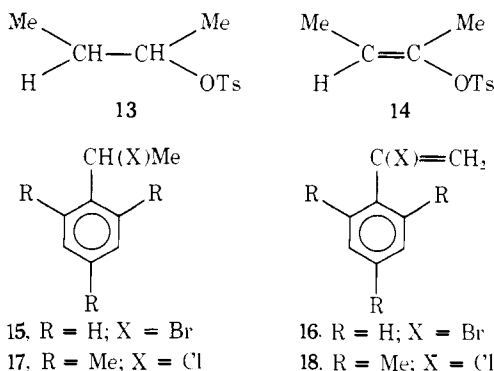


**$\alpha$ -(9-Anthryl) as an Activating Group.** Two factors determine the relative reactivity of an  $\alpha$ -9-anthryl group compared with an  $\alpha$ -anisyl group, which is our standard  $\alpha$  substituent.<sup>6</sup> These are the inherent positive charge stabilizing ability of the two groups and the extent of ground-state conjugation between the aryl group and the double bond.

The inherent charge dispersal ability of the 9-anthryl group is much higher than that of an  $\alpha$ -phenyl group and probably also exceeds that of an  $\alpha$ -anisyl group as judged by the 9-anthryl/phenyl reactivity ratio of  $2.4 \times 10^4$  for the solvolysis of ArCHMeCl in 80% acetone.<sup>14b</sup> More extensive delocalization is possible for the polycyclic aryl group, and correlation of the solvolytic reactivity with the MO delocalization energies of the hydrocarbons was obtained for  $\alpha$ -arylmethyl chlorides.<sup>14</sup>

Conjugation of the  $\pi$  system of an  $\alpha$ -aryl group with the  $\pi$  system of the double bond stabilizes the ground state, and consequently reduces the solvolytic reactivity of a vinylic compound compared with its saturated analogue. This is reflected by the increased solvolysis rate when the presence of bulky  $\beta$  substituents or ortho-substituted  $\alpha$ -aryl groups<sup>9</sup> results in an extensive  $\pi$ - $\pi$  deconjugation. The extent of the rate decrease caused by the  $\pi(\alpha\text{-Ar})-\pi(\text{C}=\text{C})$  conjugation can be estimated from the data of Table VI.

The saturated-RX/vinyl-RX relative reactivity in the absence of  $\pi$ - $\pi$  conjugation is estimated as  $10^6$  from the data for compounds **13** and **14**.<sup>27,28</sup> The  $\pi$ - $\pi$  conjugation increases this ratio by ca.  $10^4$  as shown by the solvolysis rates of compounds **15** and **16**.<sup>20</sup> Steric interaction of the ortho methyl groups of

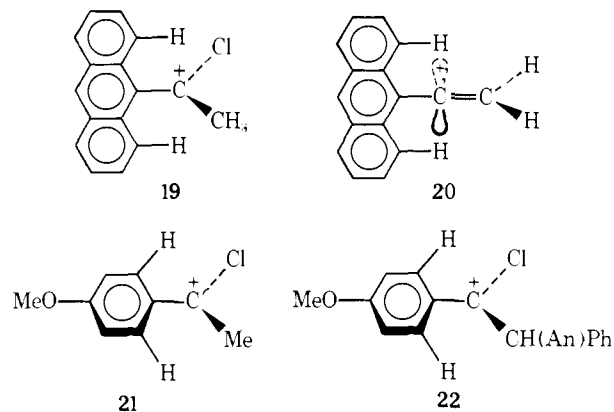


**18** with the side chain results in almost complete deconjugation, and the  $k(\mathbf{17})/k(\mathbf{18})$  reactivity ratio is again ca.  $10^6$ .<sup>9,29</sup> In spite of the extrapolations over extended temperature range and other extrapolations applied for the **17-18** pair,<sup>9</sup> it is clear that large steric interactions of the ortho substituents with the vinylic side chain result in an appreciably lower  $k_{\text{sald-RX}}/k_{\text{vinylic-RX}}$  reactivity ratio. The ratio obtained now for the  $\alpha$ -9-anthryl substituent is the lowest known, being 16 times lower than that for the reference compounds **13** and **14**.<sup>28</sup>

Applying the arguments used by Charlton and Hughes<sup>29</sup> for the solvolysis of **17**, the transition state for the solvolysis of **4** will be more sterically retarded than that for the solvolysis of **13**, owing to the steric interactions between the 1 and 8 hydrogens and the  $\alpha$  hydrogen and methyl in the close to planar transition state. The tetrahedral ground state of both compounds will be relatively unhindered. On the other hand, owing to the rigidity of the anthracene system, the  $\pi$ - $\pi$  deconjugation of the ground state due to interaction of the  $\beta$  hydrogens of **3** with the 1 and 8 aromatic hydrogens will be higher than the  $\pi$ - $\pi$  deconjugation for **16** and even for **18**. Steric effects therefore decrease the solvolysis rate of the saturated compound and increase it for the unsaturated compound. Consequently, the gap between the two types of compounds as measured by the  $k_{\text{sald-RX}}/k_{\text{vinylic-RX}}$  is the smallest for the  $\alpha$ -9-anthryl-substituted systems.

When two  $\alpha$ -aryl groups (e.g., phenyl and 9-anthryl) are compared, the comparison involves four ground states (e.g., **3**, **4**, **15**, **16**) and four transition states and this analysis is necessarily oversimplified since it neglects steric acceleration for the congested saturated compounds, and steric hindrance to solvation which has different geometrical requirements for the vinylic and the saturated systems. Nevertheless, this approximation gives the correct order of the  $k_{\text{sald-RX}}/k_{\text{vinylic-RX}}$  ratios.

Moreover, similar argument is also capable of rationalizing some of the results on the competition between the Ad<sub>E</sub>-E and the S<sub>N</sub>1 routes discussed above. For  $\pi(\text{Ar})-\pi(\text{C}^+)$  stabilization of the ion **19** formed by electrophilic addition, H-1, H-8, R, and

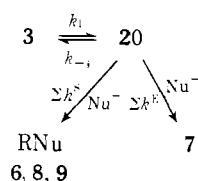


Cl should be in the same plane and steric interaction between H-1, H-8, and R and Cl will obviously reduce the stability of the ion. On the other hand,  $\pi(\text{Ar})-\pi(\text{C}^+)$  conjugation in the vinyl cation **20** puts the ortho hydrogens and the  $\beta$  hydrogens in perpendicular planes.

Apparently, the similar steric interactions in the ion **21** (derived by Ad<sub>E</sub> to compound **11**) are not sufficiently strong to turn the reaction completely to S<sub>N</sub>1,<sup>4</sup> but the bulky  $\alpha$  substituent of the ion **19** and the bulky  $\beta$  substituents of the ion **22** (derived by electrophilic addition to **12**)<sup>5a</sup> are sufficient to completely hinder the Ad<sub>E</sub>-E route.

As a result of its electronic and steric effects the  $\alpha$ -9-anthryl group is the best stabilizing  $\alpha$ -aryl group studied so far in the solvolysis of  $\alpha$ -arylvinylic systems. The relative reactivities  $\alpha$ -phenyl: $\alpha$ -anisyl: $\alpha$ -mesityl: $\alpha$ -9-anthryl are  $1:5 \times 10^3:5.8 \times$

Scheme III



$10^4$ : $5.2 \times 10^5$  for  $\text{ArC}(\text{Cl})=\text{CH}_2$  in 80% EtOH at  $120^\circ\text{C}$  when a  $k_{\text{Br}}/k_{\text{Cl}}$  ratio of 50 is assumed. These ratios are solvent and temperature dependent since both the Winstein–Grunwald  $m$  values<sup>13b</sup> and the activation energies<sup>9,16</sup> differ for the different compounds.

**$\text{S}_{\text{N}}1$  vs. E1 Reactions.** The reaction products in the three solvents studied consist of the  $\text{S}_{\text{N}}1$  products (**6**, **8**, **9**) obtained by capture of the ion by the solvent or its conjugate base and the E1 elimination product, 9-ethynylantracene (**7**).

The capture products are  $\text{sp}^2$  hybridized at  $\text{C}_\alpha$  and  $\text{C}_\beta$  (**6** only at  $\text{C}_\alpha$ ) and are therefore subject to steric interaction of substituents either on the same carbon atom or at *cis* positions on  $\text{C}_\alpha$  and  $\text{C}_\beta$ . The elimination product is  $\text{sp}$  hybridized and is free of such steric interactions. Steric effects which are so significant in various phenomena related to vinylic solvolysis<sup>6</sup> should be also important in determining the substitution/elimination ratios, predicting an increased percentage of elimination for bulkier vinylic substituents.

This prediction was borne out in the solvolysis of  $\alpha$ -anisyl mono- $\beta$ -substituted vinyl bromides, where the percentage of elimination increased with the bulk of the  $\beta$  substituent in the order  $\text{H} < \text{Me} < \text{An}$ .<sup>3c,4,17</sup> The lower extent of elimination for **3** in 80% EtOH (ca. 20%) in the presence of 2,6-lutidine than for **11** (ca. 44% elimination) in the presence of NaOAc, and the higher extent of elimination in 90% acetone compared with 80% EtOH, indicate the importance of base strength and solvent nucleophilicity in determining the substitution/elimination ratio.

The elimination reaction introduces several difficulties in the interpretation of the selectivity values obtained for **3**. While Scheme I is applicable for calculating  $\alpha$  and  $\alpha'$  values in the case of exclusive substitution, the more generalized Scheme III is the appropriate one for calculating selectivities in a system which also shows elimination. Since either the solvent or its conjugate base (both designated as  $\text{Nu}^-$ ) can be the capturing nucleophile in the substitution (S) or the base in the elimination (E), the general reaction scheme involves all the rate constants for the substitution ( $\Sigma k^{\text{S}}$ ) and the elimination ( $\Sigma k^{\text{E}}$ ). It is assumed that both the E1 and the  $\text{S}_{\text{N}}1$  products are formed from the free  $\text{R}^+$ .

The first-order titrimetric rate constant is then given by

$$k_{\text{obsd}} = \frac{k_1}{1 + \frac{k_{-1}[\text{X}^-]}{\Sigma k^{\text{S}}[\text{Nu}^-] + \Sigma k^{\text{E}}[\text{Nu}^-]}} \quad (8)$$

and the application of eq 3 and 4 is permitted only under limiting conditions. Since each solvent imposes specific problems we will discuss this question independently for each of our solvents.

**Selectivity of the  $\alpha$ -(9-Anthryl)vinyl Cation **20**.** Common ion rate depression was never observed previously for  $\beta,\beta$ -unsubstituted vinyl cations.<sup>4,9,30</sup> However, the expectation that an increased bulk of the  $\alpha$ -aryl substituent will lead to a more selective  $\beta,\beta$ -unsubstituted  $\alpha$ -arylvinyl cation was realized with the  $\alpha$ -(9-anthryl)vinyl system which showed common ion rate depression in three solvents.

**A. In Aqueous EtOH.** In contrast with the absence of common ion rate depression for *p*-methoxy- $\alpha$ -bromo- (or  $\alpha$ -chloro-) styrene,<sup>4,30</sup> and  $\alpha$ -mesitylvinyl chloride<sup>9</sup> in aqueous EtOH, there is a weak mass law effect for **3** in 80% EtOH. In

a solvent containing 0.1 M  $\text{Et}_4\text{NCl}$ ,  $k_1$  is somewhat lower than in the absence of salt, although it is expected to be higher owing to a "normal" salt effect.<sup>31</sup>

Four nucleophiles ( $\text{EtOH}$ ,  $\text{H}_2\text{O}$ ,  $\text{EtO}^-$ ,  $\text{OH}^-$ ) can participate in the  $k^{\text{S}}$  process in the buffered solvent and all of them and 2,6-lutidine can serve as bases in the  $k^{\text{E}}$  process. However, since the concentrations of the solvent components are constant and the  $[\text{OH}^-]$  and  $[\text{EtO}^-]$  concentrations are negligible,  $k^{\text{S}}_{\text{EtOH}}[\text{EtOH}] + k^{\text{S}}_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$  can be designated  $k^{\text{S}}$  and  $k^{\text{E}}_{\text{EtOH}}[\text{EtOH}] + k^{\text{E}}_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$  can be designated  $k^{\text{E}}$ . To a first approximation, a small change in the 2,6-lutidine concentration does not affect the extent of elimination (i.e.,  $k^{\text{E}}_{2,6\text{-lutidine}}[2,6\text{-lutidine}] \ll k^{\text{E}}$ ) as judged by the moderate change in the elimination/substitution ratio for 4-amino- $\alpha$ -bromostyrene over a high pH range.<sup>32</sup>

Under these limiting conditions, eq 8 becomes

$$k_{\text{obsd}} = \frac{k_1}{1 + \frac{k_{-1}[\text{Cl}^-]}{k^{\text{S}} + k^{\text{E}}}} \quad (9)$$

and comparison with eq 3 shows that the value obtained by the NOA program under these conditions is  $k_{-1}/(k^{\text{E}} + k^{\text{S}})$  and not  $k_{-1}/k_2 (= k_{-1}/k^{\text{S}})$ . The  $\alpha$  value which measures the selectivity of the ion for capture processes should then be obtained by multiplying the  $\alpha$  value of eq 3 by  $(1 + k^{\text{E}}/k^{\text{S}})$  (eq 10). This  $\alpha$  value, which is designated  $\alpha^{\text{S}}$ , is the appropriate selectivity constant for comparison with  $\alpha$  values for systems where elimination does not compete with the substitution.

$$\alpha^{\text{S}} = \alpha(1 + k^{\text{E}}/k^{\text{S}}) \quad (10)$$

An  $\alpha$  value of 1–3.3 was calculated from the data of Table I and eq 7. If we introduce a correction for a "normal" salt effect, using a  $b$  value<sup>31</sup> of 4 for  $\text{Et}_4\text{NBr}$ ,  $\alpha$  becomes 5.4–8.7. By using an average  $k^{\text{E}}/k^{\text{S}}$  value of 0.25,  $\alpha^{\text{S}} = 6.8\text{--}11$ .

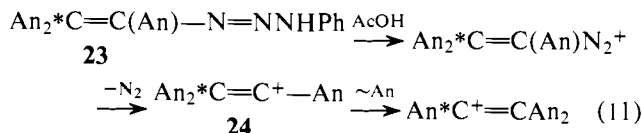
These very approximate values can still enable us to draw some qualitative conclusions. First, with a sufficiently bulky  $\alpha$ -aryl group, even a  $\beta,\beta$ -unsubstituted ion shows selectivity, albeit low, in a nucleophilic solvent such as aqueous ethanol. However, the  $\alpha^{\text{S}}$  value is still lower than those for  $\beta,\beta$ -disubstituted systems carrying a less bulky  $\alpha$  substituent. Second, by using eq 5 it can be estimated that  $\geq 12\%$  of the products are formed from the free ion **20**. This is a lower limit and the bulk of the reaction may proceed either via **20** or via the corresponding ion pair. Finally, the absence of common ion rate depression for  $\alpha$ -mesitylvinyl bromide<sup>9</sup> may be due to the lower bulk of mesityl compared with 9-anthryl, but is more probably due to the different reaction conditions: Yates and Périé buffered the system with NaOAc and used RBr concentrations 200-fold lower than in our system. The use of  $\text{AcO}^-$ —a better nucleophile than the solvent—and much lower concentrations of the liberated  $\text{Br}^-$  are expected to result in a negligible external ion return.

The product distribution gives ratios of several of the rate constants of eq 8. The **7**/(**6** + **8**) ratio of ca. 0.25 is identical with  $k^{\text{E}}/k^{\text{S}}$ , while the **6**/**8** ratio is identical with  $k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]/k_{\text{EtOH}}[\text{EtOH}]$  in the absence of specific solvation. Based on the average distribution of 21% of **6** and 60% of **8** in 80% EtOH,  $k_{\text{EtOH}}/k_{\text{H}_2\text{O}} = 23$ , i.e., ethanol is more nucleophilic toward **20** than water, as expected.<sup>33</sup>

**B. In AcOH.** The common ion rate depression by  $\text{Cl}^-$ , either formed in a run or added externally, indicates an appreciable selectivity of the ion **20**. This is again in contrast to the behavior of other  $\alpha$ -aryl  $\beta,\beta$ -unsubstituted vinylic systems in buffered AcOH, where  $k_1$  remains constant during the reaction.<sup>9,30</sup> However, the problems associated with the quantitative evaluation of the selectivity in AcOH are much more severe than in aqueous ethanol for two reasons. Neither the extent of the

capture by the different nucleophiles nor the extent of elimination to **7** is clearly known.

A major question is whether AcOH or AcO<sup>-</sup> is the capturing nucleophile of the ion **20** in buffered AcOH, i.e., whether eq 3 or eq 4 is applicable. Since both nucleophiles give the same product, the nature of the product cannot aid in answering this question. AcO<sup>-</sup> is presumably much more nucleophilic than AcOH, but its concentration in the medium is much lower and a priori either nucleophile or both can be involved in the capture process. The available data do not justify an assumption that one of the two terms,  $k_{\text{AcOH}}[\text{AcOH}]$  and  $k_{\text{AcO}^-}[\text{AcO}^-]$ , is very small compared with the other and can therefore be neglected. From the dependence of the extent of the common ion rate depression on the NaOAc concentration it was previously argued that the capturing nucleophile of several trisubstituted vinyl cations is mainly the acetate ion,<sup>3e,5a</sup> but a recent work by Lee and co-workers<sup>34</sup> casts some doubt on this conclusion. The molarity of pure AcOH is 17.3 M and the highest stoichiometric NaOAc concentration studied is 0.0865 M, i.e., the  $[\text{AcOH}]/[\text{AcO}^-]$  ratio in the reaction medium is ca. 200. If the contribution of the reaction with AcOH is small or negligible,  $k_{\text{AcO}^-}/k_{\text{AcOH}}$  should be higher than 1000, while if the contribution of the reaction with AcO<sup>-</sup> is small,  $k_{\text{AcO}^-}/k_{\text{AcOH}}$  should be 20 or lower. Although the former value is not unreasonable when compared with the  $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$  ratios of  $10^{4.5}$  in the reactions of these two nucleophiles with stable cations,<sup>11</sup> it should be mentioned that the  $k_{\text{AcO}^-}/k_{\text{AcOH}}$  ratio for capture of the 1,2-dianisyl-2-phenylvinyl cation, where there is good evidence that capture by AcO<sup>-</sup> is dominant, is ca. 410.<sup>5a</sup> Moreover, that the capture can be mainly by AcOH can be deduced from the study of the solvolysis-degenerate  $\beta$ -anisyl rearrangement of the labeled trianisylvinyl cation **24** formed from the corresponding trianisylvinyl phenyltriazenes **23** in AcOH (eq 11).<sup>34</sup> It was found

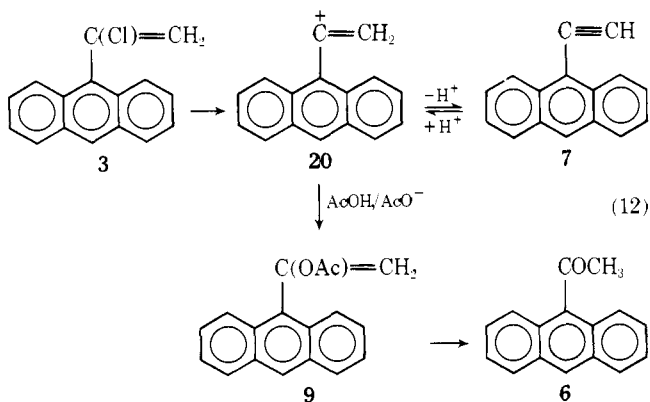


that the rearrangement can be suppressed by added AcO<sup>-</sup>, and by assuming that this is due to capture of the unrearranged ion by AcO<sup>-</sup> we calculated a  $k_{\text{AcO}^-}/k_{\text{AcOH}}$  ratio of 19 for capture of **24** by the two nucleophiles. If a similar ratio also applies for the reaction of the ion **20**, the capture by the acetate ion will be relatively insignificant and  $\alpha$  rather than  $\alpha'$  is the measured selectivity constant. However, it is doubtful whether the  $k_{\text{AcO}^-}/k_{\text{AcOH}}$  ratio for the presumably "hot" cation **24** which is formed by dediazonation is the appropriate value for the reaction of the solvolytically generated "cold" cation **20**.

A clear-cut answer to this problem is not obtained from the dependency of the extent of common ion rate depression on the base concentration. On the one hand, acetate ion is clearly involved in the capture process since the extent of common ion rate depression is higher in the presence of lower concentrations of NaOAc as shown by the higher corresponding  $\alpha$  values of Table II. The correlation coefficients of the linear regression of eq 4 for capture by OAc<sup>-</sup> are also higher than those for eq 3 for capture by AcOH. On the other hand, the  $\alpha'$  value which should be independent of the  $[\text{NaOAc}]$  if OAc<sup>-</sup> is the capturing nucleophile is lower at lower  $[\text{OAc}^-]$ . A steady-state treatment of Scheme III which takes into account the competitive capture of **20** by AcO<sup>-</sup> and AcOH will give a more complicated equation than eq 3 and 4, but such refinement was not attempted for three reasons. (a) The amount of data is too limited to justify such a treatment. (b) The difference between the salt effects of the added NaOAc and the NaBr formed, which is required for a detailed analysis is unknown. (c) Ion pairing effects were so far neglected, although ion pairing is

extensive in AcOH<sup>35</sup> and the ion pairs M<sup>+</sup>OAc<sup>-</sup> and M<sup>+</sup>Br<sup>-</sup> are presumably much less reactive toward **20** than the free OAc<sup>-</sup> and Br<sup>-</sup> ions. It is interesting that this effect, which was invoked to explain the dependency of  $\alpha'$  on  $[\text{NaOAc}]$  for the 1,2-dianisyl-2-phenylvinyl cation,<sup>5a</sup> is not reflected in a difference between the  $\alpha'$  (or  $\alpha$ ) values in the presence of NaOAc and the more dissociated Bu<sub>4</sub>NOAc, while it affects the  $k_1$  values. This may be due to a cancellation of the effect of the cation on the dissociation of the M<sup>+</sup>OAc<sup>-</sup> and the M<sup>+</sup>Br<sup>-</sup> ion pairs. As a consequence of these problems both  $\alpha$  and  $\alpha'$  values are given in Table II and comparison with other values in AcOH should take into account the above-mentioned considerations.

The second problem concerns the evaluation of the contribution of the E1 reaction to the overall reactions of **20**, i.e., to the calculation of the  $\alpha^S$  value. The solvolysis in the presence of NaOAc or the reaction at long reaction times in the presence of Bu<sub>4</sub>NOAc does not give the alkyne **7** and  $\alpha^S$  may be identified with  $\alpha$ . However, in contrast to the behavior in the nucleophilic solvents, **7** does not survive in this reaction medium, since the reversible **20**  $\rightleftharpoons$  **7** transformation is coupled with the irreversible **20**  $\rightarrow$  **9**  $\rightarrow$  **6** reaction (eq 12). This is



supported by the independent study of the **7**  $\rightarrow$  **9** reaction in AcOH/Bu<sub>4</sub>NOAc which shows that the rate constant for this reaction is approximately similar to that of the solvolysis. A mechanism for the conversion of vinylic acetates (e.g., **9**) to the corresponding ketones in dry AcOH was suggested.<sup>36</sup>

Although the formation of **7** in the above-mentioned media is hidden in the presence of NaOAc, the fraction of the elimination reaction, which is essential for calculating  $\alpha^S$ , can be roughly estimated from the product distribution at short reaction time in the presence of Bu<sub>4</sub>NOAc. Table III shows that at early reaction times the alkyne is one of the main products, and the  $k^E/k^S$  ratio is approximately unity. The detection of **7** is due to two reasons. The ionization to **20** is faster in the presence of Bu<sub>4</sub>NOAc (Table II), so that the loss of **7** becomes slower compared with the reaction with NaOAc, and the elimination **20**  $\rightarrow$  **7** is probably more extensive with the more dissociated Bu<sub>4</sub>NOAc, since the  $k^E/k^S$  ratios in the solvolysis of *p*-amino- $\alpha$ -bromostyrene increase with increase in the base concentration.<sup>32</sup>

The  $k^E/k^S$  value at early reaction time with Bu<sub>4</sub>NOAc can be taken as an approximate value for the value with NaOAc, assuming cancellation of the higher extent of elimination with Bu<sub>4</sub>NOAc and the partial loss of **7** even at these reaction times. By using eq 10,  $\alpha^S \geq 2\alpha$  (or  $\geq 2\alpha'$ ). The  $\alpha^S$  values so obtained (12–30 when based on  $\alpha'$  and 200–770 when based on  $\alpha$  at 0.084 M of NaOAc) are of the order of magnitude of the  $\alpha$  or  $\alpha'$  values obtained for  $\alpha$ -anisyl- $\beta,\beta$ -dimethyl,  $\alpha$ -anisyl- $\beta,\beta$ -diphenyl, and trianisylvinyl cations in AcOH/NaOAc.<sup>3a,g,6</sup>

**C. In 90% Acetone.** Since the concentration of hydroxide ion is negligible at the 2,6-lutidine concentrations employed, water is the only nucleophile involved in the capture of **20**. In spite of the relatively low correlation coefficients it is clear that the



**Table VII.** Solvolysis of 9-( $\alpha$ -Chloroethyl)anthracene in 90% Acetone<sup>a</sup>

| [RCI],<br>10 <sup>3</sup> M | [NaOH],<br>10 <sup>3</sup> M | T, °C | 10 <sup>5</sup> k <sub>1</sub> <sup>0</sup> , s <sup>-1</sup> <sup>b</sup> | $\alpha$  | n <sup>c</sup>  | r <sup>d</sup> | k <sub>d</sub> /k <sub>1</sub> <sup>0</sup> <sup>e</sup> |
|-----------------------------|------------------------------|-------|--|-----------|-----------------|----------------|--|
| 10.22                       | 2.80                         | 12.0  | 40.2 ± 2.41 (33.0)   | 549 ± 52  | 16              | 0.991 66       | 0.32 <sup>f</sup>  |
| 9.74                        | 2.80                         | 0.0   | 11.0 ± 1.03 (8.75)   | 630 ± 101 | 16 <sup>i</sup> | 0.975 83       | 0.23 <sup>f</sup>  |
|                             |                              |       | 11.9 ± 1.29  | 713 ± 120 | 13 <sup>g</sup> | 0.983 90       |  |
|                             |                              |       | 10.8 ± 0.08  | 619 ± 81  | 8 <sup>h</sup>  | 0.991 49       |  |

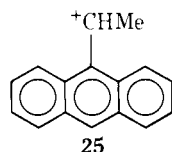
<sup>a</sup> Titrimetric data taken from N. Shieh, Ph.D. Thesis, Bryn Mawr College, June 1957. <sup>b</sup> In parentheses—data from ref *a*. <sup>c</sup> Number of points used in the calculation. <sup>d</sup> Correlation coefficient of the linear regression according to eq 3. <sup>e</sup> Ratio of the depressed rate constant at the highest reaction percentage measured to the initial rate constant. <sup>f</sup> At 85% reaction. <sup>g</sup> Three points deviating from the best line by 6–13% were not included in the calculation. <sup>h</sup> Only data at 7–63% reaction were used. <sup>i</sup> Data from 3–85% reaction.

selectivity is appreciable (Table IV). The larger  $\alpha$  value obtained in the presence of Bu<sub>4</sub>NCl suggests an increased efficiency in the capture by the more dissociated Bu<sub>4</sub>NCl as compared with 2,6-lutidinium hydrochloride.

The alkyne **7** is the main reaction product and from the product distribution  $k^E/k^S = 4$ . If an average  $\alpha$  value of 52 ± 6 is taken from Table IV, the  $\alpha^S$  value is 260 ± 30.

The importance of this  $\alpha^S$  value is that for the first time an  $\alpha$  (or  $\alpha^S$ ) value for a vinylic system can be compared with the  $\alpha$  value for the closely related saturated analogue 9-( $\alpha$ -chloroethyl)anthracene (**4**). In unbuffered 90% acetone the rate constants for **4** at 0 and 12 °C decreased with the progress of the reaction.<sup>14b</sup> Although the  $\alpha$  values were not calculated in the original work, we obtained the rate data for **4** from Professor Berliner<sup>37</sup> and calculated the  $\alpha$  values by applying eq 3 where SOH = 90% acetone. The data are given in Table VII and the best  $\alpha$  values are 630 ± 101 at 0 °C and 549 ± 52 at 12 °C.

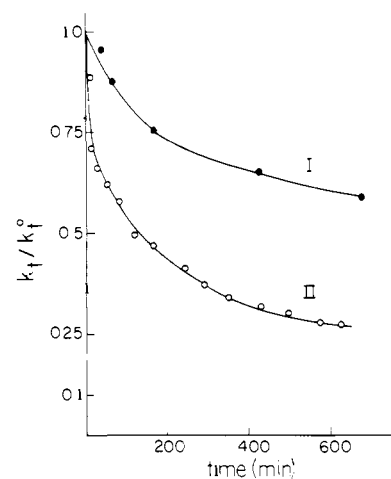
The only product isolated from the unbuffered solvolysis of **4** in 90% acetone is the corresponding carbinol.<sup>14b</sup> A control experiment on the rate of hydrochloric acid catalyzed addition of water from the solvent to 9-vinylanthracene was not conducted. Consequently, a reaction sequence analogous to that of eq 12, where the  $\alpha$ -9-anthrylethyl cation **25** forms reversibly



9-vinylanthracene, where the reverse reaction is catalyzed by the HCl formed in the reaction, cannot be excluded. The  $\alpha$  values of Table VII are therefore either identical with or lower than the corresponding  $\alpha^S$  values for **4**.

Comparison of the  $\alpha^S$  value for the solvolysis of **3** with the  $\alpha$  value for the solvolysis of **4** shows that the selectivity of the saturated compound at 0 °C is 2.4 times higher than that of the vinylic compound at 140 °C. This is shown graphically in Figure 5, which shows that the relative decrease of the rate constant with the progress of the reaction for 0.0097 M of **4** is larger than for a higher concentration (0.038 M) of **3**. This comparison suffers from two drawbacks: first, from the uncertainty discussed above concerning a possible elimination from **25**; second, from the widely different temperatures at which the solvolyses of **3** and **4** were conducted. However, if the trend for a lower selectivity at higher temperature which is indicated by the data of Table VII is real, the selectivity of **4** will be much closer to that of **3** or even lower at the same temperature.<sup>38</sup>

Table VI shows that **4** is  $6.9 \times 10^4$  more reactive than **3** in a solvent where the selectivities differ very little. It could be argued that this is another manifestation of Ritchie's "constant selectivity" rule<sup>11</sup> which was found to be applicable to the reactions of nucleophiles with various cations which differ much in their stabilities. However, since the reactivity of  $\alpha$ -arylvinyl



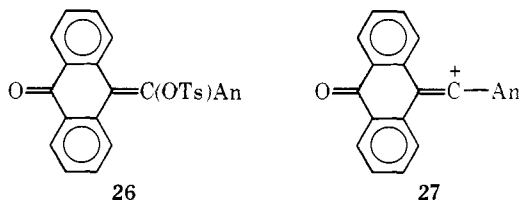
**Figure 5.**  $k_t/k_t^0$  values for the solvolyses in 90% acetone of (I) 0.038 M of **3** with 0.09 M 2,6-lutidine at 140 °C and (II) 0.0097 M of **4** at 0 °C.

halides is much more affected by ground-state effects than the reactivities of  $\alpha$ -arylalkyl halides,<sup>6</sup> reactivity–selectivity comparisons of the two classes of compounds are unjustified. Nevertheless, it is important that while calculations on simple systems suggest a much lower stability for the vinyl than for the trigonal cation,<sup>39</sup> the selectivity probe for the stability of the cations indicates that an  $\alpha$ -arylvinyl cation with a bulky  $\alpha$ -aryl group (**20**) is almost as stable as its sp<sup>2</sup>-hybridized analogue (**25**).<sup>48</sup> We emphasized previously that shielding of the cationic orbital by the  $\beta$  substituents is mainly responsible for the selectivity of these ions<sup>6</sup> and we predict on the basis of the present data that  $\alpha$ -arylvinyl cations substituted by bulky  $\beta$  substituents will be more selective than their trigonal analogues.

The  $\alpha$  values in the three solvents decrease with an increase in the nucleophilicity of the solvent:<sup>33</sup>  $\alpha^S(90\% \text{ Me}_2\text{CO}) \sim \alpha(\text{AcOH}) > \alpha(90\% \text{ Me}_2\text{CO}) > \alpha(80\% \text{ EtOH})$ . This is the expected trend since the rate constant with the nucleophilic solvent appears in the denominator of the defining equation for  $\alpha$ . It is noteworthy that the solvent nucleophilicity more than compensates for the decrease of the dielectric constant in the solvent series, which should reduce the stability of the ion and consequently decrease  $\alpha$ .

**Solvent Effect.** An interesting feature of the solvolysis of  $\alpha$ -arylvinyl halides and tosylates is that in these reactions, which are clearly of the solvent-unassisted  $k_c$  type,<sup>40</sup> the Winstein–Grunwald  $m$  values change strongly with changes in the bulk of the  $\beta$  substituents.<sup>6</sup> The  $m$  value of 0.77 at 120 °C for compound **3** and the extrapolated value of 1.01 at 25 °C support this generalization. The  $m$  value is higher than those for any other  $\alpha$ -arylvinyl halide, except one.<sup>41</sup> The importance of steric effects is realized when the  $m$  value for **3** is compared with the  $m$  value of 0.28 in aqueous ethanol at 105

°C for the anthronylidene derivative **26**.<sup>6</sup> The  $\alpha$ -9-anthryl group of **3** is perpendicular to the vacant orbital in the ion **20** and the steric hindrance to solvation of either the ion or the transition state for its formation is small. In contrast, in the structurally related compound **26** where a  $\beta$ -9-oxodihydroanthracene moiety is constrained into the plane of the C-OTs bond of **26** or the vacant orbital of the ion **27**, the steric



hindrance to solvation is high and this is reflected in the *m* values.<sup>6,13b</sup>

### Experimental Section

Melting points were determined with a Fisher-Johns or a Büchi apparatus and are uncorrected. NMR spectra were measured with a Varian T-60 or EM-360 instrument with tetramethylsilane as an internal standard. UV spectra were recorded with a Unicam SP 800 spectrophotometer, IR spectra with a Perkin-Elmer 337 spectrophotometer, and mass spectra on a MAT 311 instrument. Potentiometric titration was conducted with a PHM63 (Radiometer) instrument. TLC was carried out on a silica gel Kieselguhr-6F-25A plate, and elution was with light petroleum (bp 40–60 °C) which contained 2% ethanol in several cases.

**Solvents and Materials.** Acetic acid, containing 2–3% of acetic anhydride, was purified as previously described,<sup>42</sup> and sodium acetate solutions in acetic acid were prepared by dissolving analytical grade dry Na<sub>2</sub>CO<sub>3</sub> in AcOH. *O*-Deuterioacetic acid was prepared according to Weltner<sup>43</sup> and contained (by NMR) ca. 3% of the undeuterated acid. Acetone was dried according to Vogel<sup>44</sup> and acetone (90% v/v) was prepared with conductivity water. Ethanol was purified according to Lund and Bjerrum,<sup>45</sup> and EtOH (80% v/v) was prepared with conductivity water. Tetraethylammonium chloride (Fluka) was crystallized from acetonitrile-acetone, filtered rapidly, and dried for 24 h at 100 °C over P<sub>2</sub>O<sub>5</sub>. Tetrabutylammonium acetate was prepared according to the literature.<sup>46</sup> Catechyl phosphorus trichloride was prepared according to Gross and Gloede,<sup>19</sup> and 9-acetylanthracene and 9-vinylnanthracene were prepared according to Bergmann and Katz.<sup>47</sup>

**9-( $\alpha$ -Chlorovinyl)anthracene (3).** 9-Acetylanthracene (7.7 g, 35 mmol) was melted together with catechyl phosphorus trichloride (8.6 g, 35 mmol), and the mixture was kept at 100 °C for 5 h. After cooling, ether (100 mL) was added, ice-cooled water was added slowly, until the evolution of HCl ceased, and the two layers were separated. After additional extraction with ether (50 mL), the combined organic fraction was washed with aqueous NaHCO<sub>3</sub> and with water and dried (MgSO<sub>4</sub>), the solvent was evaporated, the remainder was distilled, and the fraction boiling at 160–170 °C at 1 mmHg was collected. The best results were obtained with a preheated, short distillation system and when the rate of distillation was such that the product was slowly accumulated in the receiver. Crystallization of the oil obtained from ethanol gave 4.5 g (54%) of yellow crystals of 9-( $\alpha$ -chlorovinyl)anthracene, mp 60–61 °C.

Similar yield was obtained when thin layer chromatography (eluent: petroleum ether, bp 40–60 °C) was used instead of distillation, and the main fraction was extracted with methylene chloride and crystallized from ethanol.

$\delta$  (CDCl<sub>3</sub>) 5.58 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 6.17 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 7.28–8.42 (9 H, m, Ar);  $\lambda_{\max}$  (EtOH) 254 nm ( $\epsilon$  154 000), 320 (1500), 333 (3200), 346 (6400), 367 (9300), 386 (8100);  $\nu_{\max}$  (KBr) 3050–2850 (C–H, s), 1640 cm<sup>-1</sup> (C=C, vs); *m/e* 240, 238 (M – <sup>37</sup>Cl, M – <sup>35</sup>Cl, 7.6%, 22.6%), 203 (anthryl-<sup>+</sup>C=CH<sub>2</sub>, B), 202 (anthryl-C $\equiv$ CH, 74%), 175 (anthracene – 3 H, 4.7%).

Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Cl: C, 80.50; H, 4.61; Cl, 14.88. Found: C, 80.29; H, 4.66; Cl, 14.23.

Preliminary experiments to prepare 9-( $\alpha$ -chlorovinyl)anthracene from the reaction of 9-acetylanthracene and phosphorus pentachloride gave a black oil, which according to the NMR contained **3** admixed with additional compound.

**9-Ethynylantracene (7).** 9-( $\alpha$ -Chlorovinyl)anthracene (4.5 g, 19 mmol) was added in small portions to a solution of 60 mM of sodamide in liquid ammonia (50 mL) at –33 °C. After 3 h water was added slowly, the solid obtained was filtered, dissolved in methylene chloride, washed with acetic acid and then with water, and dried (MgSO<sub>4</sub>), and the solvent was evaporated, giving 2.87 g (75%) of yellow crystals of 9-ethynylantracene: mp 71–75 °C;  $\delta$  (CDCl<sub>3</sub>) 3.9 (1 H, s,  $\equiv$ CH), 7.2–8.7 (9 H, m, Ar);  $\lambda_{\max}$  (EtOH) 258 nm ( $\epsilon$  150 000), 250 sh (82 000), 325 (1200), 342 (3100), 355 (7000), 378 (11 200), 400 (11 200);  $\nu_{\max}$  (KBr) 3280 cm<sup>-1</sup> (C $\equiv$ CH, s), 3050–2840 (C–H, s), 1640 (C=C, s);  $\nu_{\max}$  (Nujol) 2100 cm<sup>-1</sup> (C $\equiv$ C, w); *m/e* 202 (M, 65%), 201 (M – H, 100%), 176 (anthracene – 2 H, 3.2%), 175 (anthracene – 3 H, 16%), 152 (C<sub>12</sub>H<sub>8</sub>, 10%), 101 (M<sup>2+</sup>, 14%).

Anal. Calcd for C<sub>16</sub>H<sub>10</sub>: C, 95.02; H, 4.98. Found: C, 94.94; H, 4.81.

A lower yield was obtained if the base to substrate ratio was 2:1, when the sodamide concentration was 20 mM, or when the reaction time was shorter (30 min).

**9-( $\alpha$ -Bromovinyl)anthracene (5).** To a solution of 0.05 M of hydrogen bromide in dry chloroform (100 mL) at 0 °C, 9-ethynylantracene (1 g, 5 mmol) and mercuric bromide (1.8 g, 5 mmol) were added. After 30 min the mixture was washed with water, then with NaHCO<sub>3</sub> and again with water, and dried (MgSO<sub>4</sub>). The solvent was evaporated, and the oil obtained was purified by thin layer chromatography, in an analogous way as described for the corresponding vinyl chloride. Since the *R<sub>f</sub>*'s of 9-( $\alpha$ -chlorovinyl)anthracene and of 9-( $\alpha$ -bromovinyl)anthracene are identical, this method cannot be used for separation of the two compounds, and the 9-ethynylantracene should be carefully purified from traces of the 9-( $\alpha$ -chlorovinyl)anthracene precursor.

Crystallization of the solid obtained from the TLC from ligroin gave orange crystals, mp 78–79 °C, of 9-( $\alpha$ -bromovinyl)anthracene:  $\delta$  (CDCl<sub>3</sub>) 5.95 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 6.38 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 7.25–8.65 (9 H, m, Ar);  $\lambda_{\max}$  (EtOH) 255 nm ( $\epsilon$  126 000), 320 (1200), 335 (3000), 352 (6300), 370 (8500);  $\nu_{\max}$  (KBr) 3050–2850 (C–H, s), 1660–1640 (C=C, s), 730 cm<sup>-1</sup> (C–Br, vs); *m/e* 283, 281 (M – <sup>81</sup>Br, M – <sup>79</sup>Br, 30%, 30%), 203 (anthryl-<sup>+</sup>C=CH<sub>2</sub>, 52%), 202 (anthryl-C $\equiv$ CH, 100%), 201 (anthryl-C $\equiv$ C<sup>+</sup>, 100%), 176 (anthracene – C<sub>2</sub>H<sub>2</sub>, 9%), 100 (B<sup>2+</sup>, 94%).

Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Br: C, 67.83; H, 3.88; Br, 28.26. Found: C, 67.90; H, 3.99; Br, 28.65.

**9-( $\alpha$ -Ethoxyvinyl)anthracene (8).** An ampule containing a solution of 9-( $\alpha$ -chlorovinyl)anthracene (238 mg, 1 mmol) in 25 mL of 0.08 M of 2,6-lutidine in 80% EtOH (v/v) was kept at 120 °C for 3 h. The mixture was cooled, water was added, the mixture was extracted twice with methylene chloride, the organic phase was washed with aqueous ammonium chloride solution, then with water, and dried (CaCl<sub>2</sub>), and the solvent was evaporated. NMR showed that the oil formed is a mixture of 30% 9-acetylanthracene and 70% 9-( $\alpha$ -ethoxyvinyl)anthracene. Purification by TLC using 98% petroleum ether (bp 40–60 °C)–2% methanol as eluent gave ca. 100 mg of crude 9-( $\alpha$ -ethoxyvinyl)anthracene, which crystallized from ethanol as yellow crystals: mp 97 °C;  $\delta$  (CDCl<sub>3</sub>) 1.30 (3 H, t, *J* = 14 Hz, Me), 4.03 (2 H, q, *J* = 14 Hz, CH<sub>2</sub>), 4.31 (1 H, d, *J* = 3.5 Hz,  $\beta$ -CH), 4.80 (1 H, d, *J* = 3.5 Hz,  $\beta$ -CH), 7.2–8.4 (9 H, m, Ar);  $\lambda_{\max}$  (EtOH) 253 nm ( $\epsilon$  150 000), 315 (1300), 328 (2700), 344 (5800), 362 (8800), 381 (8000);  $\nu_{\max}$  (KBr) 1620 cm<sup>-1</sup> (C=C, vs), 1270 (C–O, vs), 1060 (C–O, vs); *m/e* 248 (M, 37%), 220 (anthryl-COMe, 41%), 202 (anthryl-C $\equiv$ CH, 25%), 192 (C<sub>14</sub>H<sub>8</sub>O, 100%), 176 (anthryl-H, 4%), 150 (anthracene – C<sub>2</sub>H<sub>2</sub>, 8%).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O: C, 87.06; H, 6.49. Found: C, 87.28; H, 6.50.

**9-( $\alpha$ -Acetoxyvinyl)anthracene (9).** A mixture of 9-( $\alpha$ -chlorovinyl)anthracene (239 mg, 4 mmol) and silver acetate (167 mg, 6.68 mmol) in acetic acid (25 mL) was refluxed for 4 h. The mixture was then cooled, water was added, and the organic material was extracted twice with methylene chloride. The organic phase was washed with a NaHCO<sub>3</sub> solution and then with water and dried (CaCl<sub>2</sub>) and the solvent was evaporated. The oil obtained was purified by TLC, using 98% petroleum ether (bp 40–60 °C)–2% methanol. The main fraction was extracted with methylene chloride, and the solvent was evaporated. White crystals, mp 72–75 °C of 9-( $\alpha$ -acetoxyvinyl)anthracene were obtained:  $\delta$  (CDCl<sub>3</sub>) 2.00 (3 H, s, OAc), 5.25 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 5.80 (1 H, d, *J* = 2 Hz,  $\beta$ -CH), 7.25–8.55 (9 H, m, Ar);  $\lambda_{\max}$  255 nm ( $\epsilon$  142 000), 322 (1220), 330 (1800), 347 (5600), 365 (8200), 384 (7100);  $\nu_{\max}$  (Nujol) 3050–2850 (C–H, s), 1700 (C=O, vs), 1650

cm<sup>-1</sup> (C=C, s); *m/e* 262 (M, 1%), 238 (M -  $\dot{C}H_2$ , 13%), 202 (anthryl-C $\equiv$ CH, 100%), 177 (anthryl<sup>+</sup>, 15%).

Anal. Calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>: C, 82.42; H, 5.38. Found: C, 82.14; H, 5.29.

**9-( $\beta$ -Bromovinyl)anthracene. A. 9-( $\alpha,\beta$ -Dibromoethyl)anthracene.**

To a cooled solution of 9-vinylanthracene (2 g, 10 mmol) in carbon tetrachloride (50 mL) a solution of bromine (1.6 g, 10 mmol) in carbon tetrachloride (20 mL) was added with mixing. The bromine color disappeared immediately, and at the end of the reaction when it was sustained for a longer time the solution was washed rapidly with an aqueous sodium thiosulfate solution, then with water, and dried (MgSO<sub>4</sub>) and the solvent was evaporated. The solid obtained was crystallized from methanol, giving 2.65 g (72%) of orange crystals of 9-( $\alpha,\beta$ -dibromoethyl)anthracene: mp 112 °C;  $\delta$  (CDCl<sub>3</sub>) 4.35 (2 H, m, CH<sub>2</sub>Br), 6.50 (1 H, q, CH), 7.1-8.8 (9 H, m, Ar);  $\lambda_{max}$  (EtOH) 258 nm ( $\epsilon$  120 000), 348 (4600), 367 (6100), 380 (7600), 400 (6000);  $\nu_{max}$  (KBr) 1640 (C=C, vs), 740 cm<sup>-1</sup> (C-Br, vs); *m/e* 365, 363, 361 (M - <sup>81</sup>Br<sub>2</sub>, M - <sup>81</sup>Br<sup>79</sup>Br, M - <sup>79</sup>Br<sub>2</sub>, 1%, 2%, 1%), 284, 282 (anthryl - C<sub>2</sub>H<sub>2</sub>Br for <sup>79</sup>Br and <sup>81</sup>Br, 11%, 11%), 202 (anthryl-C $\equiv$ CH, 68%), 176 (anthracene - 2 H, 6%), 150 (anthracene - C<sub>2</sub>H<sub>2</sub>, 4%), 82, 80 (H<sup>81</sup>Br, H<sup>79</sup>Br, 47%, 47%).

Anal. Calcd for C<sub>16</sub>H<sub>12</sub>Br<sub>2</sub>: C, 52.74; H, 3.20; Br, 43.90. Found: C, 52.84; H, 3.24; Br, 43.87.

The multiplet at  $\delta$  4.35 is composed of six lines and is unsymmetrical, suggesting an appreciable barrier for free rotation around the C $\alpha$ -C $\beta$  bond.

**B. 9-( $\beta$ -Bromovinyl)anthracene.** A mixture of 9-( $\alpha,\beta$ -dibromoethyl)anthracene (3.65 g, 10 mmol) and potassium *tert*-butoxide (1.13 g, 10 mmol) in *tert*-butyl alcohol (50 mL) was stirred for 24 h at room temperature. Water (50 mL) was added, and the mixture was extracted with chloroform. The organic phase was washed with aqueous NaHCO<sub>3</sub> solution and with water and dried (MgSO<sub>4</sub>) and the solvent was evaporated. The remaining oil was purified by TLC with petroleum ether (bp 40-60 °C) as the eluent. The second fraction from the top of the TLC plate was extracted by methylene chloride, the solvent was evaporated, and the remainder was crystallized twice from ethanol, giving 0.9 g (25%) of crystals: mp 100-101 °C;  $\delta$  (CDCl<sub>3</sub>) 6.58 (1 H, half of a AA'BB'q, *J* = 14 Hz, CH), 7.2-8.2 (11 H, m, Ar + CH);  $\lambda_{max}$  (EtOH) 255 nm ( $\epsilon$  138 000), 333 (2600), 350 (5600), 367 (8600), 386 (7600);  $\nu_{max}$  (KBr) 1640 cm<sup>-1</sup> (C=C, s), 750 (C-Br, s); *m/e* 284, 282 (M - <sup>81</sup>Br, M - <sup>79</sup>Br, 13%, 13%), 203 (anthryl-C $\equiv$ CH<sub>2</sub>, 100%), 202 (anthryl-C $\equiv$ CH, 67%), 176 (anthracene - 2 H, 4%).

Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Br: C, 67.40; H, 3.86; Br, 28.07. Found: C, 67.07; H, 3.60; Br, 27.59.

In contrast to the  $\alpha$ -bromo isomer **5**, 9-( $\beta$ -bromovinyl)anthracene is inert to acetolysis in AcOH/NaOAc for 25 h at 120 °C.

**Kinetic Procedure.** The sealed ampules technique was used. In AcOH and in 90% acetone stock solutions of **3** and the base were prepared. However, the low solubility of **3** in aqueous ethanol required the preparation of a stock solution of **3** and the base in absolute ethanol, and ethanol and conductivity water were added separately to each ampule.

The content of each ampule was first titrated for Cl<sup>-</sup> determination and then extracted with methylene chloride and dried and the NMR determinations were performed. In the reactions with excess Cl<sup>-</sup> which were followed directly by NMR, or in the determination of the product distribution where decomposition of primary products was possible, the NMR determination was performed on the crude reaction mixture.

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