preferred trans bending of ethylene.[25] The same explanation has been given, in part, by K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970).

(23) For a summary, see R. A. Firestone, *Tetrahedron*, **33**, 3009 (1977).

(24) During the course of this work, we became aware of independent investigations of ethylene bending distortions[25] and an energy decomposition analysis of the addition of the hydrogen atom to acetylene.[26]

(25) W. V. Volland, E. R. Davidson, and W. T. Borden, *J. Am. Chem. Soc.*, in press.

(26) S. Nagase and C. W. Kern, submitted for publication.

(27) On leave from the University of Pavia, Pavia, Italy.

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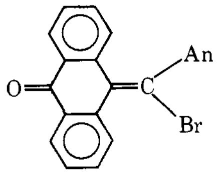
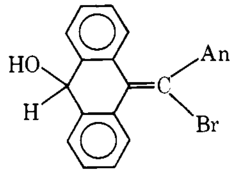
Vinylic Cations from Solvolysis. 27.[1]
Solvolysis of an Optically Active Vinyl Bromide

Sir:

Two conflicting reactivity-selectivity relationships exist for the reaction of carbonium ions with nucleophiles. For solvolytically generated ions, their selectivities, measured by the relative reaction rates with two nucleophiles, e.g., $k_{N_3^-}/k_{H_2O}$, increase with the increased solvolytic reactivity of the precursor RX.[2] By Hammond's postulate, this reflects a reactivity-selectivity relationship (i.e., lower reactivity or higher stability is associated with higher selectivity), a well-documented phenomenon.[3] In contrast, Ritchie reported many cases of a "constant selectivity" relationship for the directly measured reaction of stable carbonium ions with nucelophiles, where the rate ratio for two nucleophiles was independent of the cation.[4] Ritchie[4,5] ascribes part of this discrepancy to the derivation of the selectivity term in solvolysis from the product ratio in a competitive reaction of two nucleophiles. Since the products are probably derived from both free ions and ion pairs, their ratio does not measure the selectivity of a single species.



1



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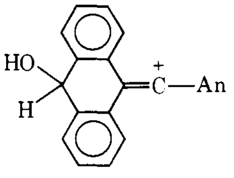


3

An = p-MeOC$_6$H$_4$

This hypothesis can be tested if the selectivity constants could be measured when the products are formed only from a solvolytically generated free cation. For such relatively stable cations, the recombination of R^+ and X^- can compete with capture of R^+ by the solvent SOH. The accompanying common ion rate depression[2c,6] is associated with capture of only the *free* cation by X^- and SOH[6b,c] and the derived "mass law constant", $\alpha = k_{X^-}/k_{SOH}$, is a selectivity constant. The α values for the benzhydryl system obey a reactivity-selectivity relationship.[2c,6]

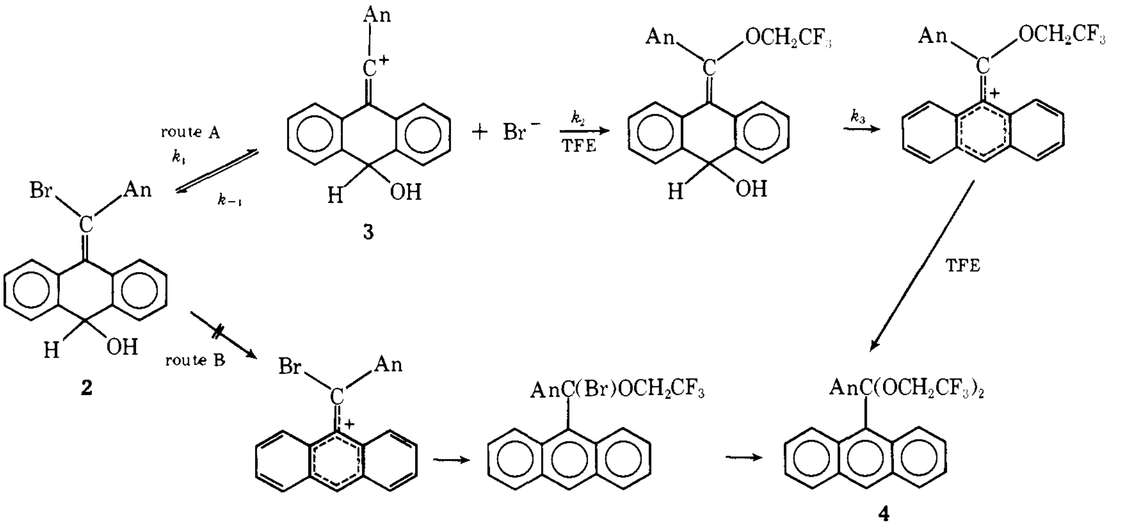
Moreover, the solvolysis rate constants which are an indirect measure of the reactivity of R^+ may differ from the ionization rate constants owing to ion-pair return,[6b,c,7] and its extent should be known for evaluation of any reactivity-selectivity relationship.

Solvolysis of triarylvinyl halides is accompanied by an extensive common ion rate depression.[8] E.g., the anthronylidene derivative **1** gives very high α values and both **1** and its p-tolyl analogue form products almost exclusively from the free ion.[8a,9] The extent of ion-pair return for several α-arylvinyl systems was evaluated by comparing the solvolysis and the cis-trans isomerization rates.[10] The more convenient comparison of titrimetric (k_t) and polarimetric (k_α) constants for optically active RX[6c,7] is usually inapplicable for the planar vinyl systems, although it was recently applied for an optically active allene.[11]

We report now the first application of this tool for a vinylic bromide which is structurally related to **1**. Reduction of **1** with $LiAlH_4$ in ether or THF in the presence of (−)-quinine, followed by chromatographic separation, gave optically active 9-(α-bromoanisylidene)-10-hydroxy-9,10-dihydroanthracene (**2**).[12] The highest rotations observed so far are $[\alpha]_{436}$ +97.5° in 2,2,2-trifluoroethanol (TFE) and $[\alpha]_{436}$ −65° in $CDCl_3$.

The solvolysis of 0.002 M **2** in TFE buffered by 0.004 M 2,6-lutidine at 49.6 °C is described in Figure 1. Extensive common ion rate depression by the formed Br^- reduces the integrated first-order rate constant k_t at 75% reaction to 25% of the extrapolated initial value k_t^0 of $3.68 \times 10^{-5}\ s^{-1}$ (line B). A selectivity constant $\alpha = 3205 \pm 99\ M^{-1}$ for competition between Br^- and TFE[13] was calculated by assuming that the product is formed only from the free vinyl cation **3**. The rate coefficient in the presence of 0.0092 M Bu_4NBr remains constant (line A) but its value ($1.52 \times 10^{-6}\ s^{-1}$) is ~4% of k_t^0, indicating that ≥96% of the product is formed from **3**.[14] The main product is anisyl 9-anthrylbis(trifluoroethyl) acetal (**4**).

Scheme I



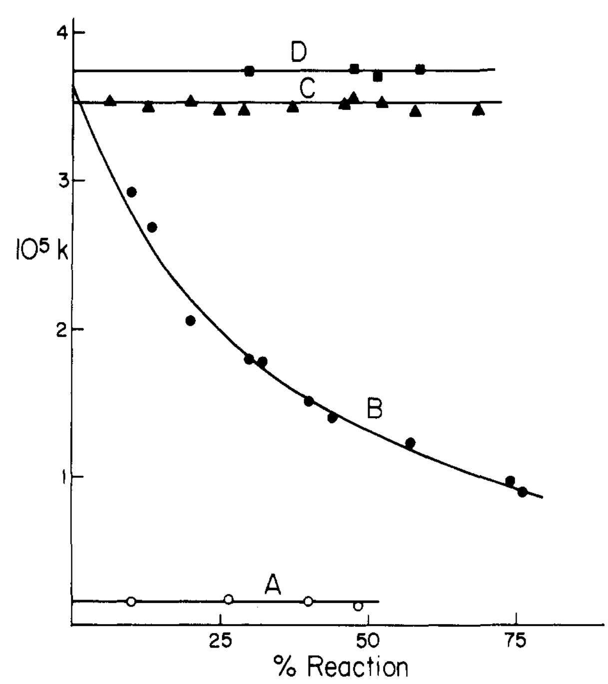
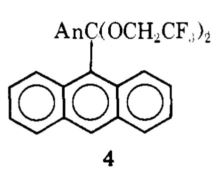


Figure 1. Change of the integrated first-order constants k_t and k_α with the progress of the reaction of 0.002 M **2** in the presence of 0.004 M 2,6-lutidine in TFE at 49.6 °C: A, k_t in the presence of 0.0092 M Bu_4NBr; B, k_t without added Br^-; C, k_α without added Br^-; D, k_α in the presence of 0.01 M Bu_4NBr.

9-Anisoylanthracene (**5**) is formed at higher reaction temperature.

The loss of optical activity is a first-order process, both in the absence (line C) and in the presence (line D) of 0.01 M Bu_4NBr. The $10^5\ k_\alpha$ values are 3.57 and 3.71 s^{-1}, respectively, almost identical with k_t^0.

Loss of optical activity by a rate-determining ionization of the secondary hydroxy group (route B, Scheme I) is excluded for three reasons: (i) by the fit of the experimental points to line B which was calculated by using k_t^0 and α for the bromide ionization model; (ii) by the similarity of k_t^0 for **2** and for **1** ($k_t^0(\mathbf{1}) = 1.08 \times 10^{-5}\ s^{-1}$ in TFE at 35 °C[15]); (iii) since the rate constant for the rearrangement of the hydrogen analogue **6** to a 9-substituted anthracene, which presumably proceeds via an initial ionization of the hydroxy group to the ion **7**, is $k_{rear} = 8.75 \times 10^{-6}\ s^{-1}$, i.e., ~4 times lower than k_t^0 for **2**.[16]



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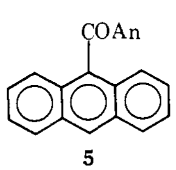

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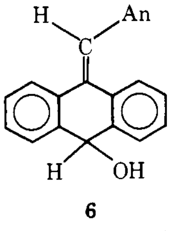

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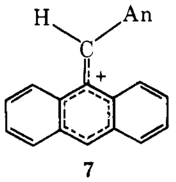

7

The extent of common ion rate depression, together with the identity of k_t^0 and k_α within the experimental error,[17] excludes both product formation from ion pairs and ion-pair return with racemization in TFE. Hence, the solvolysis proceeds by route A of Scheme I via the nonchiral ion **3**. Steps k_1, k_{-1}, and k_2 amount to Ingold's simplified ionization-solvolysis scheme.[6a] The isolation of **4** indicates that k_3 is fast compared with the rate of formation of the vinylic solvolysis product.

The present work confirms the applicability of the k_α-k_t probe for evaluating the extent of ion-pair return in vinylic solvolysis. The results agree with previous results that ion-pair return in α-arylvinyl cations is not very extensive in moderate to good ionizing solvents.[18]

If a similar behavior would be observed for other 9-(α-bromo-*p*-substituted arylidene)-10-hydroxy-9,10-dihydroanthracenes, a comparison of the resulting α values would immediately give the selectivity relationship governing the behavior of solvolytically generated sterically similar free vinyl cations. The solvolysis of **2** and related optically active vinylic systems in solvents where $k_\alpha \geqslant k_t$ is under active study.

Acknowledgment. We gratefully acknowledge the support of this research by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel.

References and Notes

(1) Part 26: Z. Rappoport, P. Shulman, and M. Thuval (Shoolman), *J. Am. Chem. Soc.*, **100,** 7041 (1978).

(2) (a) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Am. Chem. Soc.*, **88,** 2594 (1966); (b) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *ibid.*, **93,** 4821 (1971); (c) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(3) A. Pross, *Adv. Phys. Org. Chem.*, **14,** 69 (1977); B. Giese, *Angew. Chem., Int. Ed. Engl.*, **16,** 125 (1977). However, see C. D. Johnson, *Chem. Rev.*, **75,** 755 (1975).

(4) C. D. Ritchie, *Acc. Chem. Res.*, **5,** 348 (1972); C. D. Ritchie and P. O. I. Virtanen, *J. Am. Chem. Soc.*, **94,** 4966 (1972); C. D. Ritchie in "Solute–Solvent Interactions", Vol. 2, J. F. Coetzee and C. D. Ritchie, Eds., pp 259–267, Marcel Dekker, New York, 1976.

(5) C. D. Ritchie, *J. Am. Chem. Soc.*, **93,** 7324 (1971).

(6) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1968, pp 483–493; (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78,** 328 (1956); (c) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19,** 109 (1965).

(7) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. II, M. Szwarc, Ed., Wiley-Interscience, New York, 1973.

(8) For review of this behavior see (a) Z. Rappoport, *Acc. Chem. Res.*, **9,** 265 (1976); (b) P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, "Vinyl Cations", Academic Press, New York, in press.

(9) Y. Apeloig, J. Greenblatt, and Z. Rappoport, unpublished results.

(10) (a) Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **96,** 6428 (1974); (b) *ibid.*, **97,** 821 (1975); (c) *ibid.*, **97,** 836 (1975).

(11) D. Scheffel, P. J. Abbott, G. J. Fitzpatrick, and M. D. Schiavelli, *J. Am. Chem. Soc.*, **99,** 3769 (1977).

(12) Satisfactory analytical and spectroscopic data were obtained for all the new compounds.

(13) Following Ingold[6a] α does not take into account the solvent concentration. When the concentration of pure TFE is taken into account, the dimensionless α is ~44 000.

(14) Potentiometric titration was used to obtain the k_t values in the absence of added Br^- or in the presence of 0.092 M Bu_4NBr. The method is not very accurate at higher concentrations of Br^-. The different UV spectra of **2** and **4** enabled a spectrophotometric followup of the **2** → **4** reaction in the presence of 0.1 M Bu_4NBr. The k_t/k_t^0 ratio is ~0.01; i.e., ⩾99% of the products are derived from the free ion.

(15) Z. Rappoport and J. Kaspi, *J. Am. Chem. Soc.*, **96,** 4518 (1974).

(16) This is probably the route for loss of optical activity of **2** in AcOH, where $k_\alpha \gg k_t$ and $k_{rear}(\mathbf{6}) \gg k_t^0(\mathbf{2})$.

(17) The extrapolated k_t^0 value is very sensitive to the accuracy of the first kinetic points. We hope to overcome this difficulty in cooperation with Dr. G. Lodder from the University of Leiden by an independent measurement of k_t^0 by following radioactive Br^- incorporation. Until then, the similarity of k_t^0 and k_α should be regarded only as approximate.

(18) The fractions of ion-pair return 1-F are 0.63 for α-bromo-β-deuterio-*p*-methoxystyrene in AcOH,[10a] and 0.47[10b] and 0.32–0.39[10c] for 1,2-dianisyl-2-phenylvinyl bromide in AcOH and in 80% EtOH, respectively.

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On the Reported Selectivity of Olefin Bromination

Sir:

In a recent issue of the *Journal of the American Chemical Society* there appeared a report about a novel selective bro-