striking. Although both compounds have a set of four nitrogens held with their lone pairs directed outward, 5·+ shows no more stability than an ordinary tertiary amine cation, having completely irreversible cv spectrum,[2] an unusually positive $E_{1/2}$ value,[2] and a first ionization potential,[5,20] which is higher than that of adamatane itself.[20] It is clear that the number of nitrogens over which the positive charge can be spread is not as important in observing the unique stability of 1·+ and 2·+ as is the necessity for conjugating these nitrogens with C–C single bonds in favorable geometry for $n–\sigma_{CC}$ interaction. Apparently the C–N bonds of 5, which are in the best possible geometry for $n–\sigma_{CN}$ interaction, simply are too low lying to interact effectively with the nitrogen lone pair electrons.[2,5]

(20) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, 50, 654 (1969).

## Experimental Section

The preparation and purification of the materials has already been described,[2] as have the pes[5] and esr[20] experimental and data handling techniques employed.

**Esr Spectrum of 2·+.** A 5 × $10^{-3}$ M solution of 2 in butyronitrile was cooled in an ethanol slush (*ca.* −100°), with argon continuously bubbling through it. One equivalent of solid 3 was added, and the solution was agitated to hasten reaction. The solution rapidly developed a dark purple color. The mixture was transfered to a cooled 3-mm o.d. glass tube by forcing it through a steel capillary tube with pressure from the argon bubbler. After sealing, esr spectra were run at low temperature in the usual way. The purple color and the esr spectrum of 2·+ fade very rapidly above −80°.

(20) S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Amer. Chem. Soc.*, 96, 2916 (1974).

# Vinylic Cations from Solvolysis. XXII.[1] High Stereoselectivity in the Synthesis of and Ion Pair Return in the Solvolysis of (E)-α-Bromo-β-deuterio-p-methoxystyrene

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**Abstract:** Addition of HBr to α-anisyl-β-deuterioacetylene (**7-D**) in several solvents of low dielectric constants gives a mixture of (E)- and (Z)-α-bromo-β-deuterio-p-methoxystyrenes (**4-E** and **4-Z**) with little or no preference for the E isomer. More **4-E** is formed in chloroform in the presence of Et$_4$NBr, and the highest selectivity (80% **4-E**: 20% **4-Z**) is obtained in the presence of HgBr$_2$. The selectivity is ascribed to a syn addition of molecular or ion-paired HBr to **7-D**, while the nonselective addition takes place *via* the free vinyl cation **5-D**. Solvolysis of a mixture of **4-E** and **4-Z** in 50% EtOH gives mainly α-deuterio-p-methoxyacetophenone (**10-D**) and shows no 4-E ⇌ 4-Z isomerization. In AcOH, p-methoxyacetophenone (**10-H**) is formed exclusively, Et$_4$NBr enhances the solvolysis rate, a 4-E ⇌ 4-Z isomerization takes place during the solvolysis, the isotope effect $k$(**4-H**) $k$(60% **4-E** + 40% **4-Z**) is 1.21, and exchange of the vinylic deuterium with the solvent was not observed. It is suggested that the solvolysis proceeds *via* an ion pair which only gives products in 50% EtOH, while in AcOH 63% of the ion pairs give ion pair return to **4-E** and **4-Z** and 37% give **10-H**. The ion pair return in α-anisylvinyl bromides decreases on decreasing the bulk of the β substituents in aqueous EtOH, but the return in AcOH is insensitive to this factor. This is discussed in terms of capture and dissociation of the ion pairs.

The intermediacy of ion pairs in the SN1 solvolysis of vinylic substrates was suggested in several cases,[2,3] but quantitative information regarding the extent of ion pair return is scarce.[3] This is mainly due to the absence of an easy method for evaluating such return, which will be analogous to the loss of optical activity for evaluating ion pair return in the solvolysis of saturated substrates.[4]

We recently suggested[1,5] that a cis–trans isomerization of the unreacted vinyl halide can serve as such a tool for detecting ion pair return in vinylic solvolysis, depending on three prerequisites. (a) It should be shown that the isomerization is not due to a non-SN1 reaction, such as electrophilic addition–elimination (Ad$_E$–E).[6] (b) For SN1 reactions account should be taken of possible isomerization *via* external ion return. (c) The vinyl cation should be as close to symmetrical as possible. Capture of the ion by nucleophiles occurs from its less hindered side,[7] and the ion pair return may be hidden, or the extent of cis–trans isomerization will be low, if the capture

(1) Part XXI: Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, in press.
(2) (a) A. C. Day and M. C. Whiting, *J. Chem. Soc. B*, 991 (1967); (b) Z. Rappoport and Y. Apeloig, *Isr. J. Chem.*, 7, 33p (1969); (c) R. C. Macomber, *J. Amer. Chem. Soc.*, 92, 7101 (1970); (d) C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, 54, 2528 (1971); (e) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 92, 228 (1970); 93, 1941 (1971); (f) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, 94, 3626 (1972); (g) T. C. Clarke and R. G. Bergman, *ibid.*, 94, 3627 (1972); (h) R. H. Summerville and P. v. R. Schleyer, *ibid.*, 94, 3629 (1972); 96, 1110 (1974); (i) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *ibid.*, 96, 1100 (1974).
(3) (a) G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968); (b) *J. Chem. Soc. B*, 374 (1971).
(4) For an extensive review dealing with ion pairs in solvolysis reactions, see 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, N. Y., 1973.
(5) Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, in press.
(6) (a) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 90, 6515 (1968); (b) W. M. Schubert and G. W. Barfknecht, *ibid.*, 92, 207 (1970); (c) Z. Rappoport, T. Bässler, and M. Hanack, *ibid.*, 92, 4985 (1970).
(7) (a) Z. Rappoport and M. Atidia, *J. Chem. Soc., Perkin Trans. 2*, 2316 (1972); (b) A. Pross and Z. Rappoport, unpublished results.

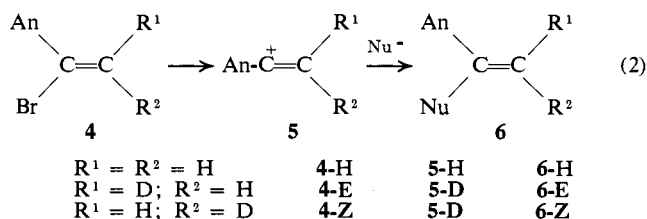occurs with high specificity from one side of the cationic orbital.

Quantitative estimate of the internal return as a function of the leaving group and the solvent was achieved in this way for the 1,2-dianisyl-2-phenylvinyl system 1.[1,5] The $Ad_E$–E route was excluded, account was taken of the extensive external ion return, and the triarylvinyl cation 2 is nearly symmetrical to approach of the nucleophile (Nu⁻), resulting in a nearly 1:1 mixture of the cis and trans products 3-E and 3-Z[8] (eq 1). Internal re-

An–C=C → An–Ċ=C Nu⁻ →

2

(1)

3-E        3-Z
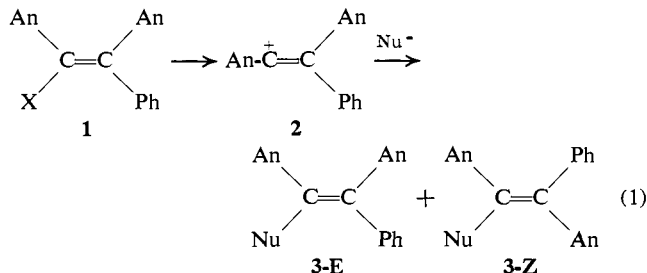
X = Br, Cl, OMs; An = $p$-MeOC₆H₄–; Nu = OAc, SR

turn is higher for the more nucleophilic leaving groups in AcOH,[1] and internal return is more important in carboxylic acid media as compared with that in aqueous EtOH.[5]

The solvolysis–isomerization is now investigated for the α-bromo-β-deuterio-$p$-methoxystyrene system (4) (eq 2). On the one hand, system 4 resembles system 1

An–C=C → An–Ċ=C Nu⁻ → C=C

4        5        6        (2)

| | | | |
|---|---|---|---|
| R¹ = R² = H | 4-H | 5-H | 6-H |
| R¹ = D; R² = H | 4-E | 5-D | 6-E |
| R¹ = H; R² = D | 4-Z | 5-D | 6-Z |

by having an activating α-anisyl group and a similar solvolysis rate,[9] and by having a highly symmetrical intermediate vinyl cation 5, thus fulfilling prerequisite c. On the other hand, this system is much less sterically hindered than 1, facilitating approach of an electrophile to 4, of a nucleophile to 5, or further reactions of the product 6. Several mechanistic criteria such as the solvent effect, the solvent isotope effect, the effect of the leaving group, and rate comparison with the rate of addition of AcOH to $p$-methoxystyrene were used previously to show that 4-H solvolyzes in AcOH almost completely via SN1 (fulfilling prerequisite a),[9] and this solvolysis does not show common ion rate depression[9,10] fulfilling prerequisite b.

## Results

**Synthesis.** The simplest stereoselective synthesis of 4-E or 4-Z[8] would be via addition of HBr to α-anisyl-β-deuterioacetylene (7-D) (eq 3). Since excess

AnC≡CD + HBr → C=C + C=C  (3)

7-D        4-E        4-Z
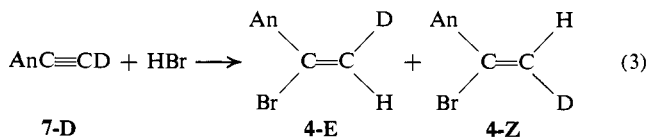
(8) For the $E$ and $Z$ nomenclature, see J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(9) Z. Rappoport and A. Gal, *J. Chem. Soc., Perkin Trans. 2*, 301 (1973).

(10) Z. Rappoport and A. Gal, *Tetrahedron Lett.*, 3233 (1970).

HBr can lead to a rapid 4-E ⇌ 4-Z isomerization via addition–elimination, the reaction was conducted with slight excess of 7-D. The product distributions are summarized in Table III in the Experimental Section.

Addition in AcOH was quantitative but nonselective, giving a 1:1 mixture of 4-E and 4-Z. The slight stereoselectivity for syn addition (52–55% of 4-E), which was obtained in benzene, CCl₄, CHCl₃, CH₂Cl₂, and petroleum ether at room temperature, increased somewhat at −20°, by using acetonitrile, or by addition of tetraalkylammonium bromides. Higher stereoselectivity was found on using the highest concentrations of R₄N⁺-Br⁻ in solvents having low dielectric constants at low temperature, but the addition rate decreased on increasing the salt concentration. On the other hand, low concentrations of HgBr₂ in chloroform increase both the addition rate and the stereoselectivity. The highest stereoselectivity obtained was in the presence of 0.002 M HgBr₂ in chloroform at −20°, where the product consisted of 80% of 4-E and 20% of 4-Z. This mixture was used for the isomerization studies.

Addition of dry HCl to 7-D in CH₂Cl₂ to form the vinyl chlorides 8-E and 8-Z was much slower than addition of HBr, but it gave similar results (see Experimental Section).

**Configuration Assignments.** Tobey's additivity rule,[11]
δ (ppm) = 5.27 + $\sigma_{cis\text{-}X}$ + $\sigma_{trans\text{-}X}$ + $\sigma_{gem\text{-}X}$, was applied for calculating the anticipated positions of the vinylic protons of 4-E and 4-Z. Space-filling models show that 4-H can achieve planarity, justifying the use of this rule. By using $\sigma_{gem\text{-}H}$ = 0, $\sigma_{cis\text{-}Br}$ = 0.33 ± 0.09, $\sigma_{trans\text{-}Br}$ = 0.53 ± 0.04,[11] and $\sigma_{cis\text{-}An}$ = 0.25 ± 0.08, $\sigma_{trans\text{-}An}$ = −0.18 ± 0.12 which are based on the data for styrene and $p$-methoxystyrene,[11,12] we calculated the δ values 6.05 ± 0.12 and 5.42 ± 0.21 ppm for the vinylic protons of 4-Z and 4-E, respectively. The observed shifts are within the error limits of the calculated values.

4-E        4-Z        8-H

8-E        8-Z
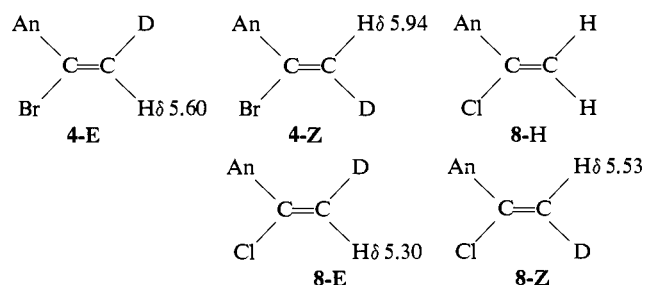
The stereochemistry of 8-E and 8-Z was assigned similarly. Additivity calculations gave δ 5.23 ± 0.20 and δ 5.61 ± 0.19 ppm for the protons of 8-E and 8-Z, respectively, which are close to the observed values of δ 5.30 and 5.53 ppm. However, we note that a recent paper by Blackborow[13] gave the opposite configurational assignments for compounds 9-E and 9-Z (X = Cl,

9-E        9-Z
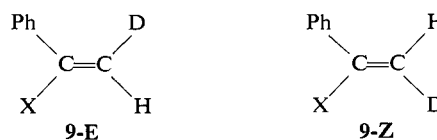
(11) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

(12) R. H. Wiley and T. H. Crawford, *J. Polym. Sci., Part A*, **3**, 829 (1965).

(13) J. R. Blackborow, *J. Chem. Soc., Perkin Trans. 2*, 1989 (1973).

**Table I.** Solvolysis and Isomerization of $\alpha$-Bromo-$p$-methoxystyrenes

| Substrate[a] | Solvent | $T$, °C | NaOAc, $M$ | Added salt, $M$ | $10^5 k_t^0$, sec$^{-1}$ | $10^5 k_t$, sec$^{-1}$ | $10^5 k_{isom}$, sec$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 65% 4-E + 35% 4-Z | 50% EtOH (v/v) | 80 | 0.023 | | | 6.80 ± 0.10 | |
| 4-H | AcOH | 120.3 | 0.087 | | 1.79[b,c] | | |
| 60% 4-E + 40% 4-Z | AcOH | 120.3 | 0.087 | | 1.48 (1.52)[c] | | |
| 60% 4-E + 40% 4-Z | AcOH | 120.3 | 0.047 | 0.04 $M$ Et$_4$NBr | | 2.37 ± 0.09[d] | |
| 60% 4-E + 40% 4-Z | AcOH | 120.3 | 0.087 | 0.04 $M$ Et$_4$NBr | | 2.37 ± 0.11 | |
| 60% 4-E + 40% 4-Z | AcOH | 120.3 | 0.087 | 0.08 $M$ Et$_4$NBr | | 3.03 ± 0.08 | |
| 80% 4-E + 20% 4-Z[e] | AcOH | 120.3 | 0.140 | | | | 2.52 ± 0.02 |

[a] [4] = 0.04 $M$. [b] Reported:[9] $k_t$ = (1.63 ± 0.02) × 10$^{-5}$ sec$^{-1}$ at 120.3° in the presence of 0.08 $M$ NaOAc. [c] From extrapolation according to eq 8. [d] Reported:[9] $k_t$ = 2.62 × 10$^{-5}$ sec$^{-1}$ for 4-H at 120.4° in the presence of 0.04 $M$ NaOAc and 0.04 $M$ NaBr. [e] [4] = 0.067 $M$.

Br, I). This was apparently based on assuming a trans addition of DBr to phenylacetylene, and the assignments are reversed if Tobey's additivity rule is applied to these compounds.[14]

Further support for the assigned geometries is based on elimination experiments. A 1:1 mixture of **4-E** and **4-Z** which was kept with 0.8 molar equiv of potassium *tert*-butoxide in *tert*-butyl alcohol at 82° gave after 48 hr $p$-methoxyphenylacetylene (**7-H**) in 80% yield, because of hydrogen–deuterium exchange of the formed **7-D** in the basic medium. In the vinylic proton region the signal at $\delta$ 5.94 disappeared almost completely, and only the signal at $\delta$ 5.60 (*ca.* 20%) was observed. Anti elimination from $p$-nitro-$\beta$-bromostyrene with $t$-BuO$^-$/$t$-BuOH is *ca.* 3000-fold faster than the syn elimination, and the deuterium isotope effects in eliminations from the $\beta$-halostyrenes in $t$-BuO$^-$/$t$-BuOH are $k_H/k_D$ = 3.2–4.6.[15] By analogy the proton at $\delta$ 5.60 ppm is that for **4-E**.

The isotope effect $k_{anti\ elimination}$(**4-Z**)/$k_{anti\ elimination}$ (**4-E**) in the reaction of equimolar concentrations of $t$-BuOK and a 1:1 mixture of **4-E** and **4-Z** was determined in a two-points run at 30% and at 60% reaction. It was calculated from eq 4 which is derived from the
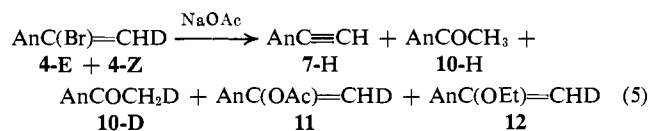
$$k_{anti\ elimination}(\text{4-Z})/k_{anti\ elimination}(\text{4-E}) =$$
$$\log[1/(1 - X_H)]/\log[1/(1 - X_D)] \quad (4)$$

second-order rate equations for elimination from **4-E** and **4-Z**, where $X_H$ and $X_D$ are the per cent reaction of **4-Z** and **4-E**, respectively, at each point. The isotope effect of 3.28 ± 0.12 at 82° is the quotient of the primary isotope effect [$k$(**4-H**)/$k$(**4-E**)] and the secondary isotope effect [$k$(**4-H**)/$k$(**4-Z**)].

**Solvolysis in 50% EtOH.** A 65:35 mixture of **4-E** to **4-Z** was solvolyzed in the presence of 0.025 $M$ NaOAc in 50% EtOH (v/v) at 80°, and the first-order rate constant is given in Table I. Nmr analysis after 3 hr showed 48% of a 65:35 mixture of **4-E** to **4-Z** (*i.e.*, no **4-E** ⇌ **4-Z** isomerization took place). The solvolysis products are $\alpha$-deuterio-$p$-methoxyacetophenone (**10-D**), $p$-methoxyacetophenone (**10-H**), and $p$-methoxyphenylacetylene (**7-H**), while the acetoxy and ethoxy signals which were observed after short reaction times were ascribed to the formation of $\beta$-acetoxy-$\alpha$-deuterio-$p$-methoxystyrene (**11**) and $\beta$-deuterio-$\alpha$-ethoxy-$p$-methoxystyrene (**12**) (eq 5). By comparing the product dis-

$$\text{AnC(Br)}=\text{CHD} \xrightarrow{\text{NaOAc}} \text{AnC}\equiv\text{CH} + \text{AnCOCH}_3 +$$
$$\text{4-E + 4-Z} \qquad\qquad \text{7-H} \qquad \text{10-H}$$
$$\text{AnCOCH}_2\text{D} + \text{AnC(OAc)}=\text{CHD} + \text{AnC(OEt)}=\text{CHD} \quad (5)$$
$$\text{10-D} \qquad\qquad \text{11} \qquad\qquad\qquad \text{12}$$

tributions after 48% reaction and after 20 half-lives (Table II), it is seen that at longer reaction times

**Table II.** Product Distribution from the Solvolysis of **4-E** + **4-Z**[a] in 50% EtOH at 80°

| Time, hr | % reaction | Product distribution, % | | | | |
|---|---|---|---|---|---|---|
| | | 7-H | 10-H | 10-D | 11 | 12 |
| 3 | 48 | 12 | 2 | 64 | 11 | 11 |
| 64 | 100[b] | 16 | 16 | 65 | 3 | |

[a] A mixture of 65% **4-E** and 35% **4-Z**. [b] Twenty solvolytic half-lives.

hydrolysis of **11** and **12** to give **10-D** and exchange of **10-D** in the basic medium to give **10-H** take place.

**Solvolysis in AcOH.** In the solvolysis of **4-H** or of a mixture of **4-E** and **4-Z**, the ketone **10-H** was the exclusive product. In the reaction in the presence of NaOAc, $10^5 k_t$ for **4-E** (60%) + **4-Z** (40%) increased during the run from 1.55 sec$^{-1}$ at 11% reaction to 1.95 sec$^{-1}$ at 65% reaction, and graphical extrapolation of a plot of $k_t$ *vs.* % reaction gave $10^5 k_t^0$ = 1.48 sec$^{-1}$. We ascribe this increase, which was also observed for **4-H**,[9] to a "normal" salt effect[16] of the NaBr formed in the reaction. By combining the equations for the first-order reaction and that for the "normal" salt effect (eq 6),[16] we obtained eq 7 and 8, where $k_t^0$ is the rate constant in the absence of the added or the formed salt. Regression analysis of eq 8 gave the best linear [log

$$k_t = k_t^0(1 + b[\text{salt}]) \quad (6)$$

$$dx/dt = k_t^0(1 + b[\text{NaBr}])(a_0 - x) \quad (7)$$

$$k_t^0 = \frac{2.3}{t(1 + a_0 b)}\left\{\log a_0 - \log\frac{a_0 - x}{1 + bx}\right\} \quad (8)$$

$(a_0 - x)/(1 + bx)$ *vs.* time plots by using a $b$ value of 11 for NaBr, whose slopes gave the $k_t^0$ values which are given in Table I. The deuterium isotope effect $k_t^0$-(**4-H**)/$k_t^0$(60% **4-E** + 40% **4-Z**) = 1.21 at 120.3°. When the reactions were conducted in the presence of both Et$_4$NBr and NaOAc, the rate constant remained reasonably constant at the first 50% of the reaction, and it was somewhat lower at higher reaction percentages.[17]

(14) Blackborow agrees now that the assignments for compounds **9-E** and **9-Z** (X = Cl, Br, I) probably should be reversed (personal communication).

(15) G. Marchese, G. Modena, F. Naso, and N. Tangari, *Boll. Sci. Fac. Chim. Ind. Bologna*, **26**, 209 (1968); *J. Chem. Soc. B*, 1196 (1970); G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).

(16) (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2763 (1956); (b) E. L. Allerd and S. Winstein, *ibid.*, **89**, 4012 (1967).

(17) The rate constants in this reaction should also fall down throughout the run due to the formation of NaBr. Apparently, the effect of added Et$_4$NBr is to reduce the effect of the formed NaBr.

**Scheme I**
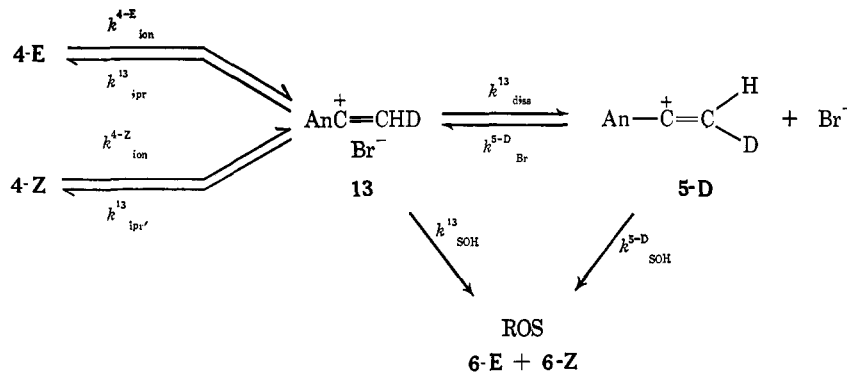


The $k_t$ values which were calculated for the first half-life of the reaction are given in Table I. The $k_t$ values increased with the $Et_4NBr$ concentrations, and a $b$ value of 14 for the "normal" salt effect of $Et_4NBr$ was obtained from the plot of $(k_t/k_t^0) - 1$ vs. [Et₄NBr] (cf. eq 6). An increase in the NaOAc concentration resulted in a negligible effect, and $b \sim 0$ for NaOAc.

The solvolysis is accompanied by a **4-E** $\rightleftharpoons$ **4-Z** isomerization. Starting from a **4-E/4-Z** ratio of 4, the ratio decreased throughout the run, until the equilibrium ratio of 1:1 was established for the unreacted **4-E** and **4-Z**. The first-order isomerization was followed by nmr, and its rate constant $k_{isom}$ is given in Table I. Exchange of the vinylic deuterium with protons from the solvent was not observed during the solvolysis. Such an exchange would lead to splitting or at least to broadening of the singlets of the vinylic protons of **4-E** and **4-Z** since each of the vinylic protons of **4-H** is a doublet with a geminal coupling constant of 1.8 Hz. Similarly, exchange of the protons of **4-H** was not observed during the solvolysis in AcOD.[9] Furthermore, using the methoxyl protons as an internal standard together with the titrimetric data, the integration of the vinylic protons of **4-E** and **4-Z** corresponded to one proton throughout the reaction, while a higher value is anticipated if some **4-H** is formed by exchange.

**Discussion**

Our results will be discussed in terms of Scheme I, where **13** is an ion pair, **5-D** is a free ("dissociated")[18] cation, and the superscripts over the $k$'s designate the species which is involved in the reaction which is designated by the subscript (ion = ionization; diss = dissociation; ipr = ion pair return; Br, SOH = capture by Br⁻ and by the solvent, respectively).[19] The actual isomerization (and capture) may occur by interconversion of the isomeric "intimate"[18] ion pairs **13-E** and **13-Z** which are formed with retained stereochemistry from **4-E** and **4-Z**, respectively, or via a common or two different "solvent separated"[18] ion pairs. How-

ever, in the absence of kinetic and stereochemical information on the **13-E** $\rightleftharpoons$ **13-Z** interconversion rate, or on the type of ion pair involved in the reaction, it is more convenient to introduce only one ion pair **13** with undefined geometry, which may be an intimate or a solvent separated ion pair, and which is formed from and returns to both **4-E** and **4-Z**.

**Intermediates in 50% EtOH.** The absence of a common ion rate depression in the solvolysis of **4-H** in 50% EtOH is consistent with two possibilities.[18] (a) $k^{13}_{SOH} \gg k^{13}_{diss}$; i.e., the free ion is not formed. (b) $k^{5-D}_{Br} \ll k^{5-D}_{SOH}$; i.e., the free ion is formed, but is it being captured before its return. We are unable to distinguish between these alternatives, but we prefer possibility a since the absence of ion pair return [which was observed for **1** (X = Br) in 80% EtOH][1] suggests a rapid capture of a tight ion pair (see below). However,
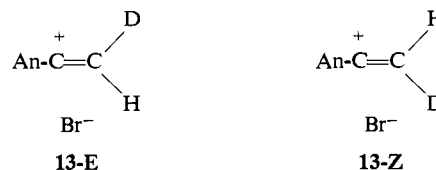


the similar acetylene ketone ratios from the solvolyses of **4-H** and **8-H** in 80% EtOH[9] argue that the product-forming intermediate is not so tight an ion pair. This question could be solved by stereochemical means since capture of **13-E** or of **13-Z** should occur with preferential inversion, while capture of **5-D** should give a 1:1 mixture of the products **6-E** and **6-Z**. Unfortunately, the stereochemistry of the vinyl acetates **11**, or of the vinyl ethers **12**, could not be studied since the signals for their vinylic protons were too weak at short reaction times and the compounds decomposed to **10-D** after long reaction times.

The important mechanistic point is the absence of a **4-E** $\rightleftharpoons$ **4-Z** isomerization. Ion pair return ($k^{13}_{ipr}$, $k^{13}_{ipr'}$) and external ion return to the isomeric vinyl halide are therefore slower than the capture of **13** by the solvent ($k^{13}_{SOH}$), and $k_t = k_{ion}$. This behavior is consistent with the lower internal return in the solvolysis of saturated substrates in alcoholic solvents as compared with AcOH.[20] We note, however, that some isomeriza-

(18) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, J. Amer. Chem. Soc., **78**, 328 (1956).

(19) A referee has suggested the use of the simpler Winstein's solvolysis scheme (ref 18) for saturated systems, instead of Scheme II. However, it should be emphasized that the solvolytic scheme for vinylic RX is necessarily more complicated than that for the saturated RX. In Winstein's scheme $k_{ion}(d$-RX$) = k_{ion}(l$-RX$)$, and each of the rate constants $k_{diss}$(ion pair), $k_{SOH}$(ion pair), $k_{SOH}$(free ion) is the same whether the $d$ or the $l$ species is involved in the reaction. In vinylic systems $k_{ion}(E$-RX$) \neq k_{ion}(Z$-RX$)$ (and their ratio is the isotope effect discussed below), and for all the rate constants ($k_{diss}$(ion pair), $k_{SOH}$(ion pair), $k_{SOH}$(free ion)), $k(E$ isomer$) \neq k(Z$ isomer$)$. Hence, more rate constants should be included in Scheme II than in Winstein's scheme.

(20) (a) S. Winstein and D. Trifan, J. Amer. Chem. Soc., **74**, 1154 (1952); (b) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, ibid., **93**, 4829 (1971); A. F. Diaz and S. Winstein, ibid., **91**, 4300 (1969); (c) S. Winstein, R. Baker, and S. Smith, ibid., **86**, 2072 (1964); S. Winstein, B. Appel, R. Baker, and A. Diaz, Chem. Soc. Spec. Publ., No. **19**, 109 (1965); (d) D. D. Roberts, J. Org. Chem., **37**, 1510 (1972).

tion may be hidden owing to a differential isotope effect (see below) and that the nmr method is less sensitive than the ir method used for following the isomerization of **1** (X = Br),[1,5] so that 5–8% of isomerization may escape detection.

Comparison can be made with the 31% of ion pair return which was observed for system **1** (X = Br) in 80% EtOH,[1] and with the lower, but nevertheless detected,[21] ion pair return (with isomerization) which was observed during the solvolysis of (E)-α-bromo-β-methyl-p-methoxystyrene (**14**) in 80% EtOH.[2d] The decrease

**14**
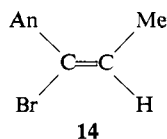
in the extent of the ion pair return in the series **1** (X = Br) > **14** > **4-E** follows the decrease in the bulk of the β substituents. It is plausible that the collapse rate of different tight ion pairs with the same α-activating group is relatively insensitive to the bulk of the β substituents, while a slower reaction with the solvent is anticipated for ions with less exposed cationic orbital. Shielding by the β substituents will be therefore responsible for the increased lifetime of the ion pair before collapse, and to a higher extent of ion pair return.[22] (However, see the results in AcOH.)

The ketone/acetylene ratio of 5.1 in 50% EtOH at infinity follows the trend for higher ratio in the more aqueous solvents; the ratios are 1.27 in 90% EtOH and 1.63 in 70% EtOH in the presence of NaOAc.[9] The corresponding ratio in the solvolysis of p-amino-α-bromostyrene decreases with the increase in the basicity of the medium,[23] and the trend may reflect a lower basicity of the more aqueous solvent. The ion pairs would be less tight in the more aqueous solvent,[4] and this may influence the ketone/acetylene ratio if Br⁻ assists in the expulsion of the proton from **13**.

The detection of the vinyl ether **12**, which was not hitherto detected in solvolysis in media containing higher molar per cent of ethanol,[9] is probably due to its reduced hydrolysis rate to **10-D** at the lower temperature used. We observed that the hydrolysis rates of α-anisyl vinyl ethers increase with the decrease in the bulk of the β substituents,[24] and **12** hydrolyzes therefore rapidly and completely to **10-D**. This ketone exchanges slowly its α-deuterium in the basic medium, giving **10-H**.

The unchanged **4-E**/**4-Z** ratio during the solvolysis argues against high differential isotope effect k(**4-Z**)/k(**4-E**). A differential isotope effect of 1.43, as found for k(**9-Z**)/k(**9-E**) when X = OSO₂F,[25] would be easily
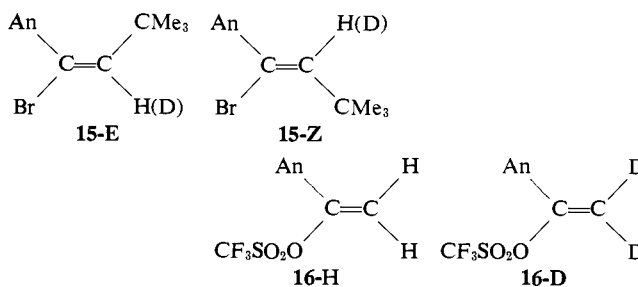
(21) This case is more complicated than ours, since the intermediate vinyl cation is unsymmetrical, and hidden return with retention (the extent of which is unknown) will predominate over return to the Z isomer.

(22) A similar factor is probably responsible for the low Grunwald–Winstein m values for triarylvinyl halides with crowded ground and transition states (e.g., Z. Rappoport and A. Gal, J. Amer. Chem. Soc., **91**, 5246 (1969); J. Org. Chem., **37**, 1174 (1972)), as compared with the monoarylvinyl systems.[9]

(23) C. A. Grob and H. R. Pfandler, Helv. Chim. Acta, **54**, 2060 (1971).

(24) Based on data in ref 2d, 5, and unpublished results, the ethers AnC(OEt)=CR¹R² formed in solvolysis are more stable when R¹ = R² = Ar than when R¹ = Me, R² = H.

detected. A better estimate for this isotope effect is based on the $k_H/k_D$ values of 1.10 and 1.26 for **15-E** and **15-Z** in 50% EtOH,[26] and the value obtained, k(4-

**15-E** **15-Z**

**16-H** **16-D**

Z)/k(4-E) = 1.15, is consistent with the k(**16-H**)/k(**16-D**) value of 1.20 estimated by Stang[27] on the basis of isotope effects for several α-arylvinyl triflates in aqueous EtOH.[28] This value is within the limits of detection by our method, but it may be reduced below this limit by a **4-E** ⇌ **4-Z** isomerization (due to internal return), which will operate in the opposite direction. It would be too great a coincidence if a high isotope effect as that for **9-E** and **9-Z** (X = OSO₂F) were exactly balanced by ion pair return, but even in this case the extent of return is still small.

**Intermediates in the Acetolysis.** Scheme I also applies for the acetolysis except that, instead of the initially formed vinyl acetates **11-E** and **11-Z**, the ketone **10-H** was the sole product. This is not surprising since the conversion of the undeuterated vinyl acetate to **10-H** and the exchange of **10-D** in AcOD/NaOAc are 314- and 18-fold faster than the solvolysis of **4-H**.[9] The absence of common ion rate depression suggests again that **5-D** is either not formed or it is captured before it returns. Common ion rate depression in the acetolysis of β-substituted α-anisylvinyl halides was previously observed,[1,5,7a,9,10,29] and, since the selectivity of the vinyl cations increases with the bulk of the β substituents,[7a,10,29] it was partially ascribed to the crowding of substituents around the cationic orbital. The absence of common ion rate depression for system **4** strengthens this interpretation and shows that the electronic effect of the α-anisyl group is not sufficient for the observation of common ion rate depression. The possibility that some rate depression is masked by the increase in $k_t$ during the run is unlikely, since eq 8, which is based on the absence of rate depression, was found to be valid.

The most important result is the observation of a concurrent **4-E** ⇌ **4-Z** isomerization during the solvolysis. There is strong evidence for little or no contribution of the electrophilic addition–elimination route (Ad_E–E) to the acetolysis of **4-H**.[9] That the Ad_E–E route for the isomerization (eq 9) is insignificant is evident by the absence of exchange of the vinylic deuterium with the solvent (via **4-E** → **17a** → **17b** → **4-H**) which will broaden the signals of the vinylic pro-

(25) D. D. Maness and L. D. Turrentine, Tetrahedron Lett., **755** (1973).

(26) Z. Rappoport, A. Pross, and Y. Apeloig, Tetrahedron Lett., 2015 (1973).

(27) P. J. Stang, Progr. Phys. Org. Chem., **10**, 205 (1973).

(28) P. J. Stang and R. J. Hargrove, unpublished results, quoted in ref 27; P. J. Stang, R. J. Hargrove, and T. E. Dueber, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. ORGN 163.

(29) (a) A. Gal, Ph.D. Thesis, The Hebrew University, Jerusalem, 1972; (b) Z. Rappoport and Y. Apeloig, unpublished results.

$$-D^+ \Big\Uparrow +D^+ \qquad\qquad -H^+ \Big\Uparrow +H^+ \qquad (9)$$
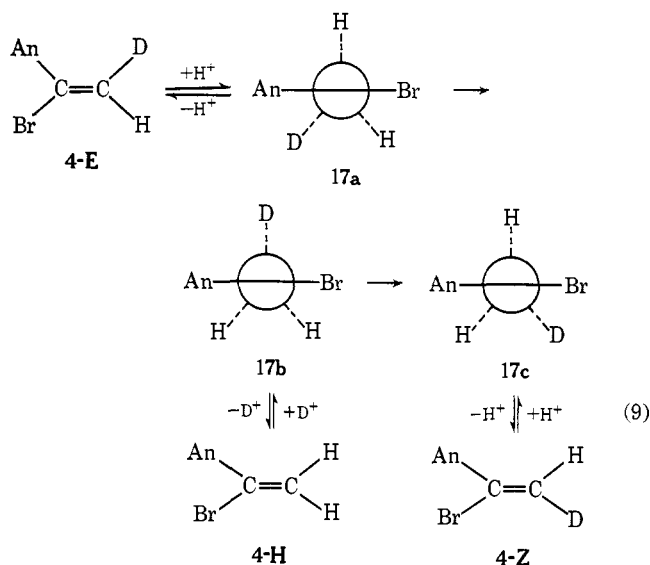


tons.[30] However, an appreciable isotope effect for the elimination of proton may favor elimination from 17c, resulting in isomerization without exchange *via* 17a → 17c → 4-Z. From the absence of exchange after 2 half-lives of 4-E, and from the absence of exchange of 4-H during solvolysis in AcOD (where the isotope effect will favor the exchange), we conclude that the main isomerization is *via* $k^{13}_{ipr}$ of Scheme I. Small contribution from an $Ad_E$–E route which will exaggerate $k_{isom}$ for the ion pair return cannot be excluded.

A differential isotope effect of cis and trans hydrogens will affect $k_{isom}$ of our experiment in the opposite direction. The isotope effect for one hydrogen in AcOH, $k_H/k_D = k(4\text{-}H)/k(60\% \ 4\text{-}E + 40\% \ 4\text{-}Z) = 1.21$, is similar to that estimated for two $\beta$ hydrogens for the solvolysis of 16-H in aqueous EtOH.[27] This is consistent with the higher kinetic deuterium isotope effects in AcOH compared with aqueous EtOH.[31] Our value is higher than the $k_H/k_D$ value of 1.10 for 9-Z ($X = OSO_2F$) in AcOH, but by analogy with Stang's results 4-Z will show a lower $k_H/k_D$ than 9-Z, and by using Stang's[28] and Maness'[25] data we estimated a $k(4\text{-}H)/k$-(4-Z) value of 1.05. From this value and the apparent isotope effect $k(4\text{-}H)/k(60\% \ 4\text{-}E + 40\% \ 4\text{-}Z) = 1.21$, we obtain a $k(4\text{-}H)/k(4\text{-}E)$ value of 1.32. The derived $k(4\text{-}Z)/k(4\text{-}E)$ ratio of 1.26 is lower than the $k(9\text{-}Z)/k$-(9-E) ($X = OSO_2F$) of 1.43. If this were the case, the change in the ratio of the signals of 4-Z to 4-E would be slower by a factor of 1.26 than anticipated for a 4-E ⇌ 4-Z isomerization in the absence of isotope effect; *i.e.*, the "true" $k_{isom}$ will be $3.18 \times 10^{-5} \text{ sec}^{-1}$.[32]

Since solvolysis and isomerization are competing

(30) There are many precedents for the absence of exchange of vinylic protons during electrophilic hydration of olefins: (a) E. L. Purlee and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 78, 5807 (1956); (b) M. J. S. Dewar and R. C. Fahey, *ibid.*, 85, 2245, 3645 (1963); (c) W. M. Schubert, B. Lamm, and J. R. Keefe, *ibid.*, 86, 4727 (1964); (d) N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, 87, 2157 (1965); (e) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965); (f) W. M. Schubert and B. Lamm, *J. Amer. Chem. Soc.*, 88, 120 (1966).

(31) *E.g.*, E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, 76, 791 (1954).

(32) A relevant question is whether a possible 9-E ⇌ 9-Z (X = OSO₂F) isomerization contributes to the observed differential isotope effect $k(9\text{-}Z)/k(9\text{-}E)$. Our study on the dependence of internal return on the leaving group[5] suggests that such contribution will be low or negligible for X = OSO₂F.

processes starting from the same substrate, the ionization rate constant $k_{ion}$ is given by eq 10. Denoting by

$$k_{ion} = k_t + k_{isom} \qquad (10)$$

$F(=k_t/k_{ion})$ the fraction of ion pairs leading to product, $F = 0.37$ (or $F = 0.32$ with "correction" for the possible isotope effect). The correction does not change materially the extent of ion pair return, and 63–68% of the ion pairs return to covalent vinyl bromide.

The fraction of ion pair return $1 - F$ (0.63) exceeds that observed in the acetolysis of compound 1 (X = Br), where $1 - F = 0.47$.[5] While the values of $k_{isom}$ for 4 and $1 - F$ for 13 may change slightly owing to the above considerations, it is clear that contrary to the behavior in aqueous EtOH the extent of ion pair return in AcOH is little affected by the bulk of the $\beta$ substituents. Ion pair return competes with dissociation of the ion pair 18 in the triarylvinyl system and with



18
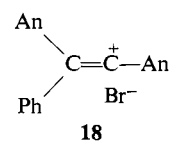
capture (and possibly with some dissociation) for 13. Dissociation will be enhanced in 18 since it will reduce the steric strain between the leaving group and the substituent cis to it, while return will be inhibited owing to the two cis interactions in 1 (X = Br). These effects are relatively unimportant for 13, while its cationic orbital is more exposed to the nucleophile, and ion pair capture (which is absent for 18) will be dominant. Apparently, the capture of 13 and the dissociation of 18 are influenced to the same extent by the different steric environment, leading to close $1 - F$ values. More work on other systems is required to decide whether this is only a coincidence or a more general behavior.

Low *b* values are common for NaOAc in vinylic[5,9] and in saturated[4,16a] solvolyses, but the *b* value of 14 for Et₄NBr is high compared with the values for halide salts in solvolyses.[4] The higher response of the $\beta,\beta$-unsubstituted compared with the $\beta,\beta$-disubstituted system to the salt effect parallels the response to the change of the solvent,[33] pointing again to an effective shielding of the incipient transition state dipole from the bulk medium by the bulky $\beta$ substituents. Perrin and Pressing[34] considered the linearity of the "normal" salt effect[16] in terms of dipole (salt)–dipole (transition state) interactions. Their model requires increase in the *b* values for a closer approach and higher dipoles of the salt and the transition state. Since the ionization rates of 4-E and 1 (X = Br) are close, the dipole moments of the corresponding transition states are probably close. We like to speculate that our high *b* value results from the unique possibility of a close proximity of the transition state and the salt ($M^+Y^-$) which may reside above the plane of the vinylic system (*cf.* transition state 19). Such an arrangement is impossible or difficult in saturated or in more crowded vinylic systems.

**Addition of HBr to *p*-Methoxyphenylacetylene.** The

(33) In aqueous EtOH $m(Ar_2C=C(X)Ar) < m(ArC(X)=CH_2)$.[9,22]

(34) C. L. Perrin and J. Pressing, *J. Amer. Chem. Soc.*, 93, 5705 (1971).

**Scheme II**





19
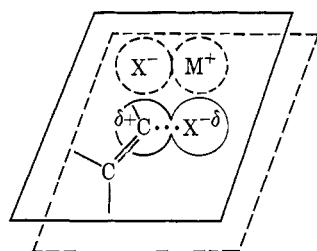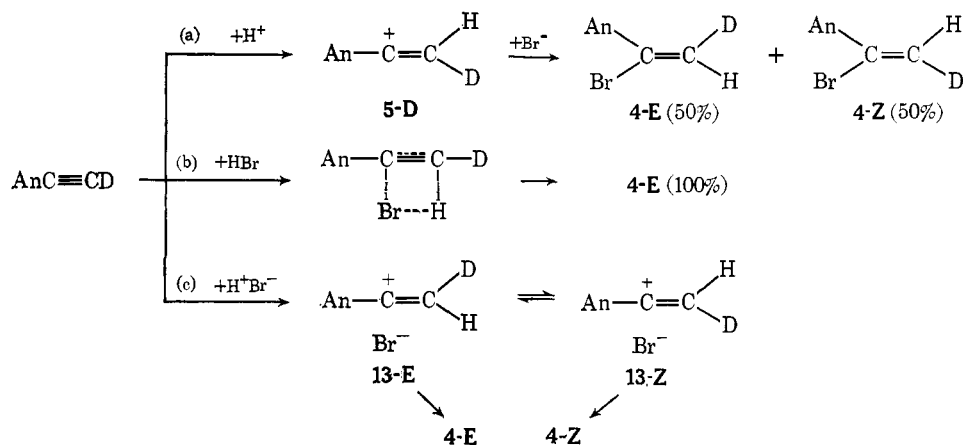
syn addition of HBr to **7-D** has a bearing on the stereochemistry of electrophilic additions to acetylenes.[35]

Dominant syn addition,[36] dominant anti addition,[36b,37,38] or nonselective addition[39] are all known, but analogies with disubstituted acetylenes may be misleading since the $E$–$Z$ product distribution from an intermediate vinyl cation is mainly determined by its capture by the nucleophile from its less hindered side. For example, the apparent syn additions of HBr to $\alpha,\beta$-dianisylacetylene[7a] or $\alpha$-anisyl-$\beta$-tert-butylacetylene[7b] give almost exclusively the more crowded, thermodynamically less stable isomer via the less hindered transition state. On the other hand, to a first approximation hydrogen and deuterium are regarded as sterically and electronically equivalent, and a $\beta$-H,$\beta$-D "symmetrical" free vinyl cation will give a 1:1 mixture of the $E$ and $Z$ isomers. This was found in the addition of fluorosulfonic acid to phenylacetylene in AcOH[25] and of HCl to phenylacetylene in sulfolane.[40] The formation of a 1:1 mixture of **4-E** and **4-Z** in the addition of HBr to **7-D** in AcOH suggests that the product-forming intermediate is the free cation **5-D**, formed by addition of proton to **7-D** (Scheme II, route a).

The preference for syn addition in solvents with low dielectric constant finds precedents in the addition of trifluoromethanesulfonic acid-O-d to 1-hexyne in pen-

tane,[2h] and in the recently studied addition of HCl to $\beta$-deuterio-$\alpha$-phenylacetylene.[40] Presumably, the syn products arise via concerted addition (Scheme II, route b), or addition of the ion pair $H^+Br^-$ with formation of the ion pair **13-E**, whose collapse to **4-E** competes favorably with rotation to **13-Z** (which in turn collapses to **4-Z**) (Scheme II, route c). It is interesting that the amount of syn products in low dielectric constant solvents apparently decreases[2h,40] with the increased stability of the vinylic cation which is formed in a route analogous to route a of Scheme II.

Syn addition of molecular or ion paired HBr is confirmed by the increased stereoselectivity and reduced rate in the presence of tetraalkylammonium bromides. Common ion rate depression reduces the concentrations of the free $H^+$ and $Br^-$ ions which are involved in the faster nonselective addition via route a, and in low dielectric constant solvents route b or c dominates. This effect of $R_4N^+Br^-$ is in contrast to the increased rate and anti stereoselectivity caused by addition of $R_4N^+$-$Cl^-$ in the addition of HCl to 1-phenylpropyne in AcOH,[41] where a termolecular reaction was invoked. The difference from our system may arise from the higher ability of AcOH to solvate the halide ion, and consequently to promote dissociation of either the $H^+Br^-$ pair or of the ion pairs **13-E** and **13-Z**.

The increased stereoselectivity in the presence of low concentrations of $HgBr_2$ may be due to a fast concerted cis addition of $HgBr_2$ analogous to route b (or c),[42] followed by an electrophilic substitution of $HgBr^+$ by $H^+$ with retention. A nonselective addition by a species such as $H^+ HgBr_3^-$ may operate at higher $HgBr_2$ concentrations.

## Experimental Section

Nmr spectra were recorded with Varian T-60 or H-100 instruments, and the data are given in $\delta$ units downfield from internal tetramethylsilane.

**Materials.** AcOH and 50% EtOH were prepared as described previously.[9] Other solvents for the addition of HBr and HCl to 7-D were dried according to the literature. $\alpha$-Anisyl-$\beta$-deuterioacetylene (**7-D**) was prepared by repeated equilibration of the

(35) R. C. Fahey, Top. Stereochem., **3**, 237 (1968).

(36) (a) R. C. Fahey and D. J. Lee, J. Amer. Chem. Soc., **88**, 5555 (1966); (b) ibid., **90**, 2124 (1968).

(37) R. C. Fahey and D. J. Lee, J. Amer. Chem. Soc., **89**, 2780 (1967).

(38) (a) M. Lépingle, Bull. Soc. Chim. Fr., **39**, 741 (1926); H. Hunziker, R. Meyer, and H. Günthard, Helv. Chim. Acta, **49**, 497 (1966); (b) R. Maroni, G. Melloni, and G. Modena, J. Chem. Soc., Perkin Trans. 1, 2491 (1973).

(39) P. E. Peterson and J. E. Duddey, J. Amer. Chem. Soc., **85**, 2865 (1963); **88**, 4990 (1966).

(40) F. Marcuzzi, G. Melloni, and G. Modena, Tetrahedron Lett., 413 (1974).

(41) R. C. Fahey, D. J. Lee, and M. Payne, unpublished results, quoted in ref 35.

(42) Hg(OAc)₂ adds syn to diphenylacetylene in AcOH [G. Derfahl, G. Hueblein, and A. Wintzer, Angew. Chem., **70**, 166 (1958)], but anti addition was observed with 2-butyne [A. E. Borisov, V. D. Vil'chevskaya, and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, **90**, 383 (1953)].

**Table III.** Addition of 0.049 $M$ HBr$^a$ or HCl$^a$ to 0.05 $M$ AnC≡CD

| Solvent | Acid | Added salt | Concn, $M$ | $T$, °C | Reaction time, hr | % reaction | Products, [4-E]/[4-Z] or [8-E]/[8-Z] |
|---|---|---|---|---|---|---|---|
| Neat | HBr | HgBr$_2$$^b$ | 0.01 | 25 | 20 | 30 | 54:46 |
| DMF | HBr | | | 0 | 1 | 100 | $c$ |
| MeCN$^d$ | HBr | | | 20 | 1 | 100 | 63:37 |
| MeCN$^d$ | HBr | Et$_4$NBr | 0.2 | 20 | 1 | 100 | 63:37 |
| AcOH | HBr | | | 20 | 0.25 | 100 | 50:50 |
| C$_6$H$_6$ | HBr | | | 20 | 1 | 100 | 55:45 |
| Petroleum ether | HBr | | | 0 | 1.5 | 100 | 55:45 |
| Petroleum ether | HBr | | | −20 | 1.25 | 40 | 60:40 |
| Petroleum ether | HBr | Et$_4$NBr$^e$ | 0.15 | 0 | 2 | 56 | 65:35 |
| Hexane | HBr | Bu$_4$NB$_1$$^e$ | 0.005 | −20 | 2 | 75 | 60:40 |
| CH$_2$Cl$_2$ | HBr | | | 20 | 1 | 100 | 52:48 |
| CH$_2$Cl$_2$ | HBr | Et$_4$NBr | 0.2 | 20 | 1 | 100 | 63:37 |
| CCl$_4$ | HBr | | | 0 | 1 | 100 | 52:48 |
| CCl$_4$ | HBr | Bu$_4$NBr | 0.1 | −20 | 2 | 85 | 70:30 |
| CCl$_4$ | HBr | Bu$_4$NBr | 0.4 | −20 | 2 | 40 | 70:30 |
| CHCl$_3$ | HBr | | | 0 | 1 | 100 | 56:44 |
| CHCl$_3$ | HBr | Et$_4$NBr | 0.25 | 0 | 2.25 | 90 | 70:30 |
| CHCl$_3$ | HBr | Et$_4$NBr | 0.6 | 0 | 1.5 | 60 | 75:25 |
| CHCl$_3$ | HBr | Et$_4$NBr | 1.2 | 0 | 4.5 | 90 | 67:33 |
| CHCl$_3$ | HBr | Et$_4$NBr | 0.5 | −20 | 4.5 | 40 | 75:25 |
| CHCl$_3$ | HBr | Bu$_4$NBr | 0.5 | 0 | 1.5 | 75 | 73:27 |
| CHCl$_3$ | HBr | HgBr$_2$$^f$ | 0.05 | 0 | 0.25 | 100 | 50:50 |
| CHCl$_3$ | HBr | HgBr$_2$$^f$ | 0.0015–0.008 | 0 | 0.25 | 100 | 73:27 |
| CHCl$_3$ | HBr | 1:1 HgBr$_2$–Et$_4$NBr$^f$ | 0.0015 | 0 | 0.25 | 100 | 75:25 |
| CHCl$_3$ | HBr | HgBr$_2$$^f$ | 0.002 | −20 | 1 | 100 | 80:20 |
| CHCl$_3$ | HBr | HgBr$_2$$^f$ | 0.002 | −45 | 1.5 | 50 | 80:20 |
| CH$_2$Cl$_2$ | HCl | | | 0 | 3 | 85 | 56:44 |
| CH$_2$Cl$_2$ | HCl | Bu$_4$NCl | 0.125 | 0 | 3 | 25 | 66:34 |
| CH$_2$Cl$_2$ | HCl | Bu$_4$NCl | 0.0125 | 0 | 3 | 0 | |
| Petroleum ether | HCl | | | 0 | 3 | 25 | 66:34 |

$^a$ Use of excess HBr or HCl resulted in 4-E and 4-Z in 1:1 ratio. $^b$ Traces of hydroquinone were added. The procedure used was that of H. Hunziker, R. Meyer, and H. H. Günthard, *Helv. Chim. Acta*, **49**, 497 (1966). $^c$ Complete exchange took place, giving 4-H. $^d$ The HBr source in MeCBr=NH which was obtained as a solid by passing gaseous HBr into cooled acetonitrile. $^e$ The salt is insoluble in the organic solvent. $^f$ HgBr$_2$ is soluble in chloroform after the addition of the HBr.

undeuterated 7-H with NaOH–D$_2$O$^{43}$ [$\delta$(CDCl$_3$) 3.77 (3 H, s, MeO), 6.95 (4 H, center of AA'BB' q, $J$ = 8 Hz, An)].

**Addition of HBr to 7-D.** Table III contains information on the product distribution in the addition of HBr or HCl to 7-D under different conditions. Since traces of water give an appreciable amounts of *p*-methoxyacetophenone, the reaction was conducted in carefully dried solvents. A general procedure for the addition is as follows.

Dry gaseous HBr or HCl was bubbled through the cooled ( −15°) solvent for 10–15 min. The concentration of the acid was determined by titration of the halide ion in aqueous media. The R$_4$NBr or HgBr$_2$ was added to the solvent (10 ml) which contained 7-D (210 mg, 1.6 mmol), and slightly less than an equimolar amount of the acid–solvent mixture was added. At the end of the reaction the mixture was washed rapidly with water, dilute NaHCO$_3$ solution, and water and dried (Na$_2$SO$_4$), and the solvent was evaporated. Nmr on the remaining oil gives (a) the 4-E/4-Z ratio and (b) the extent of addition, by comparison of the intensities of the two vinylic protons (a) with one another and (b) with the methoxyl protons.

Isolation of a mixture rich in 4-E is exemplified by the following procedure. To 7-D (210 mg, 1.6 mmol) in dry chloroform (10 ml) at −20°, mercuric bromide (12 mg) and a solution of 0.16 $N$ HBr in chloroform (10 ml) were added slowly, and the sealed reaction mixture was kept for 90 min at −20°. Work-up as above was followed by addition of methanol (12 ml) to the oil and cooling by liquid air. The white precipitate (350 mg, 94%), mp 34–35°, which contained 80% of 4-E and 20% of 4-Z (according to the nmr), was filtered rapidly, dried, and used without further purification: $\nu_{max}$ 2050 cm$^{-1}$ (C–D); $\delta$ (CDCl$_3$) 3.80 (3 H, s, MeO), 5.60 (s),

(43) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1023 (1968).

5.94 (s) ( :CH, 1 H together), 6.78, 6.87, 7.46, 7.55 (4 H, AA'BB' q, An).

**Determination of the Isotope Effect in Elimination from 4-E + 4-Z.** A 1:1 mixture of 4-E and 4-Z (250 mg, 5.5 mmol) was dissolved in *tert*-butyl alcohol (10 ml) containing potassium *tert*-butoxide (130 mg, 5.5 mmol). The mixture was kept at 82°, samples were withdrawn and poured into water (10 ml)–chloroform (20 ml), and the organic layer was separated, washed twice with water, dried (CaCl$_2$), evaporated, and analyzed by nmr. Samples taken after 4.5 hr showed 30% of 7-H and the unreacted 4-E and 4-Z in a 3:2 ratio, while after 18 hr the products were 4-E (30%), 4-Z (10%), and 7-H (60%). By using eq 4, $k_H/k_D = k_{anti\ elimination}$-(4-Z)/$k_{anti\ elimination}$(4-E) were 3.40 and 3.16, respectively.

**Solvolysis in 50% EtOH.** Solvolysis of a 65:35 mixture of 4-E to 4-Z (68 mg, 0.32 mmol) in 50% EtOH containing NaOAc (41 mg, 0.5 mmol) was conducted at 80° for 3 hr. The mixture was poured into water (50 ml) and extracted with carbon tetrachloride (2 × 30 ml), the extract was dried (CaCl$_2$) and evaporated, and the product composition was determined by nmr (CDCl$_3$) from the intensities of the following signals: $\delta$ 1.27 (3 H, $t$, Me, $J$ = 6.8 Hz), 4.19 (2 H, q, CH$_2$, $J$ = 6.8 Hz) of the ether 12, 2.51 (center of CH$_2$D, $t$, $J$ = 2.2 Hz) of 10-D, 2.52 (s, COMe) for 10-H, and 3.83 (3 H, s, MeO) of 10-H and 10-D, 2.28 (s, OAc) of 11, and 2.97 (s, ≡CH) and 3.77 (MeO) for 7-H. The aromatic protons of all the compounds merged except for the two protons ortho to the anisoyl group of 10-H and 10-D which appeared as a half of a AA'BB' quartet at $\delta$ 7.82 and 7.91.

**Solvolysis and Isomerization in AcOH.** 4-H or a mixture of 4-E and 4-Z (0.067 $M$) and NaOAc (0.14 $M$) in AcOH were kept in ampoules at 120.3°. At the appropriate time part of the mixture was poured into chloroform (20 ml); the solution was washed with water, 5% NaHCO$_3$ solution, and water, dried (CaCl$_2$), and the

solvent was evaporated. The remaining oil was analyzed by nmr. Integration of the signals of the vinylic protons was repeated several times, and the average value was used for calculating $k_{isom}$. Another part of the mixture was potentiometrically titrated with silver nitrate. Rate coefficients were calculated by using a regression program.

**Stabilities of 4-E and 4-Z.** Control experiments on the stability

of a 80:20 mixture of **4-E** and **4-Z** showed that no change in the relative intensities of the signals for the vinylic protons was observed after 48 hr at 10° in chloroform or in AcOH–NaOAc.
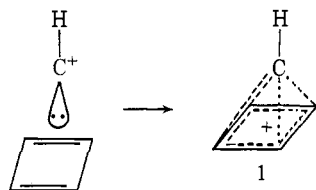
# Preparation and Reactions of a Bis-Homo-(CH)₅⁺-Type Carbocation

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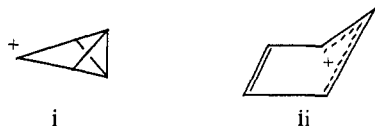
**Abstract:** The pyramidal carbocation **7** was formed in two ways, either by ionization of secondary alcohol **9** in FSO₃H–SO₂ClF (1:4) or by protonation of the alkene **43** in the same solvent, both at temperatures below −40°. The symmetry of the pmr and cmr spectra of **7** was consistent with the pyramidal structure and was not perturbed at temperatures as low as −120°; therefore, if the ion has the classical structure **18″**, equilibration between equivalent structures must be rapid at −120°. Although spectra show that the positive charge resides mainly at the "basal" carbon atoms, ion **7** is quenched exclusively at the apical position, giving either **9** (with water) or **16** (with methanol). Between −45 and −30°, **7** rearranges to **24**, whose structure was proved by quenching in methanol to give **25** which thermally eliminated methanol to give the triene **26**. The mechanism of the rearrangement of **7** to **24** was elucidated by deuterium labeling (*i.e.*, **7′** → **24′**); kinetic studies show that $\Delta F^{\neq}$ for the process is 16.7 kcal/mol. Above −30° and below 0° ion **24** rearranges to **35** whose structure was proved by quenching in methanol to give **36** which thermally eliminated methanol to give the trienes **37, 38,** and **39**. The mechanism of the rearrangement of **24** to **35**, established by deuterium labeling, involves a succession of 1,2-shifts of one five-membered ring with respect to the other (circumambulation). Treatment of alcohol **9** with trifluoroacetic acid above 10° gave the pentadienyl cation **42**, whose structure was established by quenching to a mixture of **37, 38,** and **39**. Labeling experiments establish the mechanistic sequence **9** → **7** → **24** → **35** → **37** → **42** for this series of rearrangements. Protonation of **37** in FSO₃H at −78° gives mainly **35** but in TFA at room temperature gives **42**. Irradiation of **26** in ether through Vycor gave **43** which, in addition to being a suitable precursor of **7**, gave the secondary chloride **13** or trifluoroacetate **17** with hydrochloric acid or TFA, respectively. The same chloride and trifluoroacetate were obtained from **9**, and deuterium labeling experiments show that during the latter process the relative positions of the three- and four-membered rings interchange, presumably *via* a symmetric intermediate such as **7**.

Stohrer and Hoffmann[1] made the imaginative suggestion that the most stable structure for the (CH)₅⁺ cation is the square pyramid **1**.[2] In a formal sense, **1**



1

could be formed by bringing protonated carbon (HC:⁺) toward the center of a face of square cyclobutadiene. The symmetries of the cyclobutadiene and sp-hybridized CH⁺ orbitals are correct for stabilizing this six-electron system. Experimental evidence for a disubstituted **1** with a methyl group at the apex and at one "basal" carbon has appeared.[5]

Various homologs of **1** can be envisioned; **2–6** are

and phenyl substituents are predicted[3c] to stabilize both **1** and **ii**.



iii          iv          v

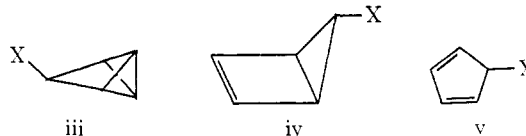(1) W-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

(2) This prediction arose from extended Hückel calculations on the cation i by examining the energy of the system as the central bicyclobutane bond is stretched. More recent calculations using the CNDO[3a] or MINDO/3[3b] methods indicate that the monocyclic nonplanar allyl cation ii also constitutes an energy minimum on the (CH)₅⁺ surface, but there is some disagreement as to which, **1** or ii, has the lower energy. The calculations do indicate that iii and iv are preferred precursors of **1** whereas ionization of v would most likely lead to ii.[4] Methyl



i          ii

(3) (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, **95**, 5836 (1973); (c) W. J. Hehre and P. v. R. Schleyer, *ibid.*, **95**, 5837 (1973).

(4) For experimental evidence, see R. Breslow and J. M. Hoffmann, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972); M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffmann, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *ibid.*, **95**, 3017 (1973).

(5) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Amer. Chem. Soc.*, **94**, 8956 (1972).