the case of the synthetic polymer catalyst, the absence of the conformational rigidity characteristic of proteins precludes a similar degree of specificity. (2) The intimate association of enzyme and substrates increases the effectiveness of hydrophobic forces. Thus, the uncharged analog of acetylcholine, 3,3-dimethyl-*n*-butyl acetate, in which a carbon is substituted for the quaternary nitrogen atom, is attacked by the enzyme only 23% more slowly than the cationic substrate.[23] Another example of the importance of hydrophobic interactions with the enzyme is provided in a comparison of its rate of attack on acetylcholine and on dimethylammoniumethyl acetate.[24] Although the two substrates have their cationic and ester groups at the same spacing, the acetylcholine, with an additional methyl group on the nitrogen, is attacked more than twice as fast. This is in sharp contrast with the lack of any indication of hydrophobic interactions in the present study with synthetic flexible chain polyions. (3) Although long-range electrostatic forces make some contribution to the substrate binding to acetylcholineesterase, this contribution is relatively small. For instance, an increase in the ionic strength from 0.025 to 0.185 produces, at low substrate concentration, a decrease of enzymatic activity by only 45%.[25] The action of synthetic polyions on oppositely charged substrates is much more sensitive to the ionic strength of the medium.

Acknowledgment. The authors are grateful for financial support by the Research Laboratory, U. S. Army, Edgewood Arsenal, under Grant DA-18-AMC-121(A), and by the National Institutes of Health under Grant No. GM 12599-02.

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[23] D. H. Adams and V. P. Whittaker, *Biochim. Biophys. Acta*, **4**, 543 (1950).

[24] I. B. Wilson, *J. Biol. Chem.*, **197**, 215 (1952).

[25] B. Mendel and H. Rudney, *Science*, **102**, 616 (1945).

Substituent Effects and Aryl Participation in β-(*syn*-9-Benzonorbornenyl)ethyl *p*-Bromobenzenesulfonate Solvolyses[1,2]

Ryonosuke Muneyuki and Hiroshi Tanida

Contribution from the Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan. *Received August 7, 1967*

Abstract: A series of 6-substituted β-(*syn*-9-benzonorbornenyl)ethyl brosylates (Ia–e-OBs), the unsubstituted *anti* isomer (IIa-OBs), and the *syn*-propyl homolog (IX-OBs) were synthesized. The acetolysis of unsubstituted Ia-OBs proceeds 20 times as fast at 100° as that of IIa-OBs and yields mainly a mixture of several benzhydrindanyl derivatives formed with rearrangements. The effects of the 6 substituents on the over-all rates, $k_{\mathrm{OCH_3}}/k_{\mathrm{NO_2}}$, amount to a factor of 146, and those on the anchimerically assisted rates, k_Δ, are well correlated by the modified Hammett relationship, $\log (k_\Delta/k_\Delta{}^0) = {}^1/_2\rho(\sigma_p{}^+ + \sigma_m{}^+)$, with $\rho = -2.88$. These are discussed as evidence for remote aryl participation under a constant steric factor. In contrast, the acetolyses of IIa-OBs and IX-OBs showed neither rate enhancement nor rearrangement.

Studies of substituent effects such as carried out by us in the solvolysis of benzonorbornenyl brosylates[3] have been evaluated as a decisive test for π-participation effects.[4] As a continuation of studies of this kind, this paper deals with the acetolysis of 6-substituted β-(*syn*- and *anti*-9-benzonorbornenyl)ethyl brosylates (Ia–e-OBs and IIa-OBs). The results provide one of the best pieces of evidence for the existence of remote aryl participation (Winstein)[5,6] and are, from a theoretical point of view, instructive for the high solvolytic reactivity of β-(*syn*-7-norbornenyl)ethyl brosylate recently found by Bly, *et al.*,[7] and for the solvolytic ring closure of ω-(Δ^3-cyclopentenyl)alkyl arenesulfonates studied by Lawton[8] and Bartlett and his coworkers.[9]

Results

Preparations. The syntheses of 6-substituted β-(*syn*-9-benzonorbornenyl)ethyl alcohols (Ia–d-OH) and the unsubstituted *anti* alcohol IIa-OH were carried out as outlined in Chart I.

9-Benzonorbornenones (IIIa–d)[10] were condensed with carbethoxymethylenetriphenylphosphorane according to the procedure of Wittig[11] to produce ethyl 9-benzonorbornenylideneacetates (IVa–d) in satisfac-

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[1] Presented, in part, at the 17th Organic Reaction Mechanism Symposium of the Chemical Society of Japan in Tokyo, Oct 1966.

[2] The numbering used in this paper is shown in the charts.

[3] (a) H. Tanida, *J. Amer. Chem. Soc.*, **85**, 1703 (1963); (b) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (c) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966); (d) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

[4] H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).

[5] For recent reviews, see (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

[6] R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **84**, 788 (1962), and references cited therein.

[7] R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *ibid.*, **89**, 880 (1967).

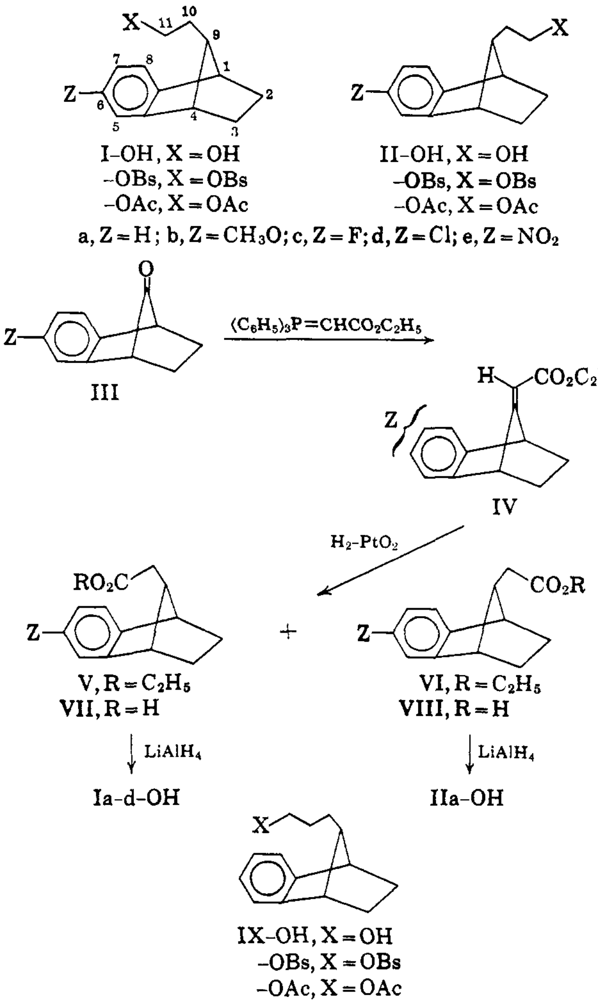
[8] R. G. Lawton, *ibid.*, **83**, 2399 (1961).

[9] (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (b) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (c) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965).

[10] (a) H. Tanida, H. Miyazaki, and H. Ishitobi, *Can. J. Chem.*, **44**, 98 (1966); (b) R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1966).

[11] Refer to A. Maercker in "Organic Reactions," Vol. 14, A. C. Cope, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 270.

Chart I



tory yields. Catalytic reduction of IVa–d over platinum oxide gave a 87:13 mixture of the corresponding saturated *syn* and *anti* esters (Va–d and VIa–d), which could be separated by preparative vpc. The use of palladium on charcoal gave mainly the *anti* isomer; the ratio was 6:4. These esters werere duced with lithium aluminum hydride to give the desired alcohols Ia–d-OH and IIa-OH. Their brosylates (Ia–d-OBs and IIa-OBs) and acetates (Ia–d-OAc and IIa-OAc) were prepared in the usual manner. The saturated *syn* acid VII could be isolated in the pure state by recrystallization of a mixture produced from IV by catalytic hydrogenation over platinum oxide followed by hydrolysis. Lithium aluminum hydride reduction of VII also gave Ia–d-OH. This method has an advantage in that no preparative vpc is required.

The assignment of configurations for the *syn* and *anti* derivatives was made by comparing the nmr spectra of I-OAc and II-OAc. The two protons at C-11 in I-OAc appeared as a triplet at τ 6.10 (J = 6.5 cps), while those in II-OAc exhibited the same pattern at τ 6.00 (J = 6.5 cps). Upon consideration of shielding effects of the benzene ring, the compounds having the high τ value should be assigned to the *syn* series. Furthermore, the products of acetolysis of the *syn* brosylates as described later confirmed this assignment.

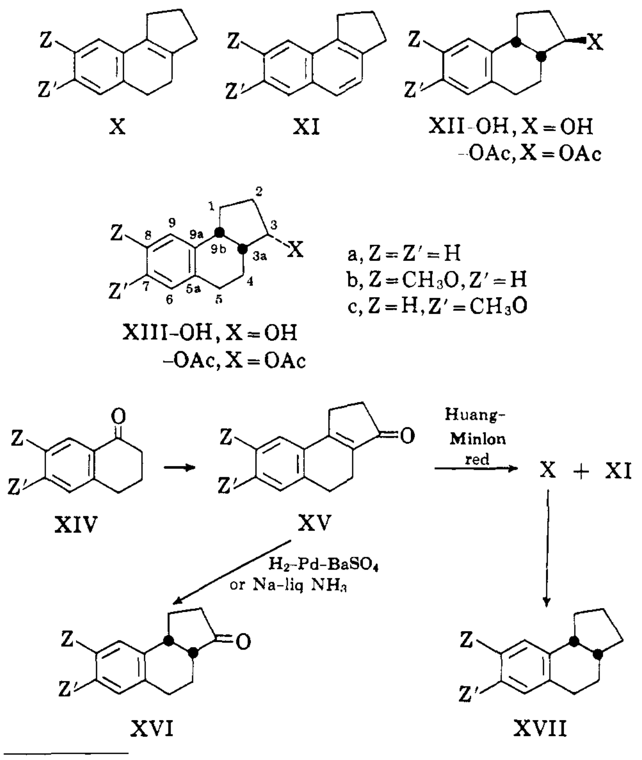
The 6-nitro *syn* derivatives, Ie-OBs and Ie-OAc, were prepared by direct nitration of Ia-OBs and Ia-OAc, respectively, with concentrated nitric acid in a medium composed of 90% aqueous sulfuric acid and nitromethane. In all cases, the almost exclusive β substitution was confirmed by the nmr pattern of aromatic protons of the mononitro products.[12]

γ-(*syn*-9-Benzonorbornenyl)propyl alcohol and its esters (IX) were prepared starting from Ia-OH through the chloride, the cyanide, and then β-(*syn*-9-benzonorbornenyl)propionic acid.

Kinetics. The rates of acetolysis were carried out in glacial acetic acid unbuffered and buffered with 1.1 equiv of sodium acetate. The theoretical infinity titers were obtained in all cases. In the unbuffered runs, the first-order plots were linear for all of the brosylates up to 80% conversion. In the presence of sodium acetate, Ia–d-OBs and IX-OBs yielded linear plots, but the plots for Ie-OBs and IIa-OBs drifted slightly downward (the rates going slower). For the latter cases, the rate constants were calculated at the first half-life. Table I summarizes the rates and the activation parameters thus obtained.

Products. The solvolysis of Ia-OBs at 100° for 18 hr in acetic acid buffered with the above amount of sodium acetate resulted in a mixture consisting of 11.5% of the retained acetate Ia-OAc and several kinds of benzindenyl derivatives formed by rearrangement. Because of the theoretical importance, the yield of Ia-OAc and those of the retained acetates in acetolysis of Ia–e-OBs were carefully determined by vpc, authentic samples and proper compounds being used as internal references. They are listed in Table II in the Discussion. The estimated error in the yield is ±1%. The structures of components and their per cent ratios in the mixture of benzindenyl derivatives were assigned by retention time analysis and integration of peak areas on vpc. Relative to 11.5% Ia-OAc, the mixture was indi-

Chart II



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(12) For a similar observation and nmr spectra of benzonorbornenes bearing substituents on the benzene ring, see H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, 87, 4794 (1965).

Table I. Kinetic Data for the Acetolysis of 6-Substituted β-(*syn*-9-Benzonorbornenyl)ethyl Brosylates and Some Related Brosylates[a]

			Calcd at 100°[c]			
6-Subst	Temp, °C[b]	$k_1 \times 10^4$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)	$k \times 10^4$, sec^{-1}	Rel rate[d]
OCH_3	68.1[d]	0.960			18.9[d]	7.3
	54.1[e]	0.270				
	68.1[e]	1.26	22.9	−9.6	24.3[e]	
	78.1[e]	3.36				
H	110.0[d]	6.49			2.61[d]	1.0
	78.8[e]	0.335				
	99.0[e]	2.51	25.2	−7.7	2.76[e]	
	110.0[e]	6.88				
F	99.0[d]	0.813			0.978[d]	0.38
	90.5[e]	0.416				
	98.8[e]	0.948	23.3	−14.7	1.00[e]	
	119.8[e]	5.09				
Cl	99.0[d]	0.400			0.439[d]	0.17
	90.5[e]	0.277	24.4	−12.6	0.672[e]	
	110.0[e]	1.63				
NO_2	99.0[d]	0.161			0.175[d]	0.067
	99.0[e,f]	0.287				
	110.0[e,f]	0.768	22.6	−18.9	0.322[e]	
	130.0[e,f]	3.30				
anti-Ethyl (IIa-OBs)	99.0[d]	0.120			0.131[d]	0.050
	99.0[e,f]	0.199	22.8	−19.2	0.217[e]	
	130.0[e,f]	2.30				
	99.0[g]	0.377				
syn-Propyl (IX-OBs)	119.95[e]	1.28	22.8	−18.8	0.268[e]	
	130.2[e]	2.69				

[a] [ROBs] = 0.045. [b] Controlled to ±0.03°. [c] Activation parameters were calculated from runs in the presence of 0.05 *M* sodium acetate. It was assumed that runs in the absence of sodium acetate have the same parameters. [d] In the absence of sodium acetate. [e] In the presence of 0.05 *M* sodium acetate. [f] Calculated from the slope of curving first-order plots at 50% reaction. [g] In the presence of 0.10 *M* sodium acetate.

cated to be composed of 17.5% unsaturated hydrocarbons (two peaks by vpc), 49.6% 2,3,4,5-tetrahydro-1H-benz[*e*]indene (Xa), 7.3% 2,3-dihydro-1H-benz[*e*]indene (XIa), 11.9% 2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]inden-3β-ol acetate (XIIa-OAc), and 2.2% 2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]inden-3α-ol acetate (XIIIa-OAc).

Hydrogenation of the first 17.5% hydrocarbons led to a single saturated compound, which was identified as 2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]indene (XVII) prepared from Xa by catalytic reduction. The three main compounds, Ia-OAc, Xa, and XIIa-OAc, were isolated by preparative vpc, and their structures were confirmed by comparison of infrared and nmr spectra with those of authentic samples. The syntheses of these samples are outlined in Chart II and detailed accounts are presented in the Experimental Section.

The acetates Ia-OAc, XIIa-OAc, and XIIIa-OAc were recovered unchanged under the reaction conditions and were verified to be the products of kinetically controlled solvolyses. The configurations for XIIa-OH and XIIIa-OH were assigned by referring to the results obtained from the reduction of *cis*-bicyclo[3.3.0]octan-2-one[13] and *cis*-bicyclo[4.3.0]nonan-4-one.[14] Lithium aluminum hydride reduction of both *cis* ketones gives predominantly the *cis,cis* alcohols (thermodynamically less stable isomer) by steric approach control,[15,16] whereas the major components in the mixture equilibrated by aluminum isopropoxide in acetone–isopropyl alcohol are the thermodynamically more stable *cis,trans* alcohols.[17] Therefore, it is reasonable to consider that lithium aluminum hydride reduction of the benzindenone XVI gives predominantly XIII-OH, while the Birch reduction produces mainly XII-OH by thermodynamic control.[18]

The acetolysis of Ib-OBs at 78° for 17.5 hr in the above buffered medium yielded 5.3% of the retained acetate Ib-OAc and a mixture of rearranged products. The mixture was indicated by vpc to involve the following nine components; in the order of retention time, 22%, two compounds of unknown structure; 28.9%, the 8-methoxytetrahydrobenzindene Xb; 10%, two compounds of unknown structure; 4%, the 8-methoxydihydrobenzindene XIb; 22.7%, the 8-methoxyhexahydrobenzinden-3β-yl acetate XIIb-OAc; 2%, unidentified compound; and 5.1%, the 8-methoxyhexahydrobenzinden-3α-yl acetate XIIIb-OAc. By preparative vpc, Ib-OAc, Xb, and XIIb-OAc were isolated, and their structures were established by comparison with authentic samples independently prepared (see Experimental Section). Further, vpc showed no appreciable amount of the 7-methoxyhexahydrobenzinden-3β-yl acetate XIIc-OAc.

In sharp contrast, Ie-OBs, IIa-OBs, and IX-OBs produced almost quantitatively the corresponding acetates of retention with no measurable amount of rearranged compounds. As exceptions, traces (<∼0.2%) of products of unknown structure were observed in the acetolyses of Ie-OBs and IX-OBs.

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(13) A. C. Cope, M. Brown, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2852 (1958).

(14) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(15) W. G. Dauben, D. G. Fonker, and D. S. Noyce, *J. Amer. Chem. Soc.*, **78**, 2579 (1956).

(16) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

(17) E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5992 (1957).

(18) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 317; W. Huckel, M. Maier, E. Jordan, and W. Seeger, *Ann.*, **616**, 46 (1958).

Table II. Dissection of Rates and Product Distribution in Acetolysis of 6-Substituted β-(*syn*-9-Benzonorbornenyl)ethyl Brosylates[a]

		From kinetic data only		From product distribution		
6-Subst	$k \times 10^4$, sec^{-1}	$k_\Delta \times 10^4$,[b] sec^{-1}	Rel k_Δ	% product of retention	$k_\Delta' \times 10^4$,[c] sec^{-1}	Rel k_Δ'
CH_3O	18.9	18.8	7.58	3.4	18.3	8.09
H	2.61	2.48	1.00	13.5	2.26	1.00
F	0.978	0.847	0.341	33.8	0.647	0.286
Cl	0.439	0.308	0.124	47.9	0.228	0.101
NO_2	0.175	0.044	1.77×10^{-2}	100	0	0

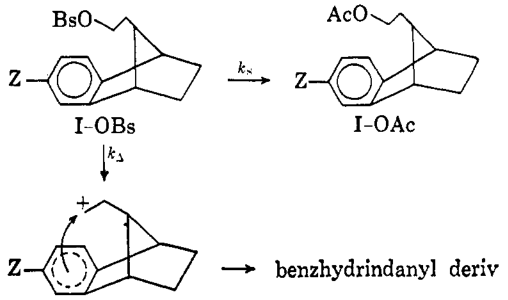
[a] At 100° in the absence of sodium acetate. [b] $k_\Delta = k - k_s$. [c] $k_\Delta' = 0.01k(100 - \%$ product of retention).

Discussion

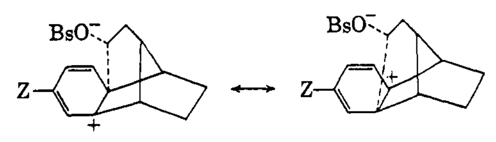
The rates of Ie-OBs, IIa-OBs, and IX-OBs are compatible with those reported for some relevent compounds of no participation: *n*-butyl brosylate (0.143×10^{-4} sec^{-1} at 99.4°),[19] 4-phenyl-*n*-butyl brosylate (0.162×10^{-4} sec^{-1} at 100°),[20] β-(cyclopentyl)ethyl brosylate (0.169×10^{-4} sec^{-1} at 100.9°),[21] and β-(2-indanyl)ethyl brosylate (0.135×10^{-4} at 100.0°).[22] Together with this fact, no formation of rearranged products clearly indicates the absence of aryl participation for Ie-OBs, IIa-OBs, and IX-OBs.

On the other hand, the acetolyses of Ia-d-OBs are aided by aryl π-electron delocalization in the transition state. At 100°, Ia-OBs is 20 times more reactive than IIa-OBs and produces mainly the rearranged compounds.[23] The effect of substituents on the rates of these *syn*-brosylates, k_{OCH_3}/k_{NO_2}, amounts to a factor of 146. The accelerating effect of the methoxy subsubstituent is 7.3, while that for a model compound, 4-phenyl-*n*-butyl brosylate, in which Winstein proposed Ar_1-5 participation, is only 1.3.[20] These values are far larger than can be accounted for in terms of a simple inductive effect of the benzene ring.

According to the method of Winstein and Grunwald,[24] the acetolysis rate constants for Ia-d-OBs may be dissected into k_Δ, the rate constant for anchimerically assisted solvolysis, and k_s, the rate constant for anchimerically unassisted solvolysis, assuming that k_s is, regardless of the substituents, equal to the rate constant for IIa-OBs. Substracting k_s from the observed rate constants for Ia-d-OBs leads to the derived values of k_Δ summarized in Table II. Another dissection will be possible on the assumption that anchimerically assisted solvolysis leads only to rearranged products and anchimerically unassisted solvolysis gives only acetates of retention. This assumes that any intermediate in the unassisted solvolysis of such a simple primary brosylate as dealt with here could be only formed with solvent participation and collapse in solvent cage leading to acetate. Calculation on this basis gives k_Δ' in Table II. By the agreement of k_Δ with k_Δ' within experimental error, it is apparent that the underlying assumptions are at least semiquantitatively valid.



The values of k_Δ and k_Δ' were linearly correlated by the modified Hammett relationship, $\log (k/k^0) = \rho(\sigma_p^+ + \sigma_m^+)/2$, yielding $\rho = -2.88$ for k_Δ (Figure 1) and $\rho = -3.07$ for k_Δ'. This type of relationship has been obtained from the substituent effects on 9-benzonornenyl brosylate solvolyses.[3] Other Hammett plots such as attempted in a previous paper[3b] provided unsatisfactory correlations. The significantly large negative ρ value indicates unequivocally that the amount of participation increases as activating substituents are introduced into the aromatic ring.[3] Further, because of the same type of Hammett relationship thus established in both of the 9-benzonorbornenyl and the present systems and, in connection with our previous observation that the effect of the 6 substituent and the 7 substituent in the 9-benzonorbornenyl system are additive, evidencing a symmetrical transition state,[3c] it is reasonable to predict a similar additivity of substituents and a symmetrical transition state in the anchimerically assisted solvolysis of Ia-d-OBs. Similar symmetrical transition states have been proposed in some related reactions, the solvolyses of β-(3,4-dimethyl-3-cyclopentenyl)ethyl arenesulfonate[9] and β-(*syn*-7-norbornenyl)ethyl brosylate.[7] However, our data provide no indication of whether the product-forming intermediate formed just after the transition state is a single symmetrical or distinct unsymmetrical ion pair(s) or cations.



In view of the cationic intermediate(s), the reaction path shown in Chart III would most simply accommodate all the products formed by rearrangement. Rearrangement of the initial intermediate(s) into the benzhydrindanyl cations by C_1-C_{8a} bond cleavage would be favored thermodynamically by strain relief

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(19) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, 77, 1117 (1955).

(20) R. Heck and S. Winstein, *ibid.*, 79, 3105 (1957).

(21) Calculated with the factor OBs:OTs = 3 from the data reported in ref 8a.

(22) H. Tanida and S. Teratake, unpublished data.

(23) It has been shown that internal return may be an important factor in acetolysis. See S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 78, 328 (1956). However, any ion-pair return that might be involved in acetolysis of the primary brosylates in Table I would not affect the solvolysis rate. This is because the expected products of ion-pair return would be secondary brosylates and solvolyze more rapidly. For example, we measured the rate constants of 0.188×10^{-4} sec^{-1} at 54.1° for XII-OBs.

(24) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, 70, 828 (1948).

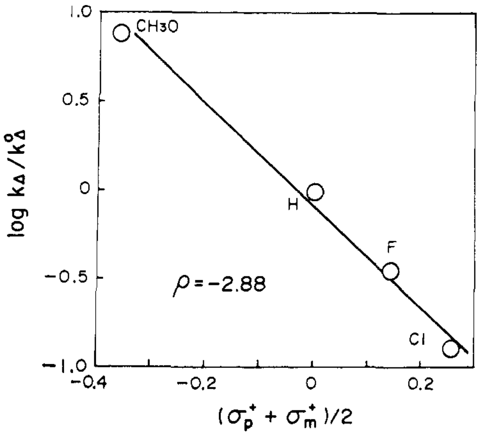
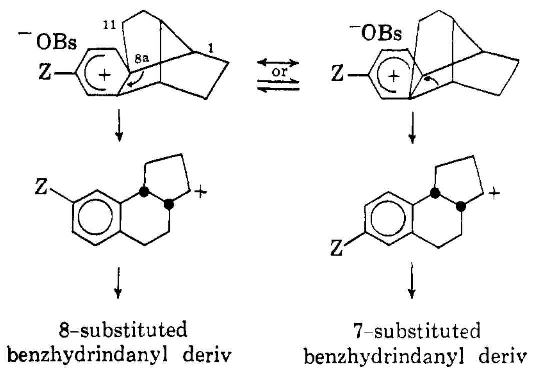


Figure 1. The ρ–σ treatment of anchimerically assisted rate constants in the acetolyses of β-(*syn*-9-benzonorbornenyl)ethyl brosylates.

rather than return to the original β-(*syn*-9-benzonorbornenyl)ethyl system by C_{11}–C_{8a} bond cleavage.

Chart III



Finally, it is pointed out that the absence of participation in the acetolysis of IX-OBs is consistent with the unimportance of Ar$_1$-6[5b,20] or Ar$_2$-7[5b,25] and with the fact that the elongation of the chain from ethyl to propyl in the solvolysis of ω-(Δ^3-cyclopentenyl)alkyl arenesulfonates brings about a large decrease in the anchimerically assisted rate.[9c]

Experimental Section[26]

9-Benzonorbornenones (IIIa–d) These ketones were prepared by the procedure reported earlier.[10b]

Ethyl 9-Benzonorbornenylideneacetate (IVa–d). General Procedure. A solution of 5.0 g (0.032 mol) of IIIa in 10 ml of dichloromethane was added to a solution of 12.0 g (0.034 mol) of carbethoxymethylenetriphenylphosphorane in 20 ml of dichloromethane. After heating under reflux for 4 hr, the reaction mixture was allowed to stand overnight at room temperature. Evaporation gave an oily residue which was dissolved in 20 ml of ether and cooled at 0°. Triphenylphosphine oxide was precipitated and was then filtered off. The ether solution was concentrated to an oil which was distilled to give 5.6 g (77%) of IVa, bp 120–123° (4 mm), n^{25}D 1.5533; ν_{max}^{neat} 3026, 1720, 1690, 1465, 1373, 1344, 1282, 1270, 1200, 1162, 1117, 1038, 760, and 706 cm^{-1}; $\lambda_{max}^{n\text{-heptane}}$ 276.0 mμ (ϵ 3930), 269.2 (3590), 263.4 (2400), 208.5 (28,700), and 192.7 (52,900).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.80; H, 7.07.

The ester IVb obtained by the same procedure boiled at 155–156° (0.1 mm), n^{25}D 1.5556.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 74.41; H, 6.97. Found: C, 74.36; H, 7.07.

The ester IVc boiled at a bath temperature of 160° (0.1 mm), n^{26}D 1.5374.

Anal. Calcd for $C_{15}H_{15}O_2F$: C, 73.15; H, 6.14. Found: C, 73.06; H, 6.43.

Catalytic reduction of IVa–d was carried out over platinum oxide with uptake of 1 molar equiv of hydrogen to yield a 87:13 mixture of the corresponding Va–d and VIa–d, which were separated by preparative vpc.

β-(*syn*- and -*anti*-9-Benzonorbornenyl)ethanols (Ia–d-OH and IIa–d-OH) were obtained from Va–d and VIa–d, respectively, by lithium aluminum hydride reduction in an ether solution followed by the usual work-up.

The *syn*-Ia-OH had bp 120–123° (4 mm) and n^{25}D 1.5533. The *anti*-IIa-OH had bp 140° (bath temperature, 2mm) and n^{25}D 1.5579.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found for Ia-OH: C, 83.06; H, 8.53. For IIa-OH: C, 82.67; H, 8.62.

The acetate Ia-OAc had bp 128–130° (4 mm) and n^{26}D 1.5243; ν_{max}^{neat} 2940, 1740, 1460, 1368, 1242, 1122, 1043, and 757 cm^{-1}; nmr τ 2.94 (4 H, aromatic, multiplet), 6.10 (2 H, C-11, triplet, J = 6.5 cps), 6.90 (2 H, C-1 and C-4, multiplet), 8.08 (3 H, OAc, singlet), 8.70 (2 H, C-10, quartet, J = 6.5 cps), 8.1 (2 H, *exo*-C-2 and -C-3, multiplet), 8.8 (2 H, *endo*-C-2 and -C-3, multiplet), and ~8.1 (1 H, C-9, overlapped with the *exo*-hydrogens).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.12; H, 7.94.

The acetate IIa-OAc had bp 135–137° (4 mm) and n^{26}D 1.5284; the same infrared absorptions as those of the *syn* isomer except at 1112 and 753 cm^{-1}; nmr τ 3.03 (4 H, aromatic, multiplet), 6.00 (2 H, C-11, triplet, J = 6.5 cps), 6.95 (2 H, C-1 and C-4, multiplet), 8.05 (3 H, OAc, singlet), 8.1 (2 H, *exo*-C-2 and -C-3, multiplet), 8.45 (2 H, C-10, quartet, J = 6.5 cps), 8.8 (2 H, *endo*-C-2 and -C-3, multiplet), and ~8.1 (1 H, C-9, overlapped with the *exo*-hydrogens).

Anal. Found: C, 78.48; H, 7.93.

The brosylates Ia–d-OBs melted at 89.7–90.7, 66.8–68.3, 73.7–74.7, and 75.2–77.2°, respectively.

Anal. Calcd for $C_{19}H_{19}BrO_3S$: C, 56.02; H, 4.70. Found: C, 56.17; H, 4.89. Calcd for $C_{20}H_{21}BrO_4S$: C, 54.93; H, 4.84. Found: C, 55.10; H, 5.08. Calcd for $C_{19}H_{18}BrFO_3S$: C, 53.66; H, 4.27. Found: C, 53.88; H, 4.55. Calcd for $C_{19}H_{18}BrClO_3S$: C, 51.65; H, 4.17. Found: C, 51.74; H, 4.39.

β-(*syn*- and -*anti*-9-Benzonorbornenyl)acetic acids (VIIa and VIIIa) were obtained by hydrolyses of Va and VIa, respectively, in methanol–water (8:1) containing sodium hydroxide. The acids, VIIa and VIIIa, melted at 104.5–105.5 and 99–99.5°, respectively.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found for VIIa: C, 76.73; H, 7.05. Found for VIIIa: C, 77.51; H, 7.14.

β-(6-Nitro-*syn*-9-benzonorbornenyl)ethyl Brosylate (Ie-OBs). A solution of 7.9 g of the nitrating reagent, prepared from 1.0 g of 60% nitric acid, 18.0 g of 98% sulfuric acid, and 1.6 g of water, was added dropwise to a stirred solution of 1.36 g of Ia–OBs in 60 ml of nitromethane under ice cooling. The reaction mixture was stirred for 30 min under ice cooling and for 50 min at room temperature, then added to ice–water. The mixture was extracted with ether, and the ether extract was washed with water, aqueous sodium bicarbonate, and again with water. Removal of the solvent followed by recrystallization from ether–*n*-pentane gave 1.05 g (70%) of Ie-OBs, mp 93–94.7°. The nmr spectrum in $CDCl_3$ shows two aromatic protons as an AB part multiplet of an ABK system centered at τ 2.03 and an aromatic proton as a second-order quartet of an ABK system centered at τ 2.8.

Anal. Calcd for $C_{19}H_{18}BrNO_5S$: C, 50.45; H, 4.00. Found: C, 50.62; H, 4.12.

β-(6-Nitro-*syn*-9-benzonorbornenyl)ethyl acetate (Ie-OAc) was similarly prepared by the nitration of Ia-OAc and boiled at a bath temperature of 160° (1 mm), n^{24}D 1.5530. The nmr spectrum of aromatic protons exhibited a typical ABK pattern.

Anal. Calcd for $C_{15}H_{17}O_4N$: C, 65.44; H, 6.22. Found: C, 65.44; H, 6.38.

β-(*syn*-9-Benzonorbornenyl)propionic Acid. To a solution of 2.36 g of Ia-OH in 5.0 ml of pyridine, 2.0 g of thionyl chloride was added under cooling with ice. After standing for 3 hr, the reaction mixture was poured onto the ice–water and extracted with ether. The ether extract was washed with about 3% cold hydrochloric acid and water, dried over sodium sulfate, and concentrated.

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(25) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3114 (1957).

(26) Melting points are corrected. Boiling points are uncorrected. Infrared spectra were determined on a Nippon Bunko Model IR-S spectrophotometer. Ultraviolet spectra were determined on a Hitachi Model EPS-2 spectrophotometer. The nmr spectra were observed at 60 Mc with a Varian Model A-60 using tetramethylsilane as an internal standard, in carbon tetrachloride unless otherwise noted.

The residual oil (2.25 g) was dissolved in 16 ml of dimethylformamide containing 2.4 g of potassium cyanide and heated at 150° for 75 min with stirring. After working up as usual, the resultant crude cyanide (2.05 g) showing $\nu_{\max}^{\text{neat}}$ 2250 cm^{-1} was hydrolyzed with a solution consisting of 12.5 ml of 20% aqueous sodium hydroxide and ethanol, enough to dissolve the cyanide, for 5 hr under reflux. The solution was diluted with 10% sodium hydroxide and extracted with ether. When acidified with hydrochloric acid under cooling, the aqueous layer became cloudy and a crystalline precipitate appeared on standing. The precipitate was collected by filtration, washed with water, and dried. Recrystallization of this material from *n*-hexane gave 1.0 g (37%), mp 132.3–133.3°.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.70; H, 7.34.

γ-(*syn*-9-Benzonorbornenyl)propyl Brosylate (IX-OBs). The acid (0.80 g) obtained above was converted to the corresponding alcohol by lithium aluminum hydride reduction in ether and the resultant oil (0.70 g) having $\nu_{\max}^{\text{neat}}$ 3335 cm^{-1} was esterified by brosyl chloride in pyridine. Recrystallization of the product from *n*-hexane gave 1.20 g (77%) of IX-OBs, mp 95.2–95.7°.

Anal. Calcd for $C_{20}H_{21}BrO_3S$: C, 57.01; H, 5.02. Found: C, 56.96; H, 5.06.

2,3,4,5-Tetrahydro-1H-benz[*e*]indene (Xa). A sample of 1.84 g of XVa (mp 81–82°) (lit.[27] mp 80.8–81.2°), prepared from α-tetralone (XIVa) by the reported method,[27] was dissolved in 20 ml of trimethylene glycol containing 1.0 g of potassium hydroxide and to this solution 1.6 ml of 85% hydrazine hydrate was added. The reaction mixture was heated gradually and the temperature allowed to rise to 195° when refluxing was continued for 4.0 hr. The cooled solution was poured into water and extracted with ether. After working up in the usual way, the ether extract gave 0.9 g of a brown oil. Analysis of the product on a 1-m column at 163° indicated two peaks, a major component (56%) at a retention time of 5.1 min and a minor component (46%) at a retention time of 9.15 min. The two components were isolated by preparative vpc at 170°. The major component, Xa, had bp 87–89° (2 mm) and n^{21}D 1.5940; $\nu_{\max}^{\text{neat}}$ 3060, 3020, 2925, 2840, 1492, 1448, 1438, 757, and 732 cm^{-1}; nmr peaks at τ 3.04 (4 H, aromatic, multiplet) and from 7.0 to 8.15 (other ten protons).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 92.01; H, 8.28.

The minor component, XIa, had bp 89–91° (2 mm) and $n^{24.5}$D 1.6274; $\nu_{\max}^{\text{neat}}$ 3045, 2935, 2840, 1515, 1436, 1378, 806, 767, and 741 cm^{-1}; $\lambda_{\max}^{95\%\,\text{ethanol}}$ 276.0 mμ (ε 5250), 281.0 (5380), 292.0 (4200), 310.3 (1260), 312.0 (915), and 324.6 (1860), and shoulders at 265.0 mμ (ε 3940), 270.0 (4550), and 286.5 (4790). These maxima are identical with those reported.[28]

2,3,3aβ,4,5,9bβ-Hexahydro-1H-benz[*e*]inden-3-one (XVIa). To a stirred solution of about 200 ml of liquid ammonia containing 0.9 g of sodium metal was added dropwise 3.00 g of XVa in 80 ml of dry ether. Ammonium chloride enough to decompose the residual sodium was added to the reaction mixture, and allowed to warm to room temperature. The residue obtained was dissolved in ether and the usual working up gave 3.0 g of a crude oil which was chromatographed on alumina. Elution with benzene–petroleum ether (bp 30–60°) (1:2) gave 2.43 g (80%) of XVIa, bp 127–129° (2 mm), n^{25}D 1.5635. This ketone showed an identical infrared spectra with an authentic sample,[29] prepared by catalytic reduction of XVa using 5% palladium–barium sulfate catalyst at 80° (80 atm). The semicarbazone melted at 232–233° (mixture melting point undepressed).

2,3,3aβ,4,5,9bβ-Hexahydro-1H-benz[*e*]inden-3β-ol (XIIa-OH). A sample of 0.87 g of XVIa was reduced by 0.17 g of sodium in 200 ml of liquid ammonia. After working up, the reaction solution yielded a mixture of XIIa-OH and XIIIa-OH. Vpc analysis of the acetate mixture derived therefrom showed relative peak areas of 92:8 due to XIIa-OAc and XIIIa-OAc, respectively. Repeated recrystallization of the mixture from *n*-pentane gave 0.34 g (39%) of XIIa-OH, mp 56.5–57°, nmr peak of 3α-proton at τ 6.00 (multiplet).

The acetate XIIa-OAc had bp 120–122° (2 mm) and n^{22}D 1.5350; $\nu_{\max}^{\text{neat}}$ 2930, 1736, 1242, 1022, 765, and 744 cm^{-1}; nmr peak of 3α-proton at τ 5.1 (multiplet).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.33; H, 7.88.

The *p*-nitrobenzoate XIIa-OPB, mp 128.7–130.7°, was prepared using *p*-nitrobenzoyl chloride in pyridine.

Anal. Calcd for $C_{20}H_{19}O_4N$: C, 71.20; H, 5.68. Found: C, 71.27; H, 5.84.

2,3,3aβ,4,5,9bβ-Hexahydro-1H-benz[*e*]inden-3α-ol Acetate (XIIIa-OAc). Lithium aluminum hydride reduction of XVIa in ether led to the mixture of XIIa-OH and XIIIa-OH. Vpc analysis of the acetate mixture derived indicated that the peak area due to XIIIa-OAc was 7.3 times that due to XIIa-OAc.

The infrared bands of XIIIa-OAc at 1054, 760, and 739 cm^{-1} are distinct from the corresponding bands of XIIa-OAc. The nmr peak of the 3β-proton in XIIIa-OAc appeared at τ 4.77 as a multiplet.

The *p*-nitrobenzoate XIIIa-OPB melted at 111.7–112.7°.

Anal. Calcd for $C_{20}H_{19}O_4N$: C, 71.20; H, 5.68. Found: C, 71.36; H, 5.80.

8-Methoxy-2,3,4,5-tetrahydro-1H-benz[*e*]inden-3-one (XVb) was prepared from 7-methoxy-1-tetralone (XIVb) (mp 63–64°) (lit.[30] mp 62–63°) and diethyl succinate by the reported method, except the use of polyphosphoric acid in the cyclizing step,[31] in 3.5% over-all yield and melted at 90–91°.

Anal. Calcd for $C_{14}H_{14}O_2$: C, 74.48; H, 6.59. Found: C, 78.33; H, 6.55.

8-Methoxy-2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]inden-3-one (XVIb) and -3β-ol (XIIb-OH). To a stirred solution of about 100 ml of liquid ammonia containing 173 mg of sodium metal was added dropwise 321 mg of XVb in 30 ml dry ether. When the blue color faded during this time, additional sodium metal (~100 mg) was added. The same working up as described for XVIa gave a crude oil which was chromatographed on alumina. Elution with petroleum ether–ether (9:1) gave 75 mg (23%) of XVIb, mp 47–48° (from *n*-hexane); $\nu_{\max}^{\text{CHCl}_3}$ 1738 cm^{-1} (C=O). Elution with ether gave 70 mg (22%) of XIIb-OH, mp 67–68° (from *n*-hexane); $\nu_{\max}^{\text{CHCl}_3}$ 3400 cm^{-1} (OH).

Anal. Calcd for $C_{14}H_{16}O_2$ (XVIb): C, 77.75; H, 7.46. Found: C, 77.47; H, 7.61.

Anal. Calcd for $C_{14}H_{18}O_2$ (XIIb-OH): C, 77.03; H, 8.31. Found: C, 77.28; H, 8.32.

The acetate XIIb-OAc boiled at a bath temperature of 180° (0.1 mm), n^{23}D 1.5470; $\nu_{\max}^{\text{neat}}$ 2930, 1735, 1612, 1505, 1250, and 1038 cm^{-1}; nmr peak of the 3α-proton at τ 5.1 (multiplet).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 74.22; H, 7.67.

8-Methoxy-2,3,4,5-tetrahydro-1H-benz[*e*]indene (Xb). The same procedure on XVb as described for Xa led to Xb and XIb, in the ratio of 4:1, which were separated by preparative vpc at 170°. The major component had bp 160° (bath temperature, 2 mm) and n^{23}D 1.5907; $\nu_{\max}^{\text{neat}}$ 2910, 2820, 1607, 1500, 1216, 1038, and 815 cm^{-1}; nmr peaks of aromatic protons at τ 3.09 (1 H, C-6, $J_{7,6}$ = 8.5 cps), 3.42–3.57 (2 H, C-7 and C-9, $J_{7,9}$ = 2.5 cps).

Anal. Calcd for $C_{14}H_{16}O$ (Xb): C, 83.96; H, 8.05. Found: C, 83.75; H, 8.38.

8-Methoxy-2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]indene-3α-ol Acetate (XIIIb-OAc). Reduction of XVIb with sodium borohydride led to XIIIb-OH which was converted to XIIIb-OAc, bp 180° (bath temperature, 0.1 mm). Vpc shows that the acetate contains about 8% of XIIb-OAc.

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.70; H, 7.83.

7-Methoxy-2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]inden-3-one (XVIc). The starting unsaturated ketone XVc, mp 97–97.5° (lit.[32] mp 96°), was prepared from 6-methoxy-1-tetralone (XIVc) and diethyl succinate by the reported method. The saturated ketone XVIc was obtained from XVc by the same manner as described for XVIa. The semicarbazone of XVIc melted at 237.5–238.5° (from ethanol) (lit.[32] mp 245° from acetic acid).

Anal. Calcd for $C_{15}H_{19}O_2N_3$: C, 65.91; H, 7.01. Found: C, 66.08; H, 7.00.

7-Methoxy-2,3,3aβ,4,5,9bβ-hexahydro-1H-benz[*e*]inden-3α-ol (XIIc-OH), mp 62–63.5°, was prepared from XVIc by the same method as described for XIIa-OH.

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The acetate, XIIe-OAc, boiled at a bath temperature of 180° (0.1 mm), $n^{24}D$ 1.5370.

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.83; H, 7.87.

Kinetic Measurements. The kinetic procedure for the acetolysis studies was essentially the same as that employed previously.[3b] The glacial acetic acid contained 1 wt % of acetic anhydride.

Vapor Phase Chromatography. Vpc analyses were carried out on a Hitachi Perkin-Elmer Model F-6 equipped with a hydrogen flame ionization detector using either a 1 m × 3 mm stainless steel column packed with 10% diethylene glycol succinate polyester on 60–80 mesh Chromosorb W or a 45 m × 0.5 mm stainless steel capillary coated with SE-30. Helium was used as a carried gas at a pressure of approximately 1 kg/cm². In preparative vpc, each material separated on a 5 m × 14 mm stainless steel column packed with 5% diethylene glycol succinate polyester on 30–60 mesh Chromosorb W was divided into two parts. The minor part was introduced to a flame detector and the main one was trapped in the tube cooled in Dry Ice–acetone. Helium was used as a carrier gas (200 cc/min).

Separation of Acetolysis Products. In a typical procedure, a sample of 5.78 g of Ia-OBs in 142 ml of glacial acetic acid containing 0.105 *M* sodium acetate and 1 wt % acetic anhydride was thermostated in a sealed tube at 86° for 18 hr. The solution was poured into ice-water and extracted three times with *n*-pentane. The combined extracts were washed with water and aqueous sodium bicarbonate and dried. After removal of the solvent, the residual oil was distilled (2 mm) to give 3.20 g of the products which were separated on a preparative vpc column at 200°.

Acknowledgment. We thank Mr. Toshisada Yano for his skillful technical assistance and Mr. Katsuto Okuno for the partial fulfillment of the preparative vpc.

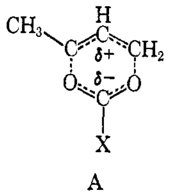
Rearrangement of Esters in the Gas Phase. II. Substituent Effects on the Rate of Isomerization of Allylic Esters[1]

Edward S. Lewis, James T. Hill, and Edward R. Newman

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received August 21, 1967*

Abstract: The earlier studies on rearrangement of crotyl esters are extended to the study of α- and γ-trifluoromethylallyl trifluoroacetates (IV and V), allyl-α-d_2 trifluoroacetate (I), allyl-^{18}O trifluoroacetate (III), α,β-dimethylallyl acetate (VII), and α,γ-dimethylallyl acetate (X). In some cases a minor but detectable rearrangement to *cis*- as well as *trans*-γ-substituted allyl derivatives is observed. The rate of rearrangement of allyl acetate is within experimental error the same whether followed by deuterium or ^{18}O labeling. The results are consistent with the transition state with carbonium carboxylate character proposed earlier.

The preceding paper of this series[2] showed that the rearrangement rates of crotyl esters increased in the order acetate < methyl carbonate < trifluoroacetate, and the less precisely determined rate for crotyl chloroformate was still faster.[3] A transition state was proposed (based upon the relation of the rates to the acid strengths) with substantial charge separation but with a structure resembling that of a Cope rearrangement, such as A. In this paper we explore the substituent effects on the allyl moiety to establish further the charge distribution on the transition state.

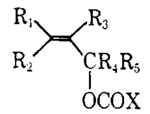


A

Results and Discussion

Rates on α- and γ-trifluoromethylallyl trifluoroacetates (IV and V) and on α,β-dimethylallyl acetate (VII) were determined using the stirred flow reactor and gas chromatographic analysis described before.[2,3] The rearrangement of allyl-α-d_2 trifluoroacetate (I) to allyl-γ-d_2 trifluoroacetate (II) was followed in the stirred flow system using an nmr analysis. The conversion of allyl-^{18}O trifluoroacetate (III) to allyl trifluoroacetate-carbonyl-^{18}O was followed by hydrolysis to the alcohol

Table I. Structures of Compounds Studied of General Formula



Compd	R_1	R_2	R_3	R_4	R_5	X
I	H	H	H	D	D	CF_3
II	D	D	H	H	H	CF_3
III[a]	H	H	H	H	H	CF_3
IV	H	H	H	H	CF_3	CF_3
V	CF_3	H	H	H	H	CF_3
VI	H	CF_3	H	H	H	CF_3
VII	H	H	CH_3	H	CH_3	CH_3
VIII[b]	CH_3	H	CH_3	H	H	CH_3
IX[b]	H	CH_3	CH_3	H	H	CH_3
X[c]	CH_3	H	H	H	CH_3	CH_3
XI	H	CH_3	H	H	CH_3	CH_3
XII[d]	H	H	H	H	CH_3	CF_3
XIII[d]	CH_3	H	H	H	H	CF_3
XIV[d]	H	H	H	H	CH_3	OCH_3
XV[d]	CH_3	H	H	H	H	OCH_3
XVI[d]	H	H	H	H	CH_3	CH_3
XVII[d]	CH_3	H	H	H	H	CH_3

[a] This compound was labeled with ^{18}O. [b] These two compounds are geometrical isomers, but the structural assignment is not rigorous. [c] This compound was used in optically active form. [d] From ref 2.

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(1) From portions of the 1967 Ph.D. theses of J. T. Hill, National Defense Education Act Fellow, 1964–1967, and E. R. Newman, National Aeronautics and Space Administration Trainee, 1965–1967.

(2) E. S. Lewis and J. M. MacDonald, submitted for publication.

(3) E. S. Lewis and K. Witte, submitted for publication.