Substituent Effects on the Solvolysis of Benzonorbornen-2-*endo*-yl *p*-Bromobenzenesulfonates and Comparison with the Results from the Corresponding *exo* Epimers[1-3]

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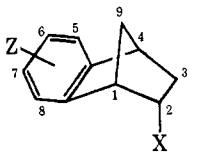
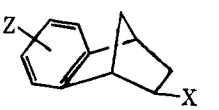
Abstract: A series of aromatic-substituted benzonorbornen-2-*endo*-yl *p*-bromobenzenesulfonates was solvolyzed and the effects of substituents on rate and products were studied. The relative rates in acetolysis of 6-CH_3O, 7-CH_3O, H, 7-CH_3O-6-NO_2, 7-NO_2, and 6,7-$(NO_2)_2$ brosylates at 77.60° were 2.7, 1.2, 1, 0.16, 0.10, and 0.012, respectively. The rate variation, $k_{6\text{-}CH_3O}/k_{6,7\text{-}(NO_2)_2}$, by a factor of 230 is compared with the corresponding variation in the *exo* epimers by a factor of 1.6×10^7. The acetolyses yield predominantly the *exo*-substituted products (benzonorbornen-2-*exo*-ols or their esters) with inversion of configuration, besides the minor olefins and *endo*-substituted products, and the apparent product distribution is not significantly influenced by the substituents in the benzene ring. The H, 7-NO_2, and 6,7-$(NO_2)_2$ brosylates deuterated at C_2 (α to the brosyl groups) were synthesized and their deuterium distributions after acetolyses analyzed by nmr. The fact that migration percentages of the deuterium toward C_1 were 44 for H, 25 for 7-NO_2, and 16 for 6,7-$(NO_2)_2$ demonstrate that, although the Wagner–Meerwein rearrangement plays a major role in the acetolysis of the H compound, the role decreases with introduction of deactivating groups into the benzene ring. The Hammett ρ-σ treatments of the observed rates and the partial rates for the deuterium scrambling afford straight lines with ρ −1.31 and −1.60, respectively. Implications of these lines and mechanisms of the scrambling are discussed. In addition, the trifluoroacetolyses of 6,7-dinitrobenzonorbornen-2-*exo*- (and -*endo*-)yl tosylates were studied.

The nature of benzonorbornenyl ions is a subject of current interest. Since a pioneering work by Bartlett and Giddings,[4] we have carried out an extensive study of solvolyses of aromatic-substituted benzonorbornen-9-*anti*- (and -*syn*-)yl brosylates.[5] More recently, the substituent effects in solvolysis of benzonorbornen-2-yl derivatives were communicated by three independent groups including us (the methoxy effects by Syracuse–UCLA, Shionogi, and Purdue, and the nitro effects by Purdue).[1,6,7] Our subsequent full paper dealt with a detailed study of benzonorbornen-2-*exo*-yl derivatives.[8] With the results, the benzonorbornene system was described by Schleyer as one of the extreme model systems revealing features of neighboring aryl participation.[9] As a continuation of our works, this paper reports a detailed account of solvolyses of benzonorbornen-2-*endo*-yl derivatives, with some additional works on the *exo* epimers. The solvolyses of tertiary 2-methyl- and 2-arylbenzonorbornen-2-*exo*- (and -*endo*-)yl derivatives are also under active research.[10,11] Combination of all the results will lead to a full understanding of benzonorbornenyl cations.

Results

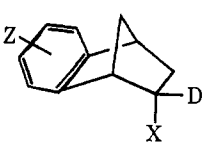
The syntheses of benzonorbornen-2-*endo*- (and -*exo*-) ols containing substituents in the aromatic ring were reported:[8] the substituents were 6-methoxy (**2n**- and **2e**-OH), 7-methoxy (**3n**- and **3e**-OH), 7-methoxy-6-nitro (**4n**- and **4e**-OH), and 6,7-dinitro (**6n**- and **6e**-OH). As an additional derivative, 7-nitrobenzonorbornen-2-*endo*-ol (**5n**-OH) was prepared by nitration of benzonorbornen-2-one, separation of produced 6- and 7-nitrobenzonorbornen-2-one, and then reduction of the





1n-X, Z = H
2n-X, Z = 6-CH_3O
3n-X, Z = 7-CH_3O
4n-X, Z = 7-CH_3O-6-NO_2
5n-X, Z = 7-NO_2
6n-X, Z = 6,7-$(NO_2)_2$

1e-X, Z = H
2e-X, Z = 6-CH_3O
3e-X, Z = 7-CH_3O
4e-X, Z = 7-CH_3O-6-NO_2
5e-X, Z = 7-NO_2
6e-X, Z = 6,7-$(NO_2)_2$



7n-X, Z = H
8n-X, Z = 7-NO_2
9n-X, Z = 6,7-$(NO_2)_2$

(1) A portion of the results of this paper appeared in preliminary communications and accounts: (a) H. Tanida, H. Ishitobi, and T. Irie, *J. Amer. Chem. Soc.*, **90**, 2688 (1968); (b) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(2) H. Tanida presented a part of this work at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

(3) The numbering used in this paper is shown in the charts.

(4) (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) also, see W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

(5) (a) H. Tanida, *ibid.*, **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).

(6) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968).

(7) H. C. Brown and G. Tritle, *ibid.*, **90**, 2689 (1968).

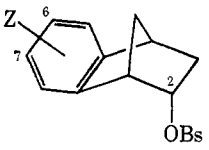
(8) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969).

(9) C. J. Lancelot and P. von R. Schleyer, *ibid.*, **91**, 4291 (1969).

(10) (a) J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5905 (1969); (b) *ibid.*, **91**, 5907 (1969).

(11) H. C. Brown and K.-T. Liu, *ibid.*, **91**, 5909 (1969); H. C. Brown, S. Ikegami, and K.-T. Liu, *ibid.*, **91**, 5911 (1969).

Table I. Acetolysis Rates of Aromatic-Substituted Benzonorbornen-2-*endo*-yl Brosylates[a]



Substituent	Temp, °C	k_t, sec^{-1}	Calcd at 77.6° $\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal/deg	k_t, sec^{-1}	Rel rate	k_t, sec^{-1} (77.6°) of *exo* brosylates[b]	*exo*:*endo* rate ratio
H[c]	120.0	8.13×10^{-5}	29.1	−3.9	8.14×10^{-7}	1	3.74×10^{-3}	4,600
	95.0	6.12×10^{-6}						
6-CH_3O	120.5	1.93×10^{-4}	28.0	−5.0	2.18×10^{-6}	2.7	6.7×10^{-1} [d]	310,000
	77.6	2.18×10^{-6}						
7-CH_3O	120.5	8.75×10^{-5}	28.2	−6.0	9.57×10^{-7}	1.2	2.68×10^{-3}	2,800
	77.6	9.57×10^{-7}						
7-CH_3O-6-NO_2	160.0	3.60×10^{-4}	28.4	−9.5	1.29×10^{-7}	0.16	4.09×10^{-6}	32
	130.0	2.92×10^{-5}						
7-NO_2	175.0	6.83×10^{-4}	28.3	−10.7	8.18×10^{-8}	0.10	3.64×10^{-6}	45
	150.0	1.00×10^{-4}						
6,7-$(NO_2)_2$[e]	180.5	1.86×10^{-4}	29.7	−10.9	9.46×10^{-9}	0.012	3.53×10^{-8} [f]	3.7
	150.0	1.64×10^{-5}						

[a] The concentration of reactants is 0.02 *M*. The acetic acid contained 0.02 *M* AcONa and 1% acetic anhydride. [b] Reference 8. [c] Reference 4a reported $k_t = 5.49 \times 10^{-5}$ (114.8°) and 7.60×10^{-6} (95.8°). [d] Estimated from the rate constant of benzonorbornen-2-*exo*-yl brosylate and the rate ratio of benzonorbornen-2-*exo*-yl chloride to its 6-methoxyl derivative. See ref 8. [e] The rates of trifluoroacetolysis of the tosylate are presented in the text. [f] The reported value was slightly corrected.

ketonic function with diborane. Positions of the nitro substituents were determined by the analysis of nmr patterns of aromatic protons in the nitro ketones as performed in the case of 6- and 7-methoxybenzonorbornen-2-ones (Experimental Section).[8] All the brosylates were obtained by treatment of the alcohols with *p*-bromobenzenesulfonyl chloride in pyridine. For trifluoroacetolysis, **6n**-OTs and **6e**-OTs were similarly prepared with *p*-toluenesulfonyl chloride.

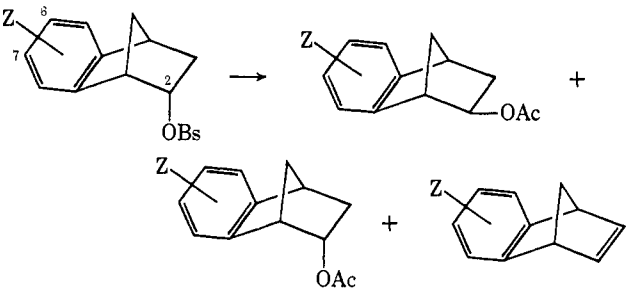
In order to investigate whether or not the products are formed involving the Wagner–Meerwein rearrangement, a few kinds of the *exo*-2-deuterio-*endo*-2-ols were prepared by reduction of the corresponding ketones with sodium borodeuteride and boron trifluoride and converted into brosylates. The brosylates thus prepared were the parent **7n**-OBs, the 7-nitro-**8n**-OBs, and the 6,7-dinitro-**9n**-OBs. No appreciable amounts of protons α to the brosyl groups were detected by nmr spectra of the deuterated compounds which were purified by recrystallization.

Solvolysis Rates. The acetolyses were carried out in glacial acetic acid containing equivalent sodium acetate by the standard procedure[12] and the rates were determined by titration of forming *p*-bromobenzenesulfonic acid. The trifluoroacetolyses of **6n**-OTs and **6e**-OTs were carried out in anhydrous trifluoroacetic acid containing equivalent sodium trifluoroacetate and the rates determined by following the disappearing nmr signal of the methyl group in the *p*-toluenesulfonyl group. The methyl signal was found to be distinguishable from that of the methyl group in the forming toluenesulfonyloxy anion. A standard procedure, rate measurements by ultraviolet spectra,[13] was unsuccessful here. Good first-order kinetics were observed in all runs and theoretical infinity titers obtained. Table I summarizes the acetolysis rates, the derived activation parameters, and, for comparison, the rate constants at 77.60° calculated by Arrhenius plots and the apparent rate ratios with the *exo* epimers.

The trifluoroacetolysis of **6n**-OTs was observed to proceed with a rate constant (k_t) of 2.28×10^{-5} sec^{-1} at 130° and that of **6e**-OTs with k_t of 3.16×10^{-4} sec^{-1} at 130°.[14] The *exo*–*endo* rate ratio is thus 14.

Solvolysis Products. For product determination, the acetolyses were carried out under the same conditions as used for the rate studies. As in the case of the *exo* epimers,[8] the solvolysis of benzonorbornen-2-*endo*-yl brosylate and its aromatic-substituted derivatives proceeds with the formation of benzonorbornen-2-*exo*-yl acetate (product of inversion), benzonorbornen-2-*endo*-yl acetate (product of retention), and benzonorbornadiene (product of elimination), or derivatives of these. No other types of products were observed. Table II presents the substituent effects on

Table II. Acetolysis Products and Yields[a]



Substituent	Temp, °C	*exo*	*endo*	Olefin
H	120	97	0.2	0.1
7-NO_2	175	98	1.0	1.0
6,7-$(NO_2)_2$	180	89	3.0	2.2

[a] Yields are per cents of theory. The yields of *exo*-acetates were determined by nmr and those of *endo*-acetates and olefins by vpc.

(12) (a) S. Winstein, C. Hanson, and E. Grunwald, *J. Amer. Chem. Soc.*, 70, 812 (1948); (b) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70,821 (1948).

(13) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid.*, 87, 5169 (1965).

(14) H. C. Brown suggested to carry out this experiment at the Conference on Carbonium Ions.[2]

Table III. Dissection of Rates and Products in Acetolysis of Aromatic-Substituted Benzonorbornen-2-yl Brosylates[a]

Substituent	Total rate at 77.6°, k_t, sec^{-1}	% H in *exo*-acetate[b] at C_2	at C_1	Partial rate[c] k_1 (SN1)	k_{SN2}
endo-OBs					
6-CH_3O	2.18×10^{-6}	50[d]	50[d]	2.18×10^{-6}	~0
H	8.14×10^{-7}	44	56	7.16×10^{-7}	9.77×10^{-8}
7-NO_2	8.18×10^{-8}	25	75	4.24×10^{-8} [e]	3.94×10^{-8}
6,7-$(NO_2)_2$	9.46×10^{-9}	16	84	3.50×10^{-9} [f]	5.96×10^{-9}
exo-OBs[g]					
6-CH_3O	6.7×10^{-1}			6.7×10^{-1}	0
H	3.74×10^{-3}			3.74×10^{-3}	0
7-NO_2	3.64×10^{-6} [h]			2.00×10^{-5}	~0
6,7-$(NO_2)_2$	3.53×10^{-8}			2.26×10^{-8} [i]	1.27×10^{-8}

[a] All runs were carried out in the presence of equivalent amounts of sodium acetate. [b] Reaction temperatures for products study are 120° for H, 150° for 7-NO_2, and 165° for 6,7-$(NO_2)_2$. [c] $k_t = k_1$ (or k_{SN1}) + k_{SN2}. k_1 is the partial rate for the "leakage" process. [d] Value estimated from data of the other compounds. [e] A total of partial rates of formations of *endo*-acetate (1%), olefin (1%), and twice **11** (2 × 25%). [f] A total of partial rates of formations of *endo*-acetate (3%), olefin (2%), and twice **11** (2 × 16%). [g] Reference 8. The value for 6,7-$(NO_2)_2$ was slightly corrected. [h] Data unpublished in ref 8. [i] $k_{SN1} = 0.01k_t \times$ (% total yield of olefin and *exo*-acetate).

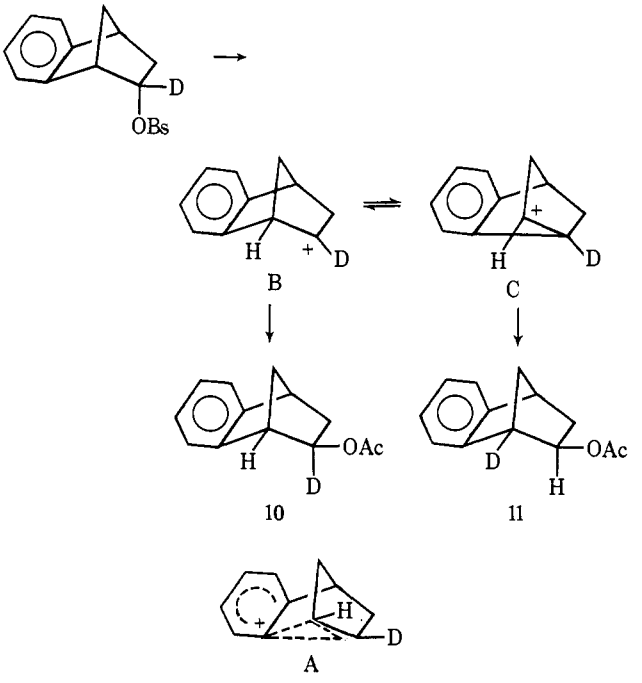
distribution of the products from **1n**-OBs, **5n**-OBs, and **6n**-OBs. The estimated errors in the yields are ±2%. Samples of the products were proved to be stable under the respective acetolysis conditions.

Discussions

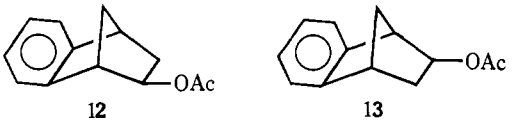
Compared to a factor of 1.6×10^7 in the *exo* series,[8] the rate range from the 6-methoxy (*homo-para*) to the 6,7-dinitro in the present *endo* series was only 230. Whereas the stereospecificity in the product formation in the *exo* series disappears dramatically with deactivation of the benzene ring, the products in the *endo* series are not greatly influenced by substituents in the ring (Table II). The contrast clearly demonstrates a major importance of participation in the *exo* and its absence in the *endo*. The substituent effects on rate in the *exo* series are just those which one would expect in electrophilic aromatic substitution reactions; however, the effects in the *endo* series are somewhat peculiar. While the *homo-meta* 7-methoxy substituent depresses the *exo* rate slightly, it shows, though very slightly, an acceleration effect on the *endo* rate. The relative rates of the 7-CH_3O-6-NO_2 *endo* and the 7-NO_2 (*homo-meta*) *endo* are 0.16 and 0.10, which are also in an unexpected order. The precise source of this rate variation is of considerable interest and we hope to explore its origin.

It was concluded that the mechanism of a major course of acetolysis of the *exo* epimers was substantially identical over the range from the 6-methoxy to the 6,7-dinitro.[8] What about acetolysis of the *endo* epimers? The deuterated brosylates, **7n**-OBs, **8n**-OBs, and **9n**-OBs, were acetolyzed, the produced *exo*-acetates were isolated,[15] and distribution of the deuterium was analyzed by nmr. The results are summarized in Table III. The Wagner–Meerwein rearrangement brings the deuterium at C_2 into C_1, in other words, the proton at C_1 into C_2. It is found that incorporation of proton in the C_2 reaction center decreases with deactivation of the benzene ring: 44% for **1n**-OBs, 25% for **5n**-OBs, and 16% for **6n**-OBs.

We assume that a mixture of equal amounts of 1- and 2-deuteriobenzonorbornen-2-*exo*-yl acetates (**10** and **11**) is produced by solvent attack toward an intermediate (a nonclassical cation, A, which is formed by leakage of an original classical ion[16]) or intermediates (classical cations, B and C, which are in a rapid equilibrium).



The fact that the acetolysis of optically active **1n**-OBs causes 94.7% racemization[16] indicates that the assumption is roughly valid for **1n**-OBs and **7n**-OBs.[17]



The yield of **11** and thereby the total yield of **10** and **11**, which is produced *via* either A or B and C, can be determined by integral of the nmr signals of the proton at C_2. Then, since the product of inversion in the acetolysis of **6e**-OBs was demonstrated to be the result of an SN2 solvolytic displacement reaction,[8] the rest of

(15) It was assumed that the isolation technique (recrystallization of the products mixture) has no significant influence upon the relative composition of the *exo*-acetates deuterated at C_1 and C_2 (**10** and **11**) in the products mixture.

(16) Proposed in the acetolysis of 1n-OBs: J. P. Dirlam, A. Diaz, S. Winstein, W. P. Giddings, and G. C. Hansn, *Tetrahedron Lett.*, 3133 (1969).

(17) Complete racemization in the acetolysis of 1n-OBs means the formation of a mixture of equal amounts of the two enantiomers, **12** and **13**, and the predominant formation of either one is the origin of a remaining optical activity of **10** and **11**.

10 (reckoned as an excess of **10** over twice the yield of **11**) may be attributed to a similar SN2 reaction. The minor formation of *endo*-acetates (products of retention) and olefins (products of elimination) from **5n**-OBs and **6n**-OBs should be considered as *via* cationic intermediates. The observed rates for **1n**-OBs, **5n**-OBs, and **6n**-OBs are thus dissected into the cationic (SN1) and SN2 components and the rates of **1e**-OBs, **5e**-OBS, and **6e**-OBs as well.

Plotting logarithms of the observed *endo* rates against σ gives a straight line with a ρ of -1.31 (correlation coefficient 0.988) (Figure 1), demonstrating that a dominant factor in the substituent effects on rates is the inductive effect. Moreover, the ρ value is of the same order of magnitude as those obtained in some models for anchimerically unassisted solvolysis of secondary β-arylalkyl arenesulfonates: $\rho = -1.06$ for the acetolysis of 1-aryl-*endo*-2-norbornyl tosylates[18] and -1.66 for the acetolysis of *cis*-2-arylcyclopentyl tosylates.[19] A noteworthy contrast is that *cis*-2-arylcyclopentyl tosylate produces predominantly olefins (95.9% yield) plus the inverted acetate in small amount (4.1%), while benzonorbornen-2-*endo*-yl brosylates give almost exclusively inverted acetates.

Following Winstein's definitions,[10,20] solvolytic processes have been widely discussed in terms of three factors:[9,21-23] (i) k_Δ, the rate constant for anchimerically assisted ionization; (ii) k_s, the rate constant for solvolysis not anchimerically assisted, but assisted by whatever nucleophilic solvent participation is appropriate for the substrate structure involved and the solvent being employed; (iii) k_c, the rate constant for an idealized process involving neither anchimeric assistance nor assistance from nucleophilic solvent participation.[20d] For the right substrate structure and solvent, k_s becomes equal to k_c;[24] in other words, k_c is a limit to which k_s tends. The k_Δ factor need not be considered in the present *endo* system. The relationship is thus expressed as $k_t = k_s$ (or k_c). Although the acetolysis of simple secondary arenesulfonates has long been postulated to be essentially limiting,[25] recent important work clearly points out that such solvolysis involves a large contribution from solvent, approaching SN2 in character.[9,22,26-28]

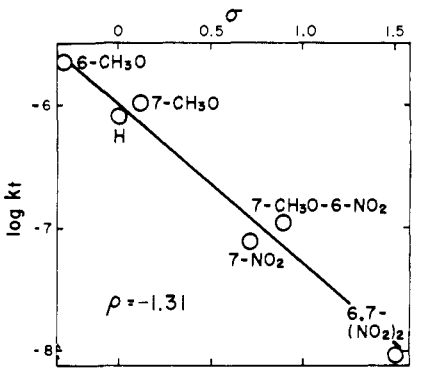


Figure 1. The ρ-σ treatment of the observed rates, k_t, of benzonorbornen-2-*endo*-yl brosylates.

Since the susceptibility of the substrate to the ionizing power of the solvent increases with increasing limiting behavior of the substrate,[29] the rate ratio in trifluoroacetic acid and acetic acid, $k_{CF_3COOH}/k_{CH_3COOH}$, may be utilized as a diagnostic tool for estimation of solvent participation. A model for the limiting behavior of secondary systems, 2-adamantyl tosylate, gives a very large ratio, 6.2×10^5 (25°), whereas a model for nonlimiting behavior, isopropyl tosylate, gives a small ratio, 269 (25°).[26c] The corresponding value for **6n**-OTs is only 25 (130°), as mentioned later. This fact indicates the importance of solvent participation. The acetolysis of primary arenesulfonates is essentially bimolecular and this is reflected in a large negative $\Delta S^{\ddagger}$ value, which is in the region of -20 eu. Thus, the value of $\Delta S^{\ddagger}$ has been used as a criterion for the presence or absence of participation in primary β-arylalkyl solvolyses.[30] The values of $\Delta S^{\ddagger}$ for **1e**-OBs–**6e**-OBs are in the range of -0.7 to -8.7 eu,[8] and those for **1n**-OBs–**6n**-OBs are not so different, from -3.9 to -10.9 eu. Since it is clear that major processes of the *exo*-brosylates are limiting and "anchimerically assisted," the values of $\Delta S^{\ddagger}$ in the *endo* acetolyses may indicate the unimportance of a bimolecular character (solvent participation) in the transition state. Under these circumstances, we consider that the *endo* acetolyses are weakly assisted by solvent, and that the assistance becomes important with introduction of deactivating substituents, being indicated by the increasing negative magnitude of $\Delta S^{\ddagger}$. It has been suggested that the two strongly assisted processes, k_s (solvent assisted) and k_Δ (anchimerically assisted), are discrete pathways, between which there is no crossover.[21c] This is not always true and should be only true if both solvent assistance and anchimeric assistance are large (k_s and k_Δ are both strongly bound). If either is small, "leakage" may occur. The weak solvent assistance in the *endo* acetolysis would permit "leakage" into the ion(s) either A or B $\rightleftharpoons$ C and then cause scrambling of the deuterium tag at the cationic center. The leakage becomes minor as the solvent

(18) D. C. Kleinfelter and P. von R. Schleyer, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstracts, p 43P; J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 182.

(19) C. J. Kim and H. C. Brown, *J. Amer. Chem. Soc.*, **91**, 4286 (1969).

(20) (a) S. Winstein, *Bull. Soc. Chim. Fr.*, 55C (1951); (b) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, **74**, 1114 (1952); (c) S. Winstein and L. L. Ingraham, *ibid.*, **77**, 1738 (1955); (d) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958); (e) S. Winstein and R. Baker, *J. Amer. Chem. Soc.*, **86**, 2071 (1964); (f) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (g) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

(21) (a) C. J. Kim and H. C. Brown, *ibid.*, **91** 4287 (1969); (b) *ibid.*, **91**, 4289 (1969).

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(24) Footnote 8a in ref 10b.

(25) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(26) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, R. C. Bingham, and P. von R. Schleyer, *ibid.*, in press; (b) J. L. Fry and P. von R. Schleyer, *ibid.*, in press; (c) P. von R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970).

(27) J. M. Harris, C. J. Lancelot, F. L. Schadt, and P. von R. Schleyer, *ibid.*, in press.

(28) Although Winstein at one time defined the k_s process as "solvent assisted,"[20d] he has been less definite in his most recent papers, and the k_s process termed merely "anchimerically unassisted" [20e,f] (cited from ref 22c).

(29) The slope m in the Grunwald–Winstein equation, $\log k = mY + \log k_0$, is a measure of the susceptibility.

(30) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); D. J. Cram, *ibid.*, **86**, 3767 (1964).

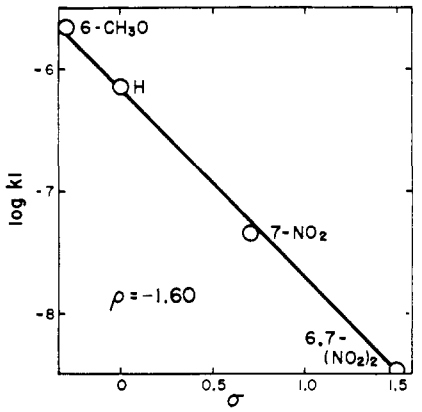


Figure 2. The ρ–σ treatment of the partial rates for the "leakage" processes, k_l, of benzonorbornen-2-*endo*-yl brosylates.

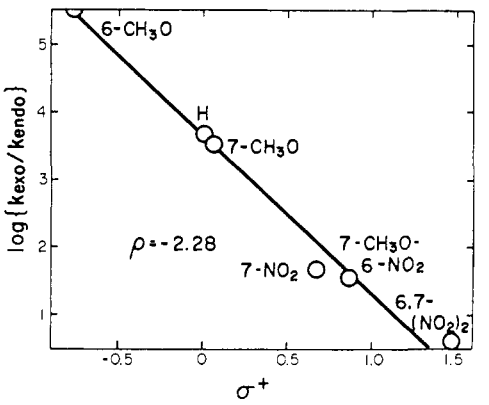
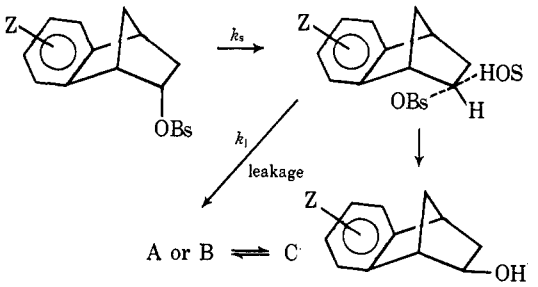


Figure 3. The ρ–σ^+ treatment of the observed *exo*–*endo* rate ratios of benzonorbornen-2-yl brosylates.

assistance increases in going from **1n**-OBs to **6n**-OBs, the deuterium scrambling decreasing accordingly. The straight line having a ρ value of -1.60 (correlation coefficient 0.999) (Figure 2), obtained from the ρ–σ treatment of the partial rates for scrambling (SN1), k_l,

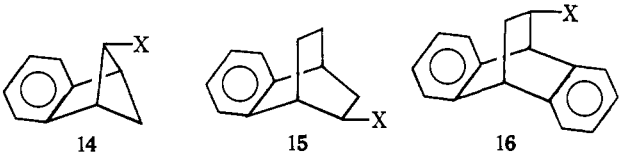


explains semiquantitatively the substituent effects on the "leakage." Therefore, anchimeric assistance by the aryl ring to this leakage step is not important.

It should be finally described that a meaningful line is obtained by plotting logarithms of the observed *exo*–*endo* rate ratios (3.07×10^5 for 6-CH_3O, 4.59×10^3 for H, 2.80×10^3 for 7-CH_3O, 4.45×10^1 for 7-NO_2, 3.17×10^1 for 7-CH_3O-6-NO_2, and 3.73 for 6,7-$(NO_2)_2$) against σ^+ with a ρ of -2.28 (correlation coefficient 0.990) (Figure 3). An ability of the aryl ring for participation is explained semiquantitatively by the constant attenuation of these *exo*–*endo* rate ratios. A similar ρ–σ^+ line, obtained from the *anti*–*syn* rate ratios in the acetolysis of benzonorbornen-9-yl derivatives, is reminded (in this case, $\rho = -3.57$).[5d]

Trifluoroacetolyses of 6,7-Dinitrobenzonorbornen-2-*exo*- (and -*endo*-)yl Tosylates (6e-OTs and 6n-OTs). Extrapolations of the observed rates by Arrhenius plots and employment of the brosylate–tosylate rate ratio by a factor of 3 give at 130° the acetolysis rate of 3.80×10^{-6} sec^{-1} for **6e**-OTs and that of 9.08×10^{-7} sec^{-1} for **6n**-OTs. The rate enhancements with a change of solvents from acetic acid to trifluoroacetic acid are, therefore, 83 for **6e**-OTs and 25 for **6n**-OTs. The reaction of **6e**-OTs was found to yield no olefin and the *exo*- and *endo*-substituted products in a ratio of 97:3, and the total yield was roughly quantitative. In contrast, the acetolysis of **6e**-OBs was reported to yield 21% (of theory) olefin and 41% the *exo*- and 35% the *endo*-substituted products.[8] These variations of rates and products with ionizing powers and nucleophilicities of the solvents suggest a still remaining ability of anchimeric assistance of the dinitrobenzene ring.

In conclusion, all the results we have so far obtained indicate that the benzonorbornen-2-*exo*-yl system is a model system which exhibits extremely the importance of neighboring aryl participation. We predict similar features in the carbonium ion reactions of 1,3-methanoindan (**14**), 1,4-ethano-1,2,3,4-tetrahydronaphthalene (**15**), dibenzobicyclo[2.2.2]octadiene (**16**), and related systems.



14 15 16

Experimental Section

Melting points were taken by capillary and are corrected. Nmr spectra were taken with a Varian A-60A and/or HA-100. The deuterium content and position were determined by the Varian A-60A spectrometer and the content was confirmed by a Hitachi RMU-6 mass spectrometer.

Kinetic Measurements. The acetolysis conditions and procedure were the same as reported.[5b]

6- and 7-Nitrobenzonorbornen-2-one. When benzonorbornen-2-one was treated at 0–5° with a solution of equivalent amounts of 95% nitric acid in acetic acid, a mixture of mononitrated ketones was obtained in a yield more than 96%. Serial recrystallizations from acetone, ether, and methanol isolated in pure states 6-nitrobenzonorbornen-2-one, mp 139.5–140°, and 7-nitrobenzonorbornen-2-one, mp 151.5°. In 100-Mc nmr spectra in acetone-d_6, the 6-nitro derivative reveals C_8-H at τ 2.46 with *ortho* coupling of 8.2 Hz and the 7-nitro derivative C_5-H at τ 2.38 with *ortho* coupling of 9.2 Hz. *Anal.* Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found for the 6-nitro: C, 64.86; H, 4.55; N, 6.89. Found for the 7-nitro: C, 65.04; H, 4.51; N, 6.75.

7-Nitrobenzonorbornen-2-*endo*-ol (5n-OH) was prepared by reduction of the corresponding ketone with diborane in tetrahydrofuran. A minor by-product, **5e-OH**, was removed during esterification with *p*-bromobenzenesulfonyl chloride.

The brosylate had mp 149.5–150°. *Anal.* Calcd for $C_{17}H_{14}BrNO_5S$: C, 48.52; H, 3.33; Br, 18.83. Found: C, 48.13; H, 3.14; Br, 19.11.

The *exo*-2-deuterio brosylate was similarly prepared through reduction with B_2D_6 and had mp 149–150°.

Properties and Analyses of Brosylates and Tosylates. 2n-OBs had mp 97–98°; **3n**-OBs had mp 110–111°. *Anal.* Calcd for $C_{18}H_{17}BrO_4S$: C, 52.81; H, 4.19. Found for **2n**-OBs: C, 52.72; H, 4.14. Found for **3n**-OBs: C, 52.91; H, 4.17. **4n**-OBs had mp 132–133°. *Anal.* Calcd for $C_{18}H_{16}BrNO_6S$: C, 47.59; H, 3.55. Found: C, 47.76; H, 3.61. **6n**-OBs had mp 171.5–172.5°. *Anal.* Calcd for $C_{17}H_{13}BrN_2O_7S$: C, 43.51; H, 2.79. Found: C, 43.55; H, 2.84. **6n**-OTs had mp 136–137°. *Anal.* Calcd for $C_{18}H_{16}N_2O_7S$: C, 53.46; H, 3.99. Found: C, 53.46; H, 4.03. **6e**-OTs had mp 188–189°. *Anal.* Calcd for $C_{18}H_{16}N_2O_7S$: C,

53.46; H, 3.99. Found: C, 53.75; H, 3.70. **7n**-OBs had mp 135–136°. **9n**-OBs had mp 168–169.5°.

Acknowledgment. We are grateful to Professor P. v. R. Schleyer for helpful comments and to Mr. Hiroyuki Ishitobi for technical assistance. H. T. thanks Professors Schleyer and G. A. Olah for the invitation to present a part of this work at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

Involvement of a Solute in a Transition State without Any Effect on Rate. The Role of Added Pyridine in Methanolysis of Triphenylmethyl Chloride in Benzene Solution[1]

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Abstract: The role of added pyridine in the methanolysis of triphenylmethyl (trityl) chloride in dilute dry benzene solutions at 25° is now clear. The rate of methanolysis in the presence of excess pyridine is first order in stoichiometric methanol below 0.005 *M* methanol, and first order in trityl chloride. Methanol in solutions more concentrated than 0.1 *M* in pyridine is appreciably associated with pyridine according to infrared and vapor-pressure data. Nevertheless, the rate of methanolysis is independent of pyridine concentration, and unchanged when pyridine is replaced by the very much more hindered 2,6-di-*t*-butylpyridine. Therefore, tritylpyridinium chloride (I) is not an intermediate, when pyridine is present. However, pyridine is involved: it prevents catalysis and reversal by HCl, by forming pyridinium chloride; it prevents otherwise serious adsorption of methanol on and reaction with the glass walls of the vessel; and it is a constituent of the transition state without HCl, to an extent that depends on pyridine concentration but has no effect on the rate. No kinetically significant amount of I is formed from reaction of trityl chloride and pyridine in benzene solution under ordinary conditions because the equilibrium is unfavorable. The "tritylpyridinium chloride" reported in the literature is a complex of triphenylcarbinol and pyridinium chloride, associated through a weak hydrogen bond in the solid state.

The methanolysis of triphenylmethyl (hereafter called trityl) chloride in benzene solution containing excess pyridine produces trityl methyl ether.

$$(C_6H_5)_3CCl + CH_3OH \xrightarrow{\text{slow}} (C_6H_5)_3COCH_3 + HCl$$

$$HCl + C_5H_5N \xrightarrow{\text{fast}} C_5H_5NHCl$$

Pyridine has been added to suppress reversal of the first reaction by combining with hydrogen chloride.[2] This also suppresses catalysis of the slow step by hydrogen chloride. Trityl chloride and pyridine do not react to a kinetically significant extent under these conditions in benzene at 25°,[3] and the rate of the reaction of trityl chloride with methanol in benzene is independent of the nature or concentration of tertiary amine when pyridine, 2,6-lutidine, triethylamine, or tribenzylamine is present, provided that any one of these amines is used in excess over the hydrogen chloride produced.[2]

Ingold and coworkers, on the other hand, stated that the reaction of trityl chloride in benzene solution with tertiary amines, *e.g.*, with pyridine to form tritylpyridinium chloride (I), although reversible, "goes forward extensively, at a rate comparable with the rate of chlorine exchange of trityl chloride with a saline radiochloride,"[4] which is much faster than the methanolysis. Leffek and Waterfield in 1967[5] reported additional kinetic data, which they interpreted as showing that pyridine very rapidly forms a "tetrahedral complex" with trityl chloride, markedly changing the reactivity of the trityl chloride.

In order to evaluate the role of pyridine in these reactions critically, 2,6-di-*t*-butylpyridine was used in the present reinvestigation of methanolysis of trityl chloride in benzene solution at 25°. 2,6-Di-*t*-butylpyridine reacts with protonic acids, but, because of extraordinarily high steric hindrance, it fails to react with Lewis acids or with alkyl halides such as methyl iodide at 1 atm.[6] Therefore, no reaction is likely between trityl chloride and 2,6-di-*t*-butylpyridine. If the formation of tritylpyridinium chloride (I) or of any tetrahedral complex of pyridine and trityl chloride were involved either in the rate-determining step or in a prior equilibrium step when pyridine is present, the rate of methanolysis of trityl chloride in the presence of 2,6-di-*t*-butylpyridine should be orders of magnitude

(1) Supported in part by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905.

(2) C. G. Swain and E. E. Pegues, *J. Am. Chem. Soc.*, **80**, 812 (1958); C. G. Swain, *ibid.*, 70, 1119 (1948).

(3) A. E. Tschitschibabin [*J. Russ. Phys. Chem.*, **33**, 249 (1902); *Chem. Zentralbl.*, **73**, No. 1, 1301 (1902)] first reported that even neat pyridine and I do not react unless equivalent water is added, whereupon a complex of pyridine and triphenylcarbinol is formed.

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 356; E. D. Hughes, C. K. Ingold, S. F. Mok, and Y. Pocker, *J. Chem. Soc.*, 1238 (1957).

(5) K. T. Leffek and R. G. Waterfield, *Can. J. Chem.*, **45**, 1497 (1967). A difficulty with their mechanism (their eq 2–4) used to explain slight retardation by tetrabutylammonium chloride is that it violates the principle of microscopic reversibility. A simpler interpretation is that this salt also suppresses catalysis by hydrogen chloride by complexing with hydrogen chloride.

(6) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953); **88**, 986 (1966).