changes in rate in this case than in that of methylal hydrolysis[52] but salt-specific effects on activity coefficients of the substrate and Hammett base are clearly still present. This is not unexpected since it has been established that salt effects on activity coefficients of anilines reflect, in part, the solvation of the basic function.[54]

[54] W. Proudlock and D. Rosenthal, *J. Phys. Chem.*, **73**, 1695 (1969).

Secondary β-Deuterium Effects on the Rates of Solvolyses of Benzonorbornen-2(*exo*)- and -2(*endo*)-yl *p*-Bromobenzenesulfonates

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Abstract: C_3-Deuterated benzonorbornen-2(*exo*)- and -2(*endo*)-yl brosylates and their aromatic nitrated derivatives were synthesized and solvolyzed in acetic and formic acids to measure the β-deuterium effects on the rates of solvolysis. Benzonorbornen-2(*exo*)-yl-*3*(*exo*)-*d* and -*3,3*-d_2 brosylates (**1-d$_1$e-OBs** and **1-d$_2$e-OBs**) showed markedly small deuterium effects in both acetolysis (1.03 for **1-d$_1$e-OBs** and 1.05 for **1-d$_2$e-OBs**) and formolysis (1.04 for **1-d$_2$e-OBs**) compared to the values for the corresponding endo epimers, which were, in acetolysis, 1.16 for the *3*(*exo*)-*d* and 1.28 for the *3,3*-d_2 and, in formolysis, 1.15 for the *3*(*exo*)-*d* and 1.24 for the *3,3*-d_2 compound. When two nitro groups were introduced into the C_6 and C_7 positions of the benzene ring, the magnitudes of the deuterium effects were raised with the *exo*-brosylates (in acetolysis, 1.10 for the dinitro-*3*(*exo*)-*d* and 1.12 for the dinitro-*3,3*-d_2), but decreased with the *endo*-brosylates (in acetolysis, 1.13 for the dinitro-*3*(*exo*)-*d* and 1.22 for the dinitro-*3,3*-d_2). A geometric dependence of the β-deuterium effects was observed in the solvolyses of the dinitro *exo*-brosylates; the increment of the effects on conversion of the dinitro-*3*(*exo*)-*d* into the dinitro-*3,3*-d_2 compound was very small, from 1.10 to 1.12 (in acetolysis). In the case of the dinitro *endo*-brosylates, such conversion raised the effects substantially, from 1.13 to 1.22. Results with the exo system are discussed in terms of competing aryl participation and hyperconjugative electron release mainly due to the exo proton at C_3, and release of steric compression at the reaction site; those with the endo system are discussed in terms of competing solvent participation and hyperconjugation due to both the exo and endo protons at C_3, as well as the release of steric compression.

Since the original findings by Lewis and Boozer[1] and by Shiner[2] that deuteration β to the leaving group could affect the reaction rate, secondary β-isotope effects have provided a subtle but powerful tool for the investigation of mechanistic details of solvolysis reactions.[3] Such a study relevant to neighboring group participation was first reported by Saunders,[4] who found that in formic acid 2-phenylethyl and 2-phenylethyl-*2,2*-d_2 *p*-toluenesulfonates (tosylates) both solvolyze at the same rate, but in acetic acid the parent tosylate reacts 4% faster than the deuterated tosylate. The absence of a β-isotope effect in formic acid was interpreted as being a result of predominant phenyl participation. However, kinetic effects due to the presence of β-phenyl groups are often extremely modest, in spite of the fact that such groups significantly affect product formation.[5,6] The group has been considered by Winstein as a "marginal" neighboring group.[6] Some controversy still exists concerning the clear description of neighboring aryl participation in solvolysis.[7-9]

A number of contrasting results of theoretical importance have been found between the solvolytic behavior of *exo*-2-norbornyl arenesulfonate (or halide) and that of its endo epimer.[10] Studies of secondary β-deuterium effects have yielded good examples of such contrasts. The effect caused by C_3 dideuteration of *exo*-2-norbornyl bromide was small, $k_H/k_D = 1.09$ (polarimetric) and 1.02 (titrimetric), while that in the case of *endo*-2-norbornyl bromide was large, $k_H/k_D = 1.16$ (conductometric).[11] A low effect ($k_H/k_D = 1.014$) was also reported for *exo*-2-norbornyl-*3,3*-d_2 brosylate and the value of k_H/k_D for *endo*-2-norbornyl-*3,3*-d_2 brosylate was 1.26.[12a] However, the nature of the norbornyl cation and the role of

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[1] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 6306 (1952).

[2] V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953).

[3] E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

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[5] D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967); **91**, 1778 (1969), and references cited therein.

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[7] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965); (b) H. C. Brown and C. J. Kim, *ibid.*, **91**, 4287, 4289 (1969).

[8] C. J. Lancelot and P. von R. Schleyer, *ibid.*, **91**, 4291 (1969), and subsequent three communications.

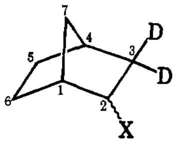
[9] M. D. Bentley and M. J. S. Dewar, *ibid.*, **92**, 3996 (1970).

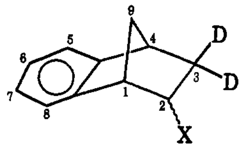
[10] As reviews, (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (b) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3; (c) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966); (d) D. Bethell and V. Gold, "Carbonium Ions, an Introduction," Academic Press, London, 1967, Chapter 7

[11] (a) J. P. Schaefer and D. S. Weinberg, *Tetrahedron Lett.*, 2491 (1965); (b) J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

[12] (a) J. M. Jerkunica, S. Borčič, and D. E. Sunko, *Chem. Commun.*, 1302 (1967); (b) *ibid.*, 1488 (1968).

participation in the transition state that lead to this cation are, at present, far from fully understood[13,14] and, consequently, their relationship with the magnitude of the β-isotope effect is quite unclear. By the nonclassical ion interpretation, the small effect of the *exo*-2-norbornyl derivatives results from the C_1–C_6 bond participation in the solvolytic transition state, which imparts S_N2 character to the C_2 reaction center and lowers the demand for hyperconjugative electron release from the site of isotopic substitution.[11,12,15] On the other hand, the classical ion school has proposed a hypothesis that the β-isotope effect results from relief of steric strain.[16,17] In a recent publication,[18] Brown has written, "numerous studies have been reported on secondary isotope effect for norbornyl derivatives containing deuterium labels. Unfortunately, general agreement as to the precise manner in which secondary isotopes exert their effects is not yet at hand. Consequently, it would appear unsafe to rely on this uncertain tool to resolve a problem (the norbornyl cation) of such complexity." In contrast to the situation with the norbornyl cation, the important existence of aryl participation in the solvolysis of benzonorbornen-*exo*-2-yl derivatives (a structural relative to the norbornyl) and its absence in the reaction of endo epimers have been well established.[19–22] This exo system was announced as one of the models revealing features of neighboring aryl participation.[8] The ability of aryl groups to participate is not "marginal" here. Further, in this system the magnitude of the π participation can be varied by the introduction of substituents into the benzo moiety, while maintaining the ground-state energy constant. Under these circumstances, we considered that the benzonorbornene system was an ideal model for testing the β-isotope effect as a diagnostic tool for participation. Also, we hoped that the present results could be instructive in indicating the real origin of the β-isotope effects reported in the norbornyl system.

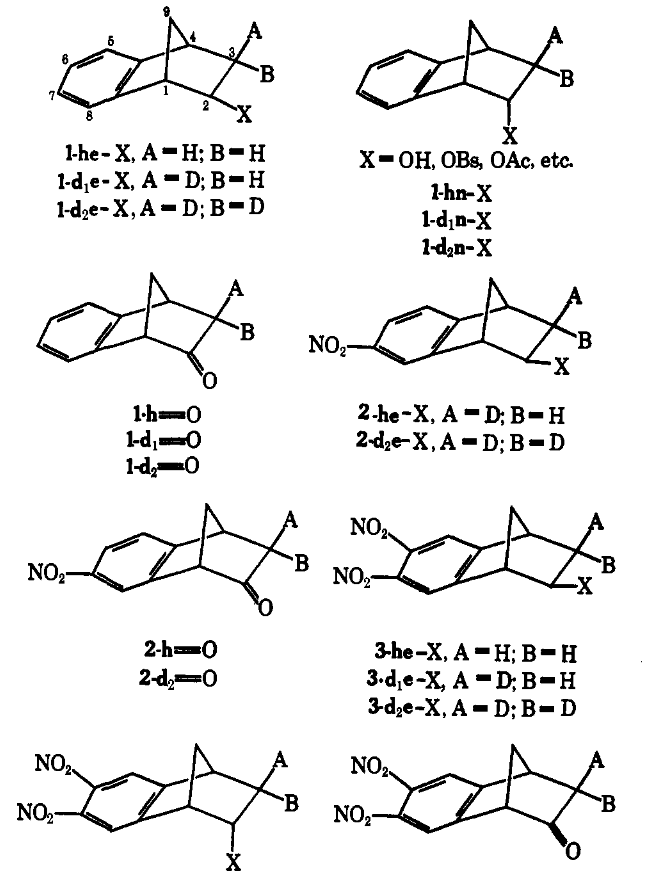




Results

Preparations. The compounds appearing in this paper are listed in Chart I. Benzonorbornen-2(*exo*)- and -2(*endo*)-ols (**1-he**-OH and **1-hn**-OH) and their esters are known.[19,21] The deuterioboration of benzonorbornadiene with sodium borodeuteride and boron trifluoride gives exclusively the cis-exo addition product,[21c] benzonorbornen-2(*exo*)-ol-*3*(*exo*)-*d* (**1-d₁e**-OH) (eq 1). Mass and nmr spectral analyses indicated the compound to be 90.4% isotopically pure. Mass spectral data for this and some relevant compounds are given in the Experimental Section. Oxidation of this alcohol with chromic anhydride in pyridine afforded benzonorbornen-2-one-*3*(*exo*)-*d* (**1-d₁**=O), the mass spectrum of which showed an identical deuterium content with that of the original **1-d₁e**-OH. The nmr signal of the exo-C_3 hydrogen in **1-d₁**=O had almost completely disappeared, while those of endo-C_3, syn-C_9, and anti-C_9 hydrogens retained their original intensities. Reduction of **1-d₁**=O with lithium aluminum hydride

Chart I



1-he-X, A = H; B = H
1-d₁e-X, A = D; B = H
1-d₂e-X, A = D; B = D

X = OH, OBs, OAc, etc.
1-hn-X
1-d₁n-X
1-d₂n-X

1-h=O
1-d₁=O
1-d₂=O

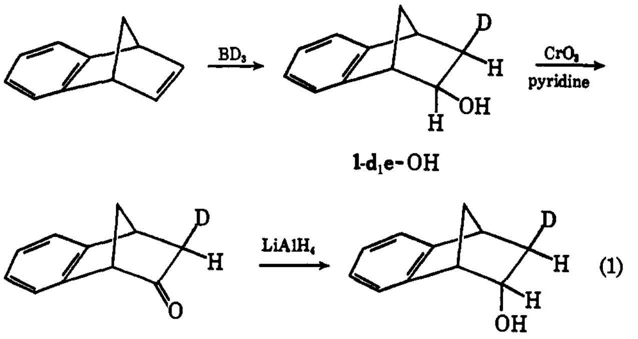
2-he-X, A = D; B = H
2-d₂e-X, A = D; B = D

2-h=O
2-d₂=O

3-he-X, A = H; B = H
3-d₁e-X, A = D; B = H
3-d₂e-X, A = D; B = D

3-hn-X
3-d₁n-X
3-d₂n-X

3-h=O
3-d₁=O
3-d₂=O



1-d₁e-OH

1-d₁=O

1-d₁n

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(13) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); *Chem. Eng. News*, **45**, 86 (Feb 13, 1967).

(14) The importance of participation was recently questioned by (a) P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **91**, 4280 (1969); (b) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *ibid.*, **91**, 4282 (1969).

(15) B. L. Murr and J. A. Conkling, *ibid.*, **92**, 3464 (1970).

(16) H. C. Brown, M. E. Azzaro, J. G. Koelling, and G. J. McDonald, *ibid.*, **88**, 2520 (1966).

(17) Steric interpretations of secondary isotope effects were originally proposed by (a) L. S. Bartell, *ibid.*, **83**, 3567 (1961); (b) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **85**, 1199 (1963).

(18) H. C. Brown, *Accounts Chem. Res.*, in press. We thank him for a preprint.

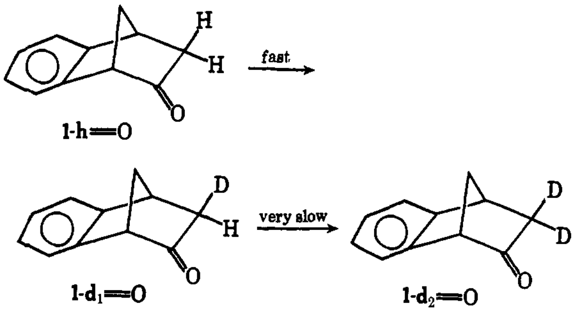
(19) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

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

(21) (a) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); (b) H. Tanida, *Account Chem. Res.*, **1**, 239 (1968); (c) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Amer. Chem. Soc.*, **91**, 4512 (1969); (d) H. Tanida, T. Irie, and T. Tshushima, *ibid.*, **92**, 3404 (1970).

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

afforded benzonorbornen-2(*endo*)-ol-*3*(*exo*)-*d* (**1-d$_1$n-OH**), whose nmr spectrum showed that these reactions affect neither the position nor the content of deuterium in the molecule. Benzonorbornen-2-one-*3,3-d$_2$* (**1d$_2$**=O) was prepared by deuterium exchange of **1-h**=O or **1-d$_1$**=O in a strongly basic solvent mixture consisting of D_2O, *O*-deuteriomethanol, tetrahydrofuran, and sodium methoxide at 100°; mass spectral analysis indicated an isotopic purity of 91.8 ± 0.7%. The nmr signals due to the C_9 and the bridgehead protons (an ABX_2 type) were in good agreement with the assignment of a solely C_3-dideuterated structure. When **1-h**=O was treated with a less basic medium, *O*-deuteriomethanol containing only a catalytic amount of sodium methoxide, it was found that deuterium was only accommodated in place of the exo-C_3 hydrogen, but not in place of the endo-C_3 (eq 2). For the exo exchange, a first-order rate constant of 1.68×10^{-4} sec^{-1} at 30.8° was obtained by both infrared and nmr spectral methods. Even after treatment under these conditions for 1 day, the spectra showed no effect upon the endo hydrogen. Such high exo:endo rate ratios for base-catalyzed deuterium exchange were recently reported by independent groups for this ketone as well as for related bicyclo[2.2.1]hexan-2-ones.[23,24] Reduction of **1-d$_2$**=O with lithium aluminum hydride gave predominantly benzonorbornen-2-(*endo*)-ol-*3,3-d$_2$* (**1-d$_2$n-OH**), which was subsequently subjected to an equilibration reaction in the presence of aluminum triisopropoxide in xylene in order to convert it into a mixture with the epimer, **1-d$_2$e-OH** (by glpc, 68% **1-d$_2$e-OH** and 32% **1-d$_2$n-OH**). The epimers were separated by passing the mixture through a column packed with deactivated neutral aluminum oxide. Mass and nmr spectral analyses of **1-d$_2$e-OH** and **1-d$_2$n-OH** showed no measurable change in either the content or position of the deuterium atom as a result of these chemical conversions.



(2)

The syntheses of 7-nitrobenzonorbornen-2(*exo*)-ol (**2-he-OH**) and the dideuterated derivative (**2-d$_2$e-OH**) were carried out by nitration of **1-he-OAc** and **1-d$_2$e-OAc**, respectively, with fuming nitric acid in acetic anhydride, hydrolysis to the alcohol mixture in aqueous methanol containing a few drops of hydrochloric acid, and separation of one major 7-nitro alcohol from the other major 6-nitro alcohol. The positions of the nitro groups were confirmed by 100-MHz nmr, as previously reported,[21c,d] after conversion into the 7-nitro ketones (**2-h**=O and **2-d$_2$**=O). The β,β'-dinitro alcohols—**3-he-OH**, **3-hn-OH**, **3-d$_1$n-OH**, **3-d$_2$e-OH**, and **3-d$_2$n-OH**—were prepared from the corresponding undeuterated and deuterated *exo*- and *endo*-alcohols by a previous method involving stepwise introduction of two nitro groups into the benzene ring.[21c,d] It is reasonable to consider that no deuterium loss or migration occurred during the preparations of any of the nitro alcohols and indeed, no inconsistency was found in the nmr spectra. The brosylates used for rate studies were prepared by treatment of the above-mentioned alcohols with *p*-bromobenzenesulfonyl chloride in pyridine and, therefore, their deuterium contents were constant enough to allow direct comparison of the β-deuterium effects on rate.

Table I. Rates by Titration in Solvolyses of C_3-Deuterated Benzonorbornen-2-yl Brosylates (or Tosylates[a])

	Acetolysis[c]			Formolysis[d]		
Compound[b]	Temp, °C	$k_1 \times 10^4$, sec^{-1}	k_H/k_D	Temp, °C	$k_1 \times 10^4$, sec^{-1}	k_H/k_D
1-he-OBs	25.0	0.0688[e]		10.0	6.33[a]	
(OTs)	60.0	5.66				
1-d$_1$e-OBs	25.0	0.0670	1.03			
	60.0	5.47	1.03			
1-d$_2$e-OBs (OTs)	25.0	0.0655	1.05	10.0	6.06[a]	1.04
1-hn-OBs	100.1	0.109		70.0	0.557	
	130.2	2.25				
1-d$_1$n-OBs	100.1	0.0943	1.16	70.0	0.486	1.15
	130.2	1.93	1.17			
1-d$_2$n-OBs	100.1	0.0849	1.28	70.0	0.449	1.24
	130.2	1.76	1.28			
2-he-OBs	95.0	0.254				
	115.0	1.94				
2-d$_2$e-OBs	95.0	0.242	1.05			
	115.0	1.88	1.03			
3-he-OBs	150.3	0.712[e]		75.0	0.0216	
	180.0	7.76[e]				
3-d$_1$e-OBs	150.3	0.648	1.10	75.0	0.0202	1.07
	180.0	7.06	1.10			
3-d$_2$e-OBs	150.0	0.638	1.12	75.0	0.0200	1.08
	180.0	6.97	1.11			
3-hn-OBs	160.1	0.382				
	170.2	0.851				
3-d$_1$n-OBs	160.1	0.333	1.15			
	170.2	0.775	1.10			
3-d$_2$n-OBs	160.1	0.314	1.22			
	170.2	0.703	1.21			

[a] For formolyses of **1-he** and **1-d$_2$e**, rate constants of tosylates are presented. In all other systems, the rate constants are for brosylates. The rate constants presented are the average of two runs. [b] The concentration is 0.02 *M*. [c] Carried out in the acetic acid containing 0.02 *M* AcONa and 1% acetic anhydride. [b] Carried out in the formic acid containing 0.02 *M* HCOONa. [e] Identical with the reported data[21c] within experimental error.

Solvolysis Rates. Table I summarizes solvolysis rates in acetic acid and formic acid, determined by titration of the *p*-bromobenzenesulfonic acid formed, and the values of secondary β-deuterium effects. The acetolyses were carried out in glacial acetic acid containing equivalent sodium acetate by the standard procedure.[25,26] Formolyses were performed by the procedure of Winstein[27] at one temperature for each substrate. Performance of temperature variation was difficult, be-

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(23) T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 1448 (1970). We thank Professor Tidwell for an exchange of related information.

(24) (a) A. F. Thomas and B. Wilhelm, *Tetrahedron Lett.*, 1309 (1965); (b) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 4465 (1965); (c) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

(25) S. Winstein, C. Hanson, and E. Grunwald, *ibid.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham *ibid.*, **70**, 821 (1948).

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(27) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

cause the solvent is not stable enough at the high temperatures required for conveniently running the aromatic-unsubstituted *endo*- and the dinitro *exo*-brosylate solvolyses, and, moreover, the aromatic-unsubstituted *exo*-brosylate was too reactive in this solvent. Good first-order kinetics were observed in all runs and theoretical infinity titers obtained. As exceptions, because of the very slow rates in formolysis of the dinitro *exo*-brosylates, the theoretical infinity values were adopted for calculation of rate constants. All the rate constants were calculated by the method of least squares and were generally reproducible to within less than ±2%. The correlation coefficients for the rate constants were in all cases within 0.999 ± 0.001.

Discussion

Correction of the deuterium effect for the deuterium content was neglected for the following reasons: first, the deuterium content of each substrate used is sufficiently high to have no serious influence on the present observations; second, since as shown in Table I, exo and endo deuterium atoms did not show the same effect, especially in the *exo*-brosylates (discussed later), each content would have to be determined for the appropriate correction. However, this could not be achieved by the nmr technique because the exo-C_3 hydrogen partially overlapped with the syn-C_9 hydrogen.

It was demonstrated that the acetolysis of the parent **1-he**-OBs is the limiting, entirely aryl-assisted (k_{Δ}[8,28]) pathway and produces only the **1-he**-OAc with complete retention of configuration.[21c] Deactivation of the benzene ring with introduction of the 7-nitro substituent is not sufficient to change the major course of the acetolysis, so that **2-he**-OBs still acetolyzes 45 times (77.6°) faster than the corresponding endo epimer **2-hn**-OBs[21d] and gives **2-he**-OAc with retention in a yield of more than 97%.[30] Introduction of two nitro groups into the 6 and 7 positions greatly diminishes the ability of the benzene ring to participate. Consequently, the acetolysis rate becomes 1.1×10^{-5} times slower than that of **1-he**-OBs, the exo:endo rate ratio turns out to be 3.7, and the products are complex. Besides 41% of the acetate of retention, 35% of the acetate of inversion and 21% of the olefin were produced. The product of inversion is considered to be a result of the solvent-assisted process k_s which is competing with the k_{Δ} process.[21c] As seen in Table I, the secondary β-deuterium effect on the acetolysis of the aromatic-unsubstituted *exo*-brosylates is very small (at 25°, $k_{\mathbf{1\text{-}he}}/k_{\mathbf{1\text{-}d_1e}} = 1.03$ and $k_{\mathbf{1\text{-}he}}/k_{\mathbf{1\text{-}d_2e}} = 1.05$). However, it increases notably with the introduction of deactivating groups: for the 7-nitro, $k_{\mathbf{2\text{-}he}}/k_{\mathbf{2\text{-}d_2e}} = 1.05$ (95°) and, for the 6,7-dinitro, $k_{\mathbf{3\text{-}he}}/k_{\mathbf{3\text{-}d_1e}} = 1.10$ (150°) and $k_{\mathbf{3\text{-}he}}/k_{\mathbf{3\text{-}d_2e}} = 1.12$ (150°). Although it is ideal to compare the deuterium effects at an identical temperature, the limited amounts of the materials did not allow us to carry out a sufficient number of runs over a wide temperature range for extrapolation of the results, without incurring any serious errors, to a temperature convenient for comparison. It is, however, fortunate for the present discussion to find that generally the β-deuterium effect in limiting solvolysis decreases with an increase in temperature.[3,31] Therefore, if the above data are corrected for temperature, the increasing tendency of the deuterium effects with deactivation of the benzene ring would become greater. Furthermore, if, on the assumption that a reaction of the SN2 type does not contribute to the β-deuterium effect, correction is made for the k_s pathway in the acetolysis of the dinitro *exo*-brosylates, the deuterium effects, which are unmasked by k_s and reveal only the Fk_{Δ} pathway, are given by simple calculation as 1.16 (150°) for **3-d$_1$e**-OBs and 1.19 (150°) for **3-d$_2$e**-OBs.

The ground-state energies of these *exo*-brosylates are constant. The ratios of polarimetric to titrimetric rate constants in acetolysis, k_{α}/k_t, were found to be 3.9 (140°) for **1-he**-OBs and 4.1 (140°) for **3-he**-OBs,[21c] so that internal return accompanying the acetolysis shows no substantial substituent effect.[32] Absence of serious effect of internal return on the present results is also indicated by the fact that the deuterium effects on the formolyses were for all the present compounds almost the same or slightly less than on the acetolyses, even though the extent of internal return is in general quite different between acetolysis and formolysis. Accordingly, if it is assumed that the steric environments of these brosylates in the transition state are independent of the aromatic substituents or, at least, that their difference is not of primary importance, the present substituent effects on the β-deuterium effects can be discussed only on the basis of electronic difference between the substituted benzene rings. The smallness of the β-deuterium effects on **1-d$_1$e**-OBs and **1-d$_2$e**-OBs relative to those on the (di)nitro brosylates are thus ascribed to the results of significant aryl participation which overwhelms the hyperconjugative effects[33,34] of the neighboring C_3–H bonds in stabilizing the developing positive charge at the reaction center. As the potential for aryl participation is lowered by introduction of electronegative nitro group(s), delocalization of a positive charge by the benzene ring will decrease and, as a consequence, that by hyperconjugation with the neighboring C–H bonds increase. The increased β-deuterium effects on the (di)nitro brosylates reflect this increased hyperconjugation, and the formation of 21% of the olefin from **3-he**-OBs may be a relevant phenomenon.

The above assumption concerning steric environments in the transition state is not, strictly speaking,

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[28] Following Winstein's definitions,[29] solvolytic process of the β-arylalkyl systems has been widely discussed in terms of three factors:[8,21c,d] (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. For the right substrate structure and solvent, k_s becomes equal to k_c; in other words k_c is a limit to which k_s tends. In the event of internal return, only a fraction of k_{Δ}, Fk_{Δ}, yields product and the balance, $(1 - F)k_{\Delta}$, undergoes ion-pair return.

[29] S. Winstein, *Bull. Soc. Chim. Fr.*, 55C (1951); S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, 3, 1 (1958); A. F. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968); A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969).

[30] The products from 7-methoxy-6-nitrobenzonorbornen-2-(*exo*)-yl brosylate, the rate of which is almost identical with that of 2-he-OBs, were reported to be 97% the retained acetate, 2% the inverted acetate, and 1% the olefin.[21c] It is assumed that the products from 2-he-OBs are essentially the same to this case.

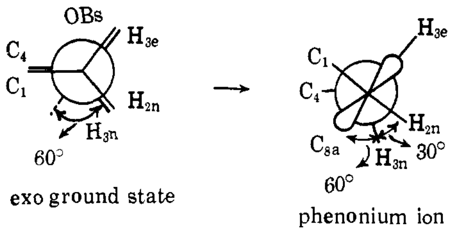
[31] V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **76**, 1603 (1954).

[32] As related data, k_{α}/k_t for the acetolysis of *exo*-2-norbornyl brosylate is 4.6 at 25°: S. Winstein, E. Clippinger, R. Howe, and E. Vogeltanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965), ref 5.

[33] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[34] V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959).

generally true. On the basis of the Hammond postulate, the more reactive **1-he**-OBs is expected to reach the transition state along the reaction coordinate earlier than the less reactive **3-he**-OBs. Judging from a Cenco–Peterson molecular model, the leaving group and the endo-C_2 hydrogen in the ground state of the *exo*-brosylates are eclipsed by the exo-C_3 and the endo-C_3 hydrogens, respectively. The situation is explained in the following Newman projections along the C_2–C_3 bond, in which H_{2n}, H_{3e}, and H_{3n} are the protons endo at C_2, and exo and endo at C_3, respectively. When a phenonium ion is formed by k_Δ, the vacant p orbital at C_2 is eclipsed (or nearly eclipsed) by H_{3e}, but H_{2n} is released from the eclipse by H_{3n} and makes a dihedral angle of 30° with H_{3n}. Therefore, the transition state leading to this ion is considered to involve release of steric compression, as far as the C_2, C_3 environment (not the whole molecule) is concerned.[35,36] Then, the degree of the release will vary from compound to compound depending upon the location of the transition state along the reaction coordinate, so that it for the less reactive dinitro exo would be relatively greater than that for the more reactive parent *exo*-brosylate.[37] It is known that decreased steric compression in the transition state leads to the normal deuterium effect ($k_H > k_D$),[3,17a] so that, as its degree becomes greater and greater, the β-deuterium effect will increase. The results from the dinitro exo are in accord with this consideration. We have not obtained enough evidence to decide which factor, hyperconjugation or release of steric compression, is more important for the observed effects on the dinitro exo, but it is evident that participation by the aryl group is a major factor for the smallness of deuterium effects on the parent *exo*-brosylates.[38]

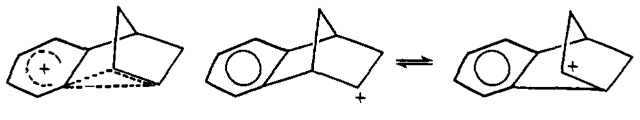


exo ground state

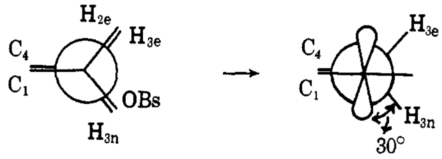
phenonium ion

It should be noted that the small effects caused by C_3 deuteration of the *exo*-2-norbornyl system[11,15] are in the same order of magnitude with the observed deuterium effects on the parent benzonorbornen-2(*exo*)-yl system. The release of steric compression is not appropriate to explain the smallness. Therefore, it is very difficult to imagine that the smallness for the *exo*-2-norbornyl system arises from a factor independent of participation.

The solvolysis of the benzonorbornen-2(*endo*)-yl derivatives proceeds only by the k_s route in the absence of aryl participation and gives almost exclusively the product of inversion. However, the solvent assistance in the transition state is not strong enough to prevent "leakage" into the nonclassical cation, A, or the rapidly equilibrating classical cations, B and C, and consequently the Wagner–Meerwein rearrangement takes place. An experiment investigating the scrambling of the deuterium label at the reaction center into the bridgehead C_1 position in the produced *exo*-acetate was employed as a probe of the Wagner–Meerwein rearrangement.[21d] Compared to those of the corresponding *exo*-brosylates, the deuterium effects of the *endo*-brosylates are very large. These large values do not indicate aryl participation as well as strong solvent assistance but are indicative of a weakly solvent-assisted transition state followed by the leakage, which requires hyperconjugative stabilization by the C_3–H bonds. As shown in the Newman projections, the steric compression in the ground state arising from the eclipsed alignments of the OBs group and H_{3n}, and H_{2e} and H_{3e}, would be relieved in the transition state. In a classical ion model, the dihedral angles of H_{3e} and H_{3n} with the vacant p orbital at the reaction center are both identical, 30°. Either the hyperconjugation or this relief of compression, or both, can be an important factor(s) for the large endo deuterium effects. Although it is unfortunate that the data obtained are not precise enough to be able to discuss the deuterium effects at a common temperature, a tendency for the effects to decrease with introduction of the nitro groups is seen: from $k_{1\text{-hn}}/k_{1\text{-d}_1\text{n}}$ (1.17 at 130°) to $k_{3\text{-hn}}/k_{3\text{-d}_1\text{n}}$ (1.15 at 160°), and from $k_{1\text{-hn}}/k_{1\text{-d}_2\text{h}}$ (1.28 at 130°) to $k_{3\text{-hn}}/k_{3\text{-d}_2\text{n}}$ (1.22 at 160°). This tendency is consistent with our proposal[21d] that, as the benzene is deactivated, the solvent assistance in the transition state becomes stronger; the leakage, and thereby deuterium scrambling, decreases accordingly. The increasing solvent assistance like aryl assistance decreases the deuterium effects.



A B C



endo ground state

classical ion

Stereospecificity Observed for the Secondary-β-Deuterium Effect of 6,7-Dinitrobenzonorbornen-2(*exo*)-yl-*3,3-d*$_2$ Brosylate (3-d$_2$e-OBs). Comparison of the results from **3-d$_1$e-OBs** with those from **3-d$_2$e-OBs** gives the respective effect per exo and endo deuterium atom at the C_3 position. The calculated k_H/k_D values for acetolysis are 1.10 for the exo and 1.02 for the endo deuterium at 150°, and 1.10 and 1.01 at 180°, respectively, and those for formolysis are 1.07 and 1.01 at 75°. The values for the exo are large and those for the endo small. As mentioned before, the deuterium content of **3-d$_2$e-OBs** used for the runs was found to be 1.92 atoms

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[35] The molecule is a cyclopentyl derivative, which has been suggested to undergo relief of steric strain in the solvolytic transition state: C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 44; A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 95–96.

[36] The reactivities of norbornyl derivatives are frequently compared with those of the corresponding cyclopentane compounds: H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1247 (1964), and papers by this group cited therein.

[37] For discussions of this kind, see H. Tanida and T. Tsushima, *ibid.*, **92**, 3397 (1970).

[38] From the standard of the data reported for *trans-* and *cis*-cyclopentyl-*2-d* tosylates,[33] the effects on the parent *exo*-brosylates can be said to be unusually small.

per molecule and shown by the nmr spectrum to be nearly equally distributed in the exo and endo positions. The k_H/k_D values from both the solvolyses indicate, therefore, a unique geometric dependence of the β-deuterium effects, although no experiment was carried out to determine the endo deuterium effects independently. It is impressed that this finding is concerned with the fact that the olefin from the acetolysis of **3-he-OBs** was formed by elimination of only the exo proton, but not of the endo proton, adjacent to the C_2 reaction center involving the Wagner–Meerwein rearrangement.[21c] A similar observation has just been reported for the solvolysis of C_3-deuterated *exo*-2-norbornyl brosylates.[15] Here also, the exo-3 deuterium has a substantial rate-retarding effect, while the endo-C_3 deuterium has a very small effect. In epimeric *endo*-2-norbornyl brosylates both the deuteriums show substantial effects. An explanation of the kind which Murr and Conkling proposed[15] is applied as follows. In the phenonium ion deriving from the *exo*-brosylates (the above Newman projections), the eclipsed alignment of H_{3e} with the vacant p orbital at C_2, though it is not optimum for maximum isotope effect, is evidently preferable to the disposition of H_{3n}, which is 60° from the plane containing H_{3e}, C_2, C_3, and the p orbital.[34,39] In the classical ion from the *endo*-brosylates, the identical dihedral angles of H_{3e} and H_{3n} with the vacant p orbital cannot cause such a geometric dependence of the β-deuterium isotope effects.

Experimental Section

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Infrared spectra were determined with a Nippon Bunko DS-201-B or DS-402-G spectrometer, and nmr spectra with a Varian A-60A and/or HA-100 with tetramethylsilane as an internal standard. The deuterium content and position were determined by a Varian A-60A nmr and a Hitachi RMU-6 mass spectrometer.

Kinetic Measurements. The acetolysis conditions and procedure were the same as previously reported.[26] The formolyses were performed by the method of Winstein and Marshall.[27] Rates of the undeuterated, the mono-, and the dideuterated brosylates were determined simultaneously so as to minimize the effect of any unavoidable temperature fluctuations during a run. As exceptions, the runs at 60° of **1-he-OBs** and **1-d$_1$e-OBs** were carried out separately, because of the fast rates. The experimental infinity titers were determined three times in each run and their average used for calculation of rate constants.

Benzonorbornen-2(*exo*)-ol-*3*(*exo*)-*d* (1-d$_1$e-OH). The synthesis was reported in ref 21c. The present sample had mp 74.5–75.5°; mass spectrum (70 eV) *m/e* (relative intensity) 158 (0.462), 159 (0.924), 160 (11.16), 161 (100.0), 162 (16.26), 163 (1.382). The isotopic purity is given as 90.4% by $100 - 11.16(12.27/100) = a$ (12.27 is a factor due to natural abundance of ^{13}C), $11.16 - 0.924 \cdot (12.27/100) = b$, $100a/(a + b) = 90.4$. The nmr spectrum supported this purity. The brosylate (**1-d$_1$e-OBs**) had mp 84–88°.

Benzonorbornen-2-one-*3*(*exo*)-*d* (1-9$_1$=O) was prepared by oxidation of **1-d$_1$e-OH**: ir (CCl_4) 2180 (w), 1740 (C=O), 1555 (s), 1265, 1123 (s), 985 (s), and 900–950 cm^{-1} (4 bands); nmr (CCl_4) δ ~7.1 (m, 4, aromatic), 3.56 (m, 1, bridgehead), 3.43 (m, 1, bridgehead), ~2.3 (m, 2 C_9-H), and 1.82 (m, 1, C_3(exo)-H); mass spectrum (70 eV) *m/e* (relative intensity) 157 (0.127), 158 (9.110), 159 (100.0), 160 (12.66), 161 (5.180), 162 (0.952), 163 (0.121); 91.9% D.

Benzonorbornen-2(*endo*)-ol-*3*(*exo*)-*d* (1-d$_1$n-OH) was prepared by reduction of **1-d$_1$=O** with lithium aluminum hydride in ether. The crude mixture of **1-d$_1$n-OH** and **1-d$_1$e-OH** in an approximate ratio of 9:1 was recrystallized from *n*-hexane to obtain a pure sample of **1-d$_1$n-OH**: mp 71–72.5°; nmr (CCl_4) δ 6.8–7.3 (m, 4, aromatic), 4.3 (m, 1, C_2(exo)-H), 3.05–3.22 (m, 2, bridgehead), 1.15–1.95 (m, 2, C_9-H), and 0.5–0.96 (two m, 2, C_3(endo)-H and OH); 91.8% D. The brosylate (**1-d$_1$n-OBs**) had mp 133.5–135.0°.

Benzonorbornen-2-one-*3,3*-*d*$_2$ (1-d$_2$=O). A homogeneous solution of **1-d$_1$=O** (7.9 g), sodium methoxide (27 g), *O*-deuteriomethanol (67 ml), deuterium oxide (150 ml), and tetrahydrofuran (60 ml) was sealed into an ampoule and kept at 100° for 48 hr. The reaction mixture was extracted repeatedly with ether and the extract was washed with deuterium oxide, dried with anhydrous sodium sulfate and molecular sieve, and then concentrated. The oily residue (a mixture of **1-d$_2$=O**, tetrahydrofuran, and *O*-deuteriomethanol) was fractionally distillated under a reduced pressure to obtain 7.5 g of **1-d$_2$=O**: bp 108° (4 mm); mass spectrum (70 eV) *m/e* (relative intensity) 158 (0.968), 159 (6.010), 160 (100.0), 161 (13.81), 162 (1.510); nmr (CCl_4) δ 6.9–7.3 (4, aromatic), 3.55 (m, 1, bridgehead), 3.41 (q, 1, bridgehead), 2.38 (d–t, 1, C_9-H, $J_{gem} = 9.8$ Hz, $J_{C_9\text{-H-bridgehead}} = 1.4$), and 2.12 (d–t, 1, C_9-H, $J_{C_9\text{-H-bridgehead}} = 1.4$). The nmr indicated 1.87 atoms of deuterium per molecule, consistent with the result from the mass spectrum (91.8 ± 0.7% isotopic purity), within accuracy of these analyses.

Benzonorbornen-2(*exo*)-ol-*3,3*-*d*$_2$ and -2(*endo*)-ol-*3,3*-*d*$_2$ (1-d$_2$e-OH and 1-d$_2$n-OH). A mixture (7.3 g) of **1-d$_2$e-OH** and **1-d$_2$n-OH** in an approximate ratio of 1:9, prepared by reduction of **1-d$_2$=O** with lithium aluminum hydride, was dissolved into a solution of 9.5 g of freshly distilled aluminum isopropoxide in 300 ml of xylene containing a few drops of acetone and heated at 125° under nitrogen atmosphere for 1 day. The reaction mixture was poured into cold 3% hydrochloric acid and extracted with ether. The ether extract was washed with cold water, dried over sodium sulfate, and concentrated. Treatment of the residue (a mixture of 68% exo and 32% endo) with elution chromatography over Merck neutral alumina containing 3% water gave 3.0 g of **1-d$_2$e-OH**, mp 74–75°, and 1.5 g of **1-d$_2$n-OH**, mp 74–75°. The mass spectra for both the alcohols showed an identical deuterium content, 1.92 atoms per molecule: *m/e* (relative intensity), for **1-d$_2$e-OH** 158 (0.252), 159 (0.401), 160 (1.720), 161 (12.07), 162 (100.0), 163 (12.75), 164 (1.017); for **1-d$_2$n-OH**, 158 (0.212), 159 (0.410), 160 (1.703), 161 (11.23), 162 (100.0), 163 (12.87), 164 (1.054). The brosylate (**1-d$_2$e-OBs**) had mp 82.5–83° and **1-d$_2$n-OBs** mp 133–134°.

Exchange of C_3-*exo*-Proton in Benzonorbornen-2-one (1-h=O) with Deuterium. The ketone (243 mg) was dissolved into 5 ml of *O*-deuteriomethanol containing 2.54 mg of sodium methoxide and maintained at 30.8°. At appropriate time intervals during the reaction, a small portion of the solution was quenched by diluting with ether, washed with cold water, dried with anhydrous sodium sulfate, and evaporated to obtain a sample for rate measurements. The resulting ketone was dissolved in carbon tetrachloride and its nmr and ir spectra were measured. For calculation of exchange rate constants by the ir method, two bands appearing at 1415 and 1125 cm^{-1} were used taking the latter band as an internal reference. The ir spectrum of the infinity sample was identical with that of the authentic sample obtained from the oxidation of **1-d$_1$e-OH**. In the nmr method, the decreasing rate of the area of overlapping signals due to the four protons at C_3 and C_9 was calculated by using the aromatic four protons as an internal reference. The rate constants were given in the text.

The Nitro Alcohols and Brosylates. The syntheses were carried out according to the reaction sequence previously reported[21c,d] and outlined in the text: **2-he-OH** had mp 91–92° (*Anal.* Calcd for $C_{11}H_{11}NO_3$: C, 64.37; H, 5.40. Found: C, 64.09; H, 5.11); **2-d$_2$e-OH** had mp 91–92°; **2-he-OBs** had mp 115–116° (*Anal.* Calcd for $C_{17}H_{14}BrNO_5S$: C, 48.52; H, 3.35. Found: C, 48.64; H, 3.44); **2-d$_2$e-OBs** had mp 115–116° (*Anal.* Calcd for $C_{17}H_{12}D_2BrNO_5S$: C, 47.90; H, 3.36. Found: C, 48.07; H, 3.40); for **3-d$_1$e-OBs**, mp 173–174°; for **3-d$_1$n-OBs**, mp 169.5–171.5°; for **3-d$_2$e-OBs**, mp 173.5–174.5°; for **3-d$_2$n-OBs**, mp 169.5–171.5°.

Acknowledgments. We thank Dr. Y. Nakagawa and Mr. M. Moriyama for mass spectral analyses.

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(39) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Amer. Chem. Soc.*, **85**, 2416 (1963).