Substituent Effects and Homobenzylic Conjugation in Benzonorbornen-2(*exo*)-yl *p*-Bromobenzenesulfonate Solvolyses[1-4]

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Abstract: A series of aromatic-substituted benzonorbornen-2(*exo*)-yl *p*-bromobenzenesulfonates was prepared and the solvolysis reactions were studied. The relative rates of acetolysis of 6-CH_3O, H, 7-CH_3O, 7-CH_3O-6-NO_2, and 6,7-$(NO)_2$ derivatives at 77.60° were 178, 1, 0.72, 1.1×10^{-3}, and 1.1×10^{-3}, respectively. The solvolyses of 6-CH_3O, H, and 7-CH_3O derivatives (**1e**, **2e**, and **3e**) proceed with retention of configuration yielding only the *exo*-substituted products (the corresponding benzonorbornen-2(*exo*)-ols or their esters). However, the strongly deactivated 7-CH_3O-6-NO_2 and 6,7-$(NO_2)_2$ derivatives (**4e** and **5e**), besides the products with retention, give the inverted *endo* products and the olefins. The analysis of the data indicates major participation by the aromatic ring, facilitating solvolysis and causing *exo* substitution in the product. When an optically active material (**8e**-OBs, the parent system) is used, the participation brings about a racemic product. When the optically active 6,7-dinitrobenzonorbornen-2(*exo*)-yl brosylate (**6e**-OBs) was acetolyzed, the produced *exo* acetate retained 4.51% of the original optical purity and the *endo* acetate retained 25.7%. By these data and the results of the acetolysis of labeled 6,7-dinitro-3(*exo*)-deuteriobenzonorbornen-2(*exo*)-yl brosylate (**7e**-OBs), it was proven that the dinitrobenzene ring is migrating. Also it was shown that the *endo* product from **5e**-OBs is partially the result of an SN2 reaction of the original brosylate and partially the result of the same reaction with the brosylate formed by internal return of an ion pair. Both the observed rates and the anchimerically assisted parts of the observed rates are correlated with good precision by using the modified Hammett relationship, $\log (k/k_0) = \rho\sigma^+$, yielding identical straight lines with $\rho = -3.26$.

The participation by the benzene ring and the nonclassical structure of the carbonium ion intermediate in the solvolysis of benzonorbornenyl derivatives was first proposed by Bartlett and Giddings.[5] The authors then discovered that, in the benzonorbornen-9(*anti*)-yl system, the effects of the 6 substituent and the 7 substituent on the reaction rate are very substantial and are additive.[6] These findings have been evaluated as one of the best pieces of evidence for the existence of participation by the benzene ring[7] and for a symmetrical transition state.[8] As an extension of studies based principally on the same ideas, the present report shows the substituent effects on the solvolysis of benzonorbornen-2(*exo*)-yl brosylate and demonstrates a $\rho\sigma^+$ relationship. Since participation by the benzene ring in the solvolysis of 6-methoxybenzonorbornen-2-(*exo*)-yl systems seems to have become a definite fact according to the recent communications submitted from three independent laboratories,[1a,3] the major attention in this paper has been focused on the effects of strongly deactivating substituents.

(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) Presented at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 1968.

(3) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1901 (1968); (b) H. C. Brown and G. Tritle, *ibid.*, **90**, 2689 (1968); working independently, these authors have published communications of work similar to that reported in our preliminary forms.[1]

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

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

(6) (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).

(7) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).

(8) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms 1967," Interscience Publishers, London, 1968, p 30.

Results

Preparations. A number of aromatic-substituted 2-benzonorbornenyl derivatives were synthesized as outlined in Chart I.

The hydrochlorination of benzonorbornadiene was reported to give solely benzonorbornen-2(*exo*)-yl chloride (**1e**-Cl).[9] Treatment of 6-methoxybenzonorbornadiene with concentrated hydrochloric acid yielded an 8:2 mixture, by vpc analysis, of 6-methoxy- and 7-methoxybenzonorbornen-2(*exo*)-yl chlorides (**2e**-Cl and **3e**-Cl) (homo-*para* and homo-*meta* chlorides, eq a).[10] The reactivity difference in solvolysis between the homo-*para* and homo-*meta*-*exo* derivatives is very large (eq c and d). It was, therefore, possible to separate these chlorides easily by hydrolysis of only the reactive **2e**-Cl into an alcohol (**2e**-OH), as was described in the communication[1a] and, in full, in the Experimental Section.[11] Oxidation of **2e**-OH and **3e**-OH by the Oppenauer method or with chromic anhydride in pyridine led to 6-methoxybenzonorbornen-2-one (**2**-O) and 7-methoxybenzonorbornen-2-one (**3**-O), respectively. Comparison of the characteristic ^1L_a bands in the ultraviolet spectra of **2**-O ($\lambda_{max}^{isooctane}$ 238 mμ (ϵ 8660)) and **3**-O (in isooctane, shoulder at 228 mμ (ϵ ~5620)) evidences the homo-*para* and homo-*meta* assignments.[12,13] In addition, the nmr patterns of aromatic

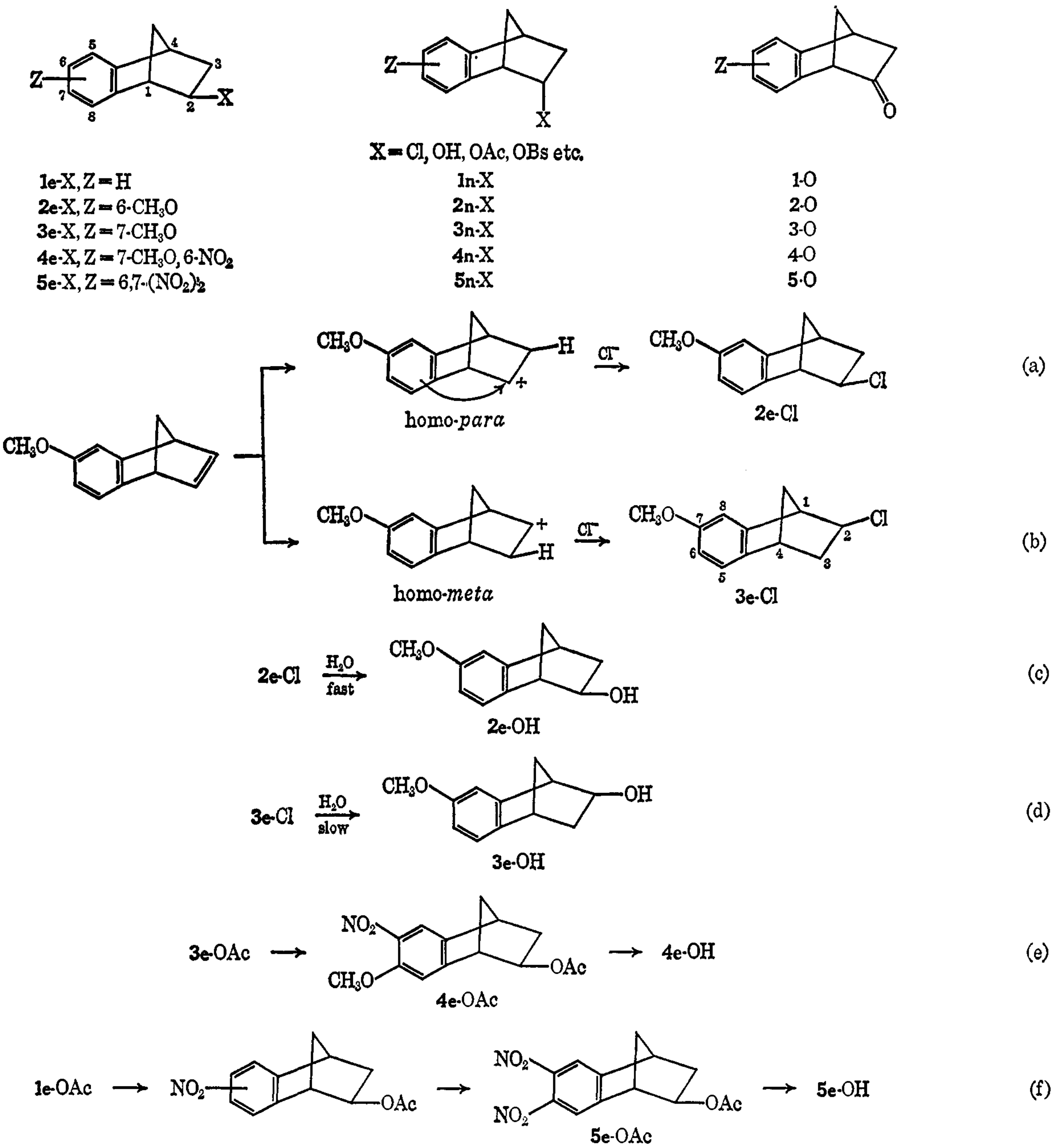
(9) S. J. Cristol and R. Caple, *J. Org. Chem.*, 31, 2741 (1966).

(10) The 7:3 ratio previously reported[1a] was the relative yields of isolated chlorides. The reason for the preferred formation of **2e**-Cl is, in substance, the same for its greater solvolytic reactivity, namely homo-*para* stabilization of the intermediate, as discussed later. We are presently investigating the substituent effects on the addition reactions of benzonorbornadienes, which will be reported later.

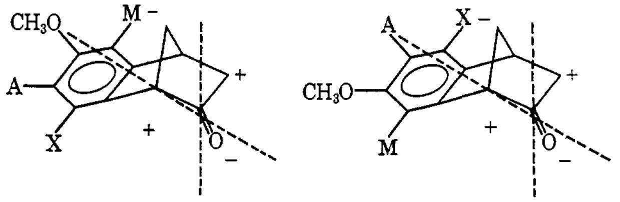
(11) *exo* and *endo* configurations in the alcohols dealt in this paper are assigned by the nature of infrared OH stretching bands as described in H. Tanida, T. Tsuji, and S. Teratake, *J. Org. Chem.*, 32, 4121 (1967).

(12) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 260.

Chart I



protons in 2-O and 3-O (AMX type, in acetone-d_6 at 100 Mc) are in agreement with the assignments. It is noted that, owing to its location in the deshielding area of the carbonyl group, the proton at C-5 in 2-O (the M part) appears at a lower field than does the corresponding proton at C-8 in 3-O, whereas, owing to their location in the shielding area, the protons at C-7 and C-8 in 2-O (the AX part) appear at a higher field than the corresponding protons at C-6 and C-5 in 3-O, respectively (see Experimental Section).



Electrophilic aromatic substitution reactions of the benzonorbornene derivatives show an unusually strong β orientation.[14] Thus, nitration of 3e-OAc with fuming nitric acid in acetic anhydride gave 7-methoxy-6-nitrobenzonorbornen-2(*exo*)-yl acetate (4e-OAc) in 96% yield, which was hydrolyzed with very dilute hydrochloric acid to obtain 4e-OH (eq e). Mononitration of 1e-OAc with fuming nitric acid in acetic anhydride followed by introduction of a second nitro group with fuming nitric acid and concentrated sulfuric acid afforded 6,7-dinitrobenzonorbornen-2(*exo*)-yl acetate (5e-OAc) in an over-all yield of about 49% (eq f). Hydrolysis gave 5e-OH. All *exo* brosylates were prepared by treatment of the alcohols with *p*-bromo-

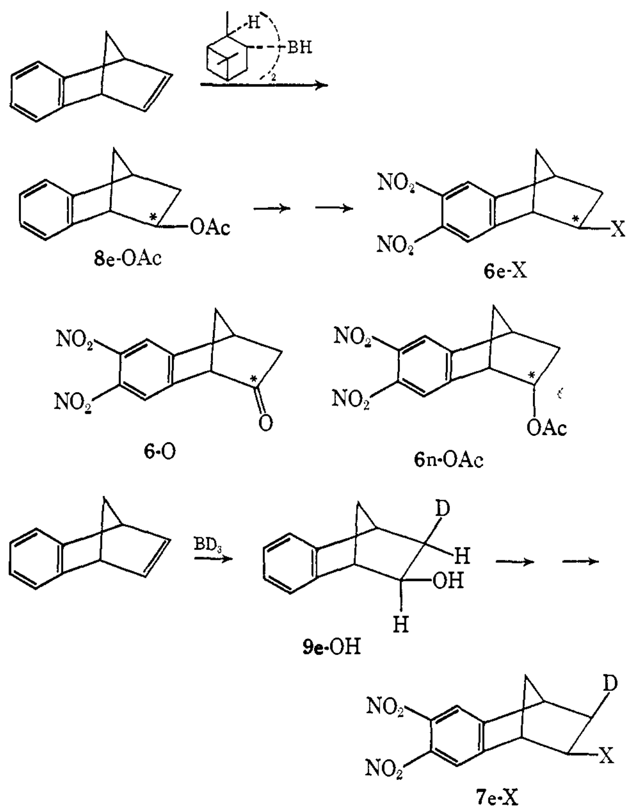
(13) The ultraviolet spectrum of 6-methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-one in *n*-heptane shows a maximum at 234 mμ (ϵ 8850) and that of 7-methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-2-one in *n*-heptane shows a shoulder at 220 mμ (ϵ ~8700) (a private communication from Dr. K. Takeda). See footnote 7 in ref 1a.

(14) H. Tanida and R. Muneyuki, *J. Amer. Chem. Soc.*, 87, 4794 (1965).

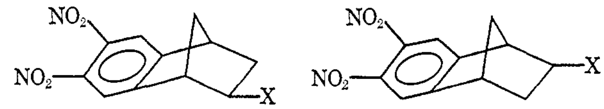
benzenesulfonyl chloride in pyridine. The *endo* alcohols (**2n**-OH, **3n**-OH, **4n**-OH, and **5n**-OH), needed as authentic samples in the products study, were prepared by oxidation of the corresponding *exo* alcohols to the respective ketones followed by reduction with diborane or lithium aluminum hydride.

In order to investigate the intermediate(s) involved in the solvolysis of **5e**-OBs, the optically active brosylate (**6e**-OBs) and the *exo*-3 deuterium-substituted brosylate (**7e**-OBs) were prepared (Chart II). Essentially using

Chart II



the same method reported recently,[15] benzonorbornadiene was allowed to react with (−)-diisocampheylborane[16] obtained from *ca.* 86% optically pure (+)-α-pinene in diglyme. Oxidation with hydrogen peroxide in aqueous sodium hydroxide and acetylation gave the optically active benzonorbornen-2(*exo*)-yl acetate (**8e**-OAc), which was purified by fractionation at a spinning-band column. Hydrolysis in ethanolic potassium hydroxide gave **8e**-OH. Subsequent transformations leading to **6e**-OAc were the same as those described for **5e**-OAc. When **6e**-OAc was hydrolyzed by treatment with lithium borohydride and then purified by recrystallization, **6e**-OH, $[\alpha]^{23}\text{D}$ +31.3 (*c* 1.014, chloroform), was obtained. For an unambiguous interpretation of the experimental results, it is necessary that the following compounds have the same optical purity as this **6e**-OH. Treatment of **6e**-OH with acetic anhydride in pyridine and *p*-bromobenzenesulfonyl chloride in pyridine gave the materials for acetolysis, **6e**-OAc and **6e**-OBs, respectively. Yields of both of these esters were almost quantitative, so that there were no changes in the optical purities of these compounds. Oxidation of **6e**-OH gave optically active 6,7-dinitrobenzonorbornen-2-one (**6**-O), which led to **6n**-OAc by treatment with diborane followed by acetylation. The origin of optical activities of these compounds is that the inactive materials are a mixture of equal amounts of the two enantiomers (for example, A and B) and in the active



A B

materials either one predominates. Since the origin is not affected by these chemical conversions, the optical purities in **6**-O and **6n**-OAc are considered to be identical with that in **6e**-OH, unless purification by crystallization is performed. The optical activities of the compounds are described in the Experimental Section.

Deuterioboration of benzonorbornadiene with sodium borodeuteride and boron trifluoride proceeds to give exclusively the *cis-exo* addition product, *exo*-3-deuteriobenzonorbornen-2(*exo*)-ol (**9e**-OH),[17] which was subsequently transformed into *exo*-3-deuterio-6,7-dinitrobenzonorbornen-2(*exo*)-ol and its brosylate (**7e**-OH and **7e**-OBs). Mass spectral analysis of **7e**-OAc indicated deuteration of 0.90 ± 0.02 atom. Since, in the nmr spectrum, the *exo*-3 proton in **7e**-OH and **7e**-OAc overlaps with the C-9 protons, it is not possible to determine whether or not the deuterium locates at a position other than the *exo*-3. However, it is reasonable to assume that the synthesis does not involve rearrangement of the deuterium from the original C-2 to other carbons.

Solvolysis Rates. The rates determined by titration of forming *p*-bromobenzenesulfonic acid are summarized in Table I, together with the derived activation parameters. The acetolyses were carried out in glacial acetic acid containing equivalent sodium acetate by the standard procedure.[6b,18] Because of the great reactivity of the **2e**-OH system, the rate of solvolysis of **2e**-Cl in 70% aqueous acetone was determined and compared with that of the parent **1e**-Cl. For discussions, **1e**-OBs and **5e**-OBs were solvolyzed in various solvents such as acetic acid, ethanol, aqueous ethanol, and aqueous dioxane, and the data obtained are listed in Table II. Good first-order kinetics were observed in all the solvolyses. Theoretical infinity titers were obtained in the acetolyses, but infinity titers in some cases of the ethanolyses and hydrolyses were to some extent less than the theoretical values. In these cases, the observed infinity titers were used for calculation.

The rate measurements of the change in the optical activities of **8e**-OBs and **6e**-OBs were carried out in the same buffered acetic acid as used for the titration rate. Linear first-order plots were found for both the brosylates. More than 99.9% racemization in the acetolysis of **8e**-OBs was reported,[5b] whereas the optical activity in the acetolysis of **6e**-OBs increased with the reaction time. The rate constants (k_α) observed were 6.94 × 10^{-4} sec^{-1} at 50° and 2.67 × 10^{-5} sec^{-1} at 25° for **8e**-OBs, and 1.08 × 10^{-4} sec^{-1} at 140° for **6e**-OBs. Com-

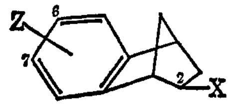
(15) D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, **90**, 4877 (1968).

(16) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397, 1071 (1964); G. Zweifel, N. R. Ayyangar, T. Munekata, and H. C. Brown, *ibid.*, **86**, 1076 (1964).

(17) P. Bruck, *Tetrahedron Lett.*, 449 (1962).

(18) (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).

Table I. Rates of Solvolysis of 6- and 7-Substituted Benzonorbornen-2(*exo*)-yl Derivatives



Substituent[a] Z	Substituent[a] X	Solvent[b]	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal/deg	Calcd at 77.6° k_1, sec^{-1}	Calcd at 77.6° Rel reactivity
H	OBs	AcOH[c]	50.0	1.75×10^{-4}	24.3	−0.7	3.74×10^{-3}	1
			25.0	6.69×10^{-6}				
H	Cl	70% Me_2CO	145.0	5.36×10^{-4}	23.7	−17.4	1.89×10^{-6}	
			120.0	8.27×10^{-5}				
6-CH_3O	Cl	70% Me_2CO	75.0	2.64×10^{-4}	21.7	−12.9	3.36×10^{-4}	178
			50.0	2.16×10^{-5}				
7-CH_3O	OBs	AcOH	60.0	3.85×10^{-4}	24.9	+0.4	2.68×10^{-3}	0.72
			40.0	3.26×10^{-5}				
7-CH_3O	Cl	70% Me_2CO	145.0	3.17×10^{-4}	25.4	−14.5	7.63×10^{-7}	
			120.4	4.46×10^{-5}				
7-CH_3O-6-NO_2	OBs	AcOH	130.0	8.70×10^{-4}	28.1	−3.6	4.09×10^{-6}	1.1×10^{-8}
			100.0	4.86×10^{-5}				
6,7-$(NO_2)_2$	OBs	AcOH	180.5	7.51×10^{-4}	29.5	−8.7	4.12×10^{-8}	1.1×10^{-5}
			150.0	6.76×10^{-5}				
			140.0	2.64×10^{-5}				

[a] The concentration of reactants is 0.02 *M*. [b] The aqueous acetone is expressed as volume per cent and the acetic acid contained 0.02 *M* AcONa and 1% acetic anhydride. [c] Reference 5a reported $k_1 = 1.88 \times 10^{-4}$ (50°) and 7.47×10^{-6} (25°) sec^{-1}.

Table II. Solvent Effects on Rates of Aromatic-Substituted Benzonorbornen-2(*exo*)-yl Brosylates

Substituent	Solvent	Temp, °C	k_1, sec^{-1}	Rel rate at 165°
H[a]	AcOH			1
	EtOH	50.0	7.61×10^{-5}	0.59
		25.0	2.64×10^{-6}	
	90% EtOH	50.0	5.74×10^{-4}	1.80
		25.0	2.66×10^{-5}	
	80% EtOH	50.0	1.81×10^{-3}	4.36
		25.0	9.12×10^{-5}	
	70% dioxane	50.0	4.28×10^{-4}	1.85
		25.0	1.79×10^{-5}	
6,7-$(NO_2)_2$	AcOH	165.0	2.30×10^{-4}	0.48×10^{-4} (1)
	EtOH	165.0	1.13×10^{-4}	0.24×10^{-4} (0.49)
	90% EtOH	165.0	3.36×10^{-4}	0.70×10^{-4} (1.46)
	80% EtOH	165.0	7.34×10^{-4}	1.53×10^{-4} (3.19)

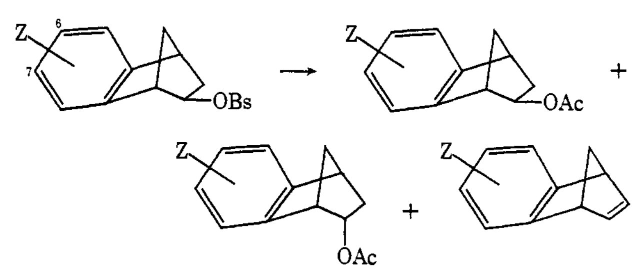
[a] k_1, sec^{-1} extrapolated to 165° are 4.79 in AcOH, 2.82 in EtOH, 8.60 in 90% EtOH, 2.09×10 in 80% EtOH, and 8.85 in 70% dioxane.

bination of the observed and extrapolated data indicated that the rates of change of the optical activities are 4.0 times faster than the rate of acid production at 25° (3.9 times at 140°) in the parent system and 4.1 times at 140° in the dinitro system (evidence for internal return).

Solvolysis Products. For product determination, the acetolyses and hydrolyses were carried out under the same conditions as used for the rate studies. In general, the solvolysis of benzonorbornen-2(*exo*)-yl brosylate and its aromatic-substituted derivatives proceeds with the formation of benzonorbornen-2(*exo*)-ol (product of retention), benzonorbornen-2(*endo*)-ol (product of inversion), and benzonorbornadiene (product of elimination), or derivatives of these. No other types of products were observed. The product composition was determined precisely by the use of vpc and nmr. Table III demonstrates the substituent effects on the distribution of the products resulting from **1e**-OBs, **4e**-OBs, and **5e**-OBs. The estimated error in the yields is ±2%. Samples of the products were isolated, treated separately under the solvolysis conditions, and recovered unchanged.

When, in the acetolysis of **5e**-OBs at 140°, the brosylate was recovered at the stages of either 40 or 60% conversion (two separate experiments), its infrared and nmr spectra were identical with those of an authentic sample of **5e**-OBs. This fact excludes rearrangement of **5e**-OBs to a brosylate of other structure before the leaving *p*-bromobenzenesulfonyloxy group is dis-

Table III. Products and Yields[a]



Substituent	Solvent	Temp, °C	*exo*	*endo*	Olefin
H	AcOH	50	96	0[b]	0[b]
H	70% dioxane	50		0.1	0.13
6-NO_2-7-CH_3O	AcOH	130	97	2	1
6,7-$(NO_2)_2$	AcOH	180	41	35	21
6,7-$(NO_2)_2$	60% dioxane	150	40	40	12

[a] Per cents of theory. [b] 0% means ≦0.1.

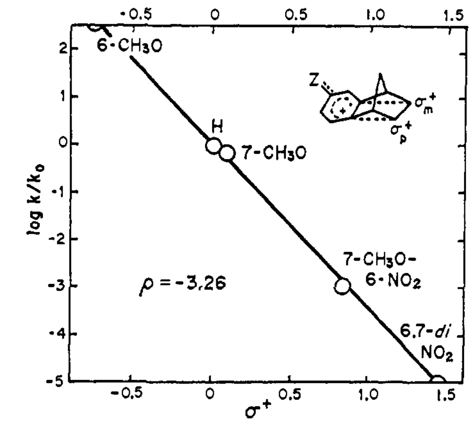
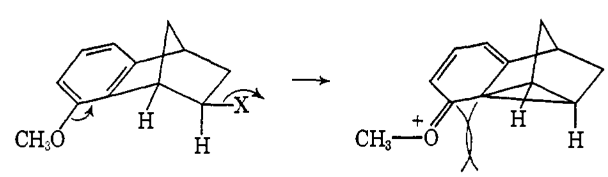


Figure 1. The ρ–σ^+ treatment of the observed rates or the anchimerically assisted rates in acetolyses of benzonorbornen-2(*exo*)-yl brosylates.

placed by the solvent. Therefore, all the products in the acetolysis of **5e**-OBs originated from the brosylate of the original *exo* structure.

Discussions

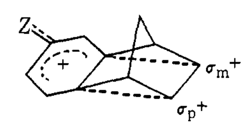
Participation Effects on Rate and Product. The importance of aryl participation in the solvolysis of the benzonorbornen-2(*exo*)-yl system was clearly evidenced by the present study. The 6-methoxy substituent (a homo-*para* system) accelerates the solvolysis rate by a factor of 178 (77.6°), whereas the homo-*meta* 7-methoxy substituent depresses it by a factor of 0.4 in a manner similar to that which we have experienced in electrophilic aromatic substitution reactions. It was pointed out that the 6-methoxy rate-accelerating effect is the largest yet observed for a neighboring *p*-anisyl group.[3b] The product formation was also highly stereospecific: **2e**-OBs as well as **1e**-OBs produced only the *exo* alcohol or its ester with retention of confiuration. Such a large rate enhancement was not observed in the *endo* brosylate system.[19] The rate-increasing factor of the 5,8-dimethoxy substituents in the *exo* system was reported to be as small as 16 at 25°.[20] This is presumably because the 8-methoxy substituent, when the reaction progresses toward the transition state of a bridged type, brings about a serious steric strain by an interaction with the bridgehead hydrogen and the hydrogen α to the leaving group, so that the participation effect of this substituent is greatly disturbed.



The combination of the 7-methoxy and the 6-nitro group decelerates the rate by the factor of 1.1×10^{-3} and a small amount of the inverted product was now found. The introduction of two of the strongly deactivating nitro groups results in a rate that is very slow, 1.1×10^{-5} times that of the parent compounds.[21] Therefore, the effect of substituents, $k_{6\text{-CH}_3\text{O}}/k_{6,7\text{-(NO}_2)_2}$, amounts to a factor of 1.6×10^7. Also, the stereospecificity in the product formation disappears dramatically with deactivation of the aromatic ring. Thus, besides 41% of the *exo* acetate, **5e**-OBs produced 35% of the *endo* acetate and 21% of the olefin.

It is conceivable that the introduction of groups such as two nitros causes a change in the mechanism of the solvolysis. However, as shown in Table II, the solvent effects on rates are not so different between **1e**-OBs and **5e**-OBs. The rate ratios in acetic acid and 97% aqueous ethanol, both of which have an identical Grunwald–Winstein Y value of -1.65,[22] were 1.3 and 1.5 at 165° for **1e**-OBs and **5e**-OBs, respectively. In addition, $\Delta S^{\ddagger}$ in acetolysis of **5e**-OBs was -8.7 eu at 165°. These results suggest that, even in the acetolysis of **5e**-OBs, nucleophilic participation by the solvent is not dominant; in other words, **1e**-OBs as well as **5e**-OBs involves carbonium ion intermediates during acetolysis. The somewhat larger solvent effects in **1e**-OBs indicate an advanced ionization in the transition state.

σ^+ Correlation of Rate Data. We have suggested that the rates at the homo-*para* position will correlate with σ_p^+ and those at the homo-*meta* position with σ_m^+.[6a] This was proven by plotting the present rate data which gave a ρ value of -3.26 (Figure 1).



A quantitative estimation of anchimeric assistance in the β-arylalkyl systems requires a separation of the rate constant into k_Δ, the rate constant for anchimerically assisted solvolysis, and k_s, the rate constant for anchimerically unassisted solvolysis, assuming that the way represented by k_Δ leads to a bridged cation and the one responsible for k_s proceeds with solvent participation or other factors.[18,23,24] We demonstrate in the next section that the production of the *exo* acetate, the olefin, and one part (26% of theory) of the *endo* acetate is *via* a cationic intermediate, involving a rearrangement of the aromatic ring, and the other part (9% of theory) of the *endo* acetate is the result of an S_N2 reaction. Therefore, it is felt that the assisted rates, k_Δ, in the **1e**–**4e** systems are equal to the rates of acid production, k_t, and k_Δ in the **5e** system amounts to 91% of k_t.[25] Replacement of k_t by k_Δ in the ρ–σ^+ treatment yields a linear relationship with the identical ρ value, -3.26.[26]

Mechanism for the *endo* Products. From the product mixtures from acetolysis of the optically active

(19) The study of the solvolysis of aromatic-substituted benzonorbornen-2(*endo*)-yl brosylates will be reported in the near future. We originally intended to include it in this paper. However, we have found that some additional work is necessary prior to publication.

(20) Literature in footnote 11.

(21) We have found that **5e**-OBs is only four times more reactive than the corresponding *endo* brosylate.

(22) *Cf.* J. F. Bunnett, "Technique of Organic Chemistry. Investigation of Rates and Mechanisms of Reactions," Vol. VIII, Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1961, Chapter VI.

(23) (a) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948); (b) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968).

(24) C. G. Lancelot and P. von R. Schleyer, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Paper ORGN-4.

(25) Our calculation involves the reasonable assumption that the yield ratios of the products are not significantly different at 77.6° (temperature for rate comparison) and at the temperatures used for the product studies.

(26) We thank Professors Winstein and Schleyer for their helpful discussions on k_Δ.

6e-OBs at 165°, the *exo* acetate was isolated in 36.4% yield, the *endo* acetate in 32.6% yield, and the olefin in 16.0% yield, and the remaining activities were measured as 4.51% for the *exo* acetate and 25.7% for the *endo* acetate. Since the yields are not significantly different from those determined by the direct analysis of the reaction mixture (Table III), it is considered that the measured activities reflect precisely the nature of the reaction products. Taking the yields in Table III, these results lead to two sets of two equations (with x = unrearranged *exo* acetate and y = *exo* acetate resulting from Wagner–Meerwein rearrangement. x' and y' are the corresponding *endo* acetates).

$$x + y = 0.41$$

$$x' + y' = 0.35$$

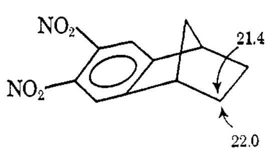
$$\frac{x}{x+y} - \frac{y}{x+y} = 0.0451$$

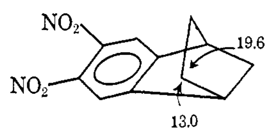
$$\frac{x'}{x'+y'} - \frac{y'}{x'+y'} = 0.257$$

These give

$$x = 0.214 \qquad x' = 0.220$$

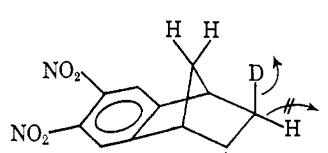
$$y = 0.196 \qquad y' = 0.130$$

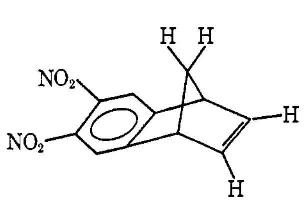




Therefore, it is shown that the *exo* acetate was formed with retention in 21.4% yield and with rearrangement in 19.6% and the *endo* acetate with retention in 22.0% and with rearrangement in 13.0%.

The *endo* acetate produced from **7e-OBs** (165°) was indicated by nmr to have deuterium at the *exo*-3 and *anti*-9 positions in a ratio of 63 to 37, which is in excellent agreement with the ratio of retention and rearrangement in the *endo* acetate obtained from **6e-OBs**. This identity demonstrates reliability of the results from **6e-OBs** and **7e-OBs**. The olefin produced was found to have 61% of the original deuterium at the *anti*-**9** position, but none at all at the vinyl positions. This means that the intermediate(s) for the formation of the olefin





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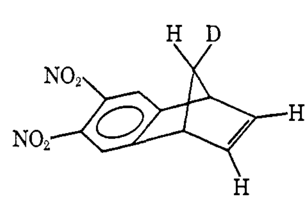

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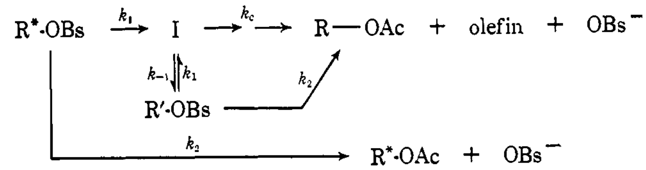
eliminates only the *exo* proton or deuterium at C-3. On the basis of the data thus obtained, we propose Scheme I.

Scheme I



The optically active brosylate (R*-OBs) produces an ion pair (I) through the path of the rate constant k_1 and the optically active *endo* acetate (R*-OAc) through an SN2 reaction with the rate constant k_2. The ion pair can undergo destruction by attack of the nucleophile to form the racemic acetate (R-OAc) and the olefin with the rate k_c, or alternatively return internally to the racemic brosylate (R′-OBs) with k_{-1}. R′-OBs should react in the same way as R*-OBs. The total amount of R*-OAc (35% (Table III) × 25.7% = 9%) was assumed to be produced by the SN2 reaction. The scheme gives the eq 1–7. Here, [R-OBs] = total

$$d[\text{R*-OBs}]/dt = -(k_1 + k_2)[\text{R*-OBs}] \quad (1)$$

$$d[\text{R}'\text{-OBs}]/dt = -(k_1 + k_2)[\text{R}'\text{-OBs}] + k_{-1}[\text{I}] \quad (2)$$

$$d[\text{I}]/dt = k_1[\text{R*-OBs} + \text{R}'\text{-OBs}] - (k_{-1} + k_c)[\text{I}] \quad (3)$$

$$d[\text{OBs}]/dt = k_c[\text{I}] + k_2[\text{R*-OBs} + \text{R}'\text{-OBs}] \quad (4)$$

$$d[\text{R*-OAc}]/dt = k_2[\text{R*-OBs}] \quad (5)$$

$$[\text{R-OBs}] = [\text{R*-OBs}] + [\text{R}'\text{-OBs}] \quad (6)$$

$$\epsilon = \alpha[\text{R*-OBs}] + \beta[\text{R*-OAc}] \quad (7)$$

amount of the reacting brosylate; ϵ is the optical activity at any time, t; α and β are constants. At time $t = 0$, [R* -OBs] = $[\text{R* -OBs}]_0$. Using the steady-state approximation, eq 1–4 gives

$$\ln\{([\text{R*-OBs}]_0 - [\text{OBs}])/[\text{R*-OBs}]_0\} = -k_t t$$

where

$$k_t = k_2 + k_1k_c/(k_{-1} + k_c) \quad (8)$$

Equations 1, 5, and 7 give

$$\epsilon = \alpha[\text{R*-OBs}]_0 e^{-(k_1+k_2)t} + \beta k_2/(k_1 + k_2)[\text{R*-OBs}]_0[1 - e^{-(k_1+k_2)t}] \quad (9)$$

At $t = 0$, $\epsilon_0 = \alpha[\text{R*-OBs}]_0$, and at $t = \infty$, $\epsilon_\infty = \beta k_2/(k_1 + k_2)[\text{R*-OBs}]_0$. Therefore

$$\epsilon = \epsilon_0 e^{-k_\alpha t} + \epsilon_\infty(1 - e^{-k_\alpha t}) \quad (10)$$

where $k_\alpha = k_1 + k_2$. This is rewritten as

$$\ln\{(\epsilon_\infty - \epsilon)/(\epsilon_\infty - \epsilon_0)\} = -k_\alpha t \quad (11)$$

Therefore, plotting ln $(\epsilon_\infty - \epsilon)$ against t should give a straight line with a slope of $-k_\alpha$, which was proven experimentally. We obtained from experiments at 140° $k_\alpha = 1.08 \times 10^{-4}$, $k_t = 2.64 \times 10^{-5}$, and k_1/k_2 91/9. Therefore, $k_1 = 9.83 \times 10^{-5}$, $k_2 = 9.72 \times 10^{-6}$, and $k_{-1}/k_c = 5$. If we propose that the racemic *endo* acetate (R_2-OAc) totally comes from R′-OBs with the rate constant k_2, the equation becomes

$$d[\text{R}_2\text{-OAc}]/dt = k_2[\text{R}'\text{-OBs}] \quad (12)$$

Since $[\text{R}'\text{-OBs}] = [\text{R*-OBs}]_0[e^{k_t t} - e^{-k_\alpha t}]$ and $[\text{R*-OBs}]_0 = 1$,

$$[\text{R}_2\text{-OAc}] = (k_2/k_t)[1 - e^{-k_t t}] - (k_2/k_\alpha)[1 - e^{-k_\alpha t}] \quad (13)$$

At $t = \infty$, $[R_2\text{-OAc}] = (k_2/k_t) - (k_2/k_\alpha) = 0.28$. This value is in good agreement with our results, a 26% yield (the *endo* yield in Table III (35%) minus R*-OAc (9%)).

Suppose that all of the *exo* acetate and of the olefin (R_1-OAc) is formed from the intermediate I with a rate constant k_c; we then obtain

$$d[R_1\text{-OAc}]/dt = k_c[I] = k_1k_c/(k_{-1} + k_c)[R^*\text{-OBs}]_0e^{-k_tt} \quad (14)$$

Therefore

$$[R_1\text{-OAc}] = k_1k_c/k_t(k_{-1} + k_c)[1 - e^{-k_tt}] \quad (15)$$

At $t = \infty$, $[R_1\text{-OAc}] = k_1k_c/k_t(k_{-1} + k_c) = 0.63$. Our experiment showed the 62% yield (the sum of 41% and 21% in Table III). These agreements between the calculations and the experimental results strongly support the proposed reaction scheme.

In summary, the present data offer the conclusions: (a) The aryl participation effects in the solvolysis of the benzonorbornen-2(*exo*)-yl system are very important in controlling the reactivity and the stereochemistry of the products. In this case, a structure of the phenyl-bridged or ethylenephenonium cation type, as suggested by Cram,[27] Winstein,[23b,28] Bartlett and Giddings in this system,[5] and others,[29,30] best visualizes the intermediate. (b) The aromatic ring, even when deactivated by two nitro groups, is still rearranging. However, the stereospecificity in products no longer exists. (c) The cationic intermediate(s) formed from **5e-OBs** collapse(s) with elimination of the *exo* proton or with solvent attack from the *exo* side. (d) Decreasing participation by the benzene ring is accompanied by an S_N2 solvolytic displacement from the *endo* side.

Experimental Section

General. 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, ultraviolet spectra with a Beckman DK-2A spectrometer, and nmr spectra with a Varian A-60A and/or HA-100. Optical rotations were determined with a Perkin-Elmer polarimeter Type 141 in a 1-dm tube. The deuterium content and position were determined by a Varian A-60A and a Hitachi RMU-6 mass spectrometer.

Kinetic Measurements. The acetolysis conditions and procedure were the same as previously reported.[6b]

6-Methoxybenzonorbornen-2(*exo*)-ol (2e-OH) and 7-Methoxybenzonorbornen-2(*exo*)-yl Chloride (3e-Cl). 6-Methoxybenzonorbornadiene[31] (56 g) was treated with concentrated hydrochloric acid (300 ml) to yield an 8:2 mixture of 6- and 7-methoxybenzonorbornen-2(*exo*)-yl chlorides (65 g) in the same way as reported for benzonorbornen-2(*exo*)-yl chloride.[8] The mixture (46.0 g) was hydrolyzed at 75° for 3 hr in 1.2 l. of 70% aqueous acetone containing 18.6 g of sodium bicarbonate. After a large portion of the acetone was removed under vacuum, the concentrated mixture was extracted with ether. The ether extract was washed with water, dried, and evaporated. Separation by elution chromatography on Merck neutral alumina yielded 22.5 g of **3e-Cl** and 20.2 g of **2e-OH**. Recrystallization from a mixture of petroleum ether (bp 30–60°) and ether gave a pure sample of **2e-OH**, mp 51–52°. When the hydrolysis reaction was repeated with the separated **3e-Cl** for 6 hr, **2e-Cl** was obtained in a pure state: bp 115° (1 mm); $n^{22}D$ 1.5670.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.79; H, 7.40.

Anal. Calcd for $C_{12}H_{13}OCl$: C, 69.06; H, 6.28. Found: C, 69.39; H, 6.28.

6-Methoxybenzonorbornen-2(*exo*)-yl Chloride (2e-Cl). To a solution of 2.65 g of **2e-OH** in 50 ml of dry ether containing one drop of pyridine was added 2.0 g of thionyl chloride. After refluxing for 2 hr, the mixture was poured into ice–water. The organic layer was extracted with ether, dried, and distilled. The chloride had bp 115° (1 mm) and $n^{25}D$ 1.5672.

Anal. Calcd for $C_{12}H_{13}OCl$: C, 69.06; H, 6.28. Found: C, 69.04; H, 6.30.

7-Methoxybenzonorbornen-2(*exo*)-ol (3e-OH). 7-Methoxybenzonorbornen-2(*exo*)-yl chloride (2.1 g) was hydrolyzed for 1.5 hr at 190° in 400 ml of 50% aqueous dimethylformamide containing 0.84 g of sodium bicarbonate. The usual work-up gave **3e-OH** as a colorless oil: bp 120° (1 mm); $n^{23}D$ 1.5684.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.62; H, 7.46.

The brosylate had mp 105–106°.

Anal. Calcd for $C_{18}H_{17}O_4BrS$: C, 52.82; H, 4.19. Found: C, 53.12; H, 4.17.

6-Methoxy- and 7-methoxybenzonorbornen-2-ones (2-O and 3-O) were prepared by substantially the same procedure as reported.[5a,20] Properties are as follows: for **2-O**, bp 110° (bath temperature, 1 mm); $n^{24}D$ 1.5668; ir (CCl_4) 1753 cm^{-1} (C=O); uv max (isooctane) 238 mμ (ε 8660), 283 (2700), 298 (1780), 310 (1680), and 322 (1010) (*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.54; H, 6.43. Found: C, 76.48; H, 6.49); for **3-O**, bp 110° (bath temperature, 1 mm); $n^{24}D$ 1.5664; ir (CCl_4) 1756 cm^{-1} (C=O); uv max (isooctane) 286 mμ (ε 2320), 300 (1720), 311 (1670), and 323 (990), with shoulder at 228 mμ (ε ~5620) (*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.54; H, 6.43. Found: C, 76.41; H, 6.49). Nmr spectra of the aromatic protons in acetone-d_6 at 100 Mc: for **2-O**, τ 2.86 (doublet, J = 8.0 Hz (*ortho* coupling), C_8H), 3.09 (doublet, J = 2.5 Hz (*meta* coupling), C_5H), and 3.37 (quartet, J = 8.0 and 2.5 Hz (*ortho* and *meta* couplings), C_7H); for **3-O**, τ 2.84 (doublet, J = 8.0 Hz (*ortho* coupling), C_5H), 3.12 (doublet, J = 2.5 Hz (*meta* coupling), C_8H), and 3.34 (quartet, J = 8.0 and 2.5 Hz (*ortho* and *meta* coupli gs), C_6H).

6-Methoxy- and 7-methoxybenzonorbornen-2(*endo*)-ols (2n-OH and 3n-OH) were prepared by reductions of **2-O** and **3-O** with lithium aluminum hydride, respectively. The crude product mixture from **2-O** consisted of 95% **2n-OH** and 5% **2e-OH**. The predominant **2n-OH** was separated by elution chromatography on alumina. Melting points were recorded as 54.5–55° for **2n-OH** and 63–63.5° for **3n-OH**.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found for **2n-OH**: C, 75.69; H, 7.38. Found for **3n-OH**: C, 75.65; H, 7.34.

7-Methoxy-6-nitrobenzonorbornen-2(*exo*)-ol (4e-OH). The alcohol **3e-OH** was acetylated. Nitration of 236 mg of **3e-OAc** was carried out at room temperature with 73 mg of 95% HNO_3 in 1 ml of acetic anhydride. The usual work-up gave 265 mg of **4e-OAc**, which was hydrolyzed with 10% aqueous hydrochloric acid to yield **4e-OH**, mp 120.5–121°.

Anal. Calcd for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.09; H, 5.55; N, 5.95.

The brosylate 4e-OBs had mp 132.5–133°.

Anal. Calcd for $C_{18}H_{16}O_6SBrN$: C, 47.59; H, 3.55; Br, 17.59. Found: C, 48.06; H, 3.54; Br, 17.90.

7-Methoxy-6-nitrobenzonorbornen-2-one (4-O) was prepared by oxidation of **4e-OH** with chromic anhydride in pyridine: mp 153–154°; ir (CCl_4) 1760 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{11}O_4N$: C, 61.80; H, 4.75. Found: C, 61.86; H, 4.78.

7-Methoxy-6-nitrobenzonorbornen-2(*endo*)-ol (4n-OH) was prepared by reduction of **4-O** with diborane in tetrahydrofuran and melted at 92.5–93.5°.

Anal. Calcd for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.19; H, 5.56; N, 5.74.

6,7-Dinitrobenzonorbornen-2(*exo*)-ol (5e-OH). Benzonorbornen-2(*exo*)-ol acetate (**1e-OAc**) was prepared by a known method.[5a,32] To a solution of 8.0 g of **1e-OAc** in 10 ml of acetic anhydride was

(27) (a) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3863 (1949); D. J. Cram, *ibid.*, **86**, 3767 (1964); (c) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

(28) (a) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (b) S. Winstein and R. Baker, *ibid.*, **86**, 2071 (1964); (c) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3504 (1965).

(29) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968), and references cited therein.

(30) The earlier literature has been critically reviewed by A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 144–152, 159, 181–182.

(31) H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Jap.*, 37, 40 (1964).

(32) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

added 4.0 g of fuming 95% nitric acid in 10 ml of acetic anhydride at 0–5°; this was allowed to stand at this temperature for 3 hr and then at room temperature overnight. The reaction mixture was poured into ice–water and extracted with ether. The ether extract was washed with aqueous sodium carbonate, dried, and evaporated. The residue (9.7 g), which consisted almost entirely of β-nitrobenzonorbornen-2(*exo*)-yl acetate, was dissolved in 112 g of concentrated sulfuric acid (*d* 1.84) and 3.23 g of fuming nitric acid in 20.2 g of concentrated sulfuric acid was added dropwise at 0–5°. After standing for 0.5 hr, the mixture was poured into ice–water and extracted with ether. The extract was washed with aqueous sodium carbonate, dried, and evaporated leaving 9.5 g of a mixture of dinitrated compounds. Recrystallization from a mixture of ether, acetone, and petroleum ether gave 5.9 g of pure **5e**-OAc, mp 133–134°, which gave a single peak on vpc. Nmr spectrum ($CDCl_3$) showed peaks at τ 2.21 and 2.35 (two singlets, aromatic), 5.23 (split triplet, C*H*OAc), and 6.40 (multiplet, bridgeheads).

Anal. Calcd for $C_{13}H_{12}O_6N_2$: C, 53.43; H, 4.14; N, 9.59. Found: C, 53.60; H, 4.25; N, 9.24.

This acetate was dissolved in 140 ml of methanol, added to 80 ml of 5% hydrochloric acid, and refluxed for 1.5 hr. The work-up gave **5e**-OH in 95% yield, mp 142–143°.

Anal. Calcd for $C_{11}H_{10}O_5N_2$: C, 52.80; H, 4.03. Found: C, 52.76; H, 3.99.

The brosylate 5e-OBs had mp 175–176°.

Anal. Calcd for $C_{17}H_{13}O_7N_2SBr$: C, 43.51; H, 2.79. Found: C, 43.51; H, 2.87.

6,7-Dinitrobenzonorbornen-2-one (5-O) was prepared by oxidation of **5e**-OH with chromic anhydride in pyridine; mp 163–164°; ir (CCl_4) 1764 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_8O_5N_2$: C, 53.23; H, 3.25; N, 11.29. Found: C, 53.41; H, 3.27; N, 11.33.

6,7-Dinitrobenzonorbornen-2(*endo*)-ol (5n-OH) was obtained by diborane reduction of **5**-O: mp 120–121°; nmr ($CDCl_3$) τ 2.21 and 2.30 (two singlets, aromatic), 5.2 (multiplet, C*H*OH), ~6.45 (broad triplet, bridgeheads), and 7.5 (multiplet, *exo*-H at C-3).

Anal. Calcd for $C_{11}H_{10}O_5N_2$: C, 52.80; H, 4.03. Found: C, 52.87; H, 4.13.

The acetate (5n-OAc): mp 120–121°; nmr ($CDCl_3$) s 2.27 (overlapping two singlets, aromatic), 4.5 (multiplet, C*H*OAc), 6.15 and 6.48 (two multiplets, bridgeheads), and 7.5 (multiplet, *exo*-H at C-3).

Anal. Calcd for $C_{13}H_{12}O_6N_2$: C, 53.43; H, 4.14. Found: C, 53.52; H, 4.12.

(+)-Benzonorbornen-2(*exo*)-yl Acetate (8e-OAc). (+)-α-Pinene, $[\alpha]^{24}D$ +43.6° (neat) (16.32 g, 0.12 mol), was added with stirring to a solution of 1.704 g (0.045 mol) of sodium borohydride in 90 ml of diglyme in a four-necked flask, equipped with a thermometer, stirrer, pressure equalizing funnel, and a nitrogen inlet tube. (−)-Diisopinocampheylborane was generated by adding 8.508 g (0.06 mol) of boron trifluoride etherate diluted with 20 ml of diglyme to the well-stirred reaction mixture over a period of 30 min at 0° under a nitrogen atmosphere. During the boron trifluoride addition, a dialkylborane precipitates. The reagent was maintained for an additional 6 hr at 0° prior to its use. To this suspension of the dialkylborane was added 8.52 g (0.06 mol) of benzonorbornadiene at 0° and the mixture was allowed to stand overnight. The organoborane was oxidized at 30–40° by adding 35 ml of 3 *N* sodium hydroxide followed by dropwise addition of 30 ml of 30% hydrogen peroxide. After stirring for an additional hour, the alcohols formed were extracted with ether. The ether extract was washed with a solution of saturated sodium chloride and with cold water until the diglyme was completely removed, and it was then dried over sodium sulfate. The alcohol mixture obtained by removal of the ether was acetylated by standing overnight in a mixture of acetic anhydride and pyridine. This mixture was poured into cold water and extracted with ether. The ether extract was washed with cold aqueous sodium bicarbonate and water and dried. The crude acetates were subjected to rectified distillation using a spinning band. The fraction at 98–100° (2 mm), $[\alpha]^{23}D$ 40.1° (*c* 0.951, chloroform), was identified as (+)-benzonorbornen-2 (*exo*)-yl acetate by nmr and ir spectra. Vpc analysis on a 1-m column packed with 10% diethylene glycol succinate polyester on Chromosorb W at 155°, helium flow pressure 1.0 atm, indicated contamination by *ca.* 1% of benzonorbornen-*endo*-2-yl acetate. The fraction was used for preparation of the dinitro derivatives.

(+)-Benzonorbornen-2(*exo*)-ol (8e-OH) was obtained by hydrolysis of the above acetate in a solution of potassium hydroxide in methanol. When purified by recrystallization from *n*-hexane (the 1% *endo* impurity was removed), it showed $[\alpha]^{23}D$ 19.2° (*c* 1.007, chloroform). This material was esterified by *p*-bromobenzenesulfonyl chloride in pyridine to obtain **8e**-OBs, $[\alpha]^{23}D$ 30.0° (*c* 1.013, chloroform), $[\alpha]^{23}D$ 35.5° (*c* 1.015, the acetolysis solvent), which was used for the measurements of k_α.

(+)-6,7-Dinitrobenzonorbornen-2(*exo*)-ol (6e-OH). The acetate of **6e**-OH (565 mg), prepared in the same manner as was **5e**-OAc, was treated with 106 mg of lithium borohydride in 20 ml of ether. The excess of hydride was decomposed by water (avoiding the use of acid). The ether extract was washed with water, dried, and evaporated to obtain crude **6e**-OH. Recrystallization from ether–*n*-hexane gave 425 mg of crystals, mp 128–129°, $[\alpha]^{23}D$ +31.3° (*c* 1.014, chloroform).

Anal. Calcd for $C_{11}H_{10}N_2O_5$: C, 52.80; H, 4.03; N, 11.20. Found: C, 52.97; H, 4.04; N, 11.02.

The Acetate (6e-OAc). The sample, which was prepared in a quantitative yield from the **6e**-OH crystals by treatment with acetic anhydride in pyridine, showed mp 143–144° and $[\alpha]^{23}D$ +36.6° (*c* 1.018, chloroform). The brosylate, mp 140.5–142°, $[\alpha]^{23}D$ +8.6° (*c* 0.95, acetic acid), was obtained in 93% yield by treatment of the crystals with *p*-bromobenzenesulfonyl chloride in pyridine.

Anal. Calcd for $C_{11}H_{10}N_2O_5$: C, 43.51; H, 2.79; N, 5.97. Found: C, 43.59; H, 2.94; N, 6.10.

(+)-6,7-Dinitrobenzonorbornen-2(*endo*)-ol (6n-OH). The complex was prepared by the slow addition of 200 mg of chromic anhydride into 2 ml of anhydrous pyridine at 10° under stirring. To this was added a solution of 90 mg of **6e**-OH under ice cooling; reaction took place overnight at room temperature. The mixture was poured into chilled water and extracted with ether. The ether extract was washed with water, dried, and evaporated to obtain 70 mg of the crude (+)-6,7-dinitrobenzonorbornen-2-one (**6**-O), mp 143–144.5°, $[\alpha]^{23}D$ +457° (*c* 1.135, chloroform). Without recrystallization, the ketone was reduced to **6n**-OH, $[\alpha]^{23}D$ 24.1° (*c* 1.11, chloroform), by treatment with diborane in tetrahydrofuran (generated from sodium borohydride and boron trifluoride) and acetylated with acetic anhydride in pyridine.

The acetate 6n-OAc thus obtained contained 1.7% of the *exo* acetate (by vpc), but not the ketone (by the absence of a carbonyl band in the infrared spectrum), and showed $[\alpha]^{23}D$ +100° (*c* 0.825, chloroform). After correction for the *exo* contamination, the optical activity of **6n**-OAc is determined as $[\alpha]^{23}D$ +102° (*c* 0.825, chloroform).

3(*exo*)-Deuteriobenzonorbornen-2(*exo*)-ol (9e-OH). To a solution of 2.64 g of sodium borodeuteride (purchased from Metal Hydrides Incorporated, Beverly, Mass.) in 600 ml of tetrahydrofuran was added at 0° benzonorbornadiene (20 g) in 200 ml of tetrahydrofuran and then boron trifluoride etherate (13.4 g) in 70 ml of tetrahydrofuran. After standing overnight at room temperature, the excess of deuteride was decomposed, and the organoborane was oxidized with 30 ml of 3 *N* sodium hydroxide and 20 ml of 30% hydrogen peroxide. After 2 hr at room temperature, the reaction mixture was extracted with ether. The ether extract was washed with saturated sodium chloride, dried, and evaporated. Recrystallization of the residue (22.5 g) gave 15.0 g of **9e**-OH.

6,7-Dinitro-3(*exo*)-deuteriobenzonorbornen-2(*exo*)-ol (7e-OH). The alcohol **9e**-OH was acetylated and then transformed into **7e**-OAc, mp 132–133°. The mass spectrum indicated deuteration of 0.90 ± 0.02 atom per molecule. Hydrolysis in 10% hydrochloric acid–ethanol gave **7e**-OH, mp 142–143°. The brosylate **7e**-OBs showed mp 175–175.5°.

Acetolysis Products from 5e-OBs. A solution of 329 mg of **5e**-OBs in 35 ml of 0.02 *N* sodium acetate–acetic acid (the kinetics solution) was heated in a sealed tube to 180° for 2 hr. The reaction mixture was concentrated under a reduced pressure and passed into ether. The ether solution was washed with aqueous sodium bicarbonate, dried, and evaporated. The product composition was investigated by nmr spectroscopy. The peaks due to the protons at carbons bearing the acetoxyl groups in **5e**-OAc and **5n**-OAc and the vinyl protons in 6,7-dinitrobenzonorbornadiene were integrated to determine the yields. Separation of the products was done by thin layer chromatography on Kieselgel GF_{254} nach Stahl (Merck) using a 35:5 mixture solvent of ether and *n*-hexane.

Acetolysis products from 7e-OBs were similarly isolated and purified by recrystallization. Mass spectral analyses showed the following amounts of remaining deuterium: 0.86 atom for the *exo* acetate, 0.83 for the *endo* acetate, and 0.54 for the olefin. Therefore, the amount in the olefin is 61% of the original contents.

6,7-Dinitrobenzonorbornadiene showed mp 157–158°.

Anal. Calcd for $C_{11}H_8O_4N_2$: C, 56.90; H, 3.47; N, 12.07. Found: C, 56.89; H, 3.52; N, 11.96.

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Kinetic Appendix to the Acetolysis Scheme of 5e-OBs

With the steady-state approximation

$$[\mathrm{I}] = k_1/(k_{-1} + k_c)[\text{R-OBs}] \tag{16}$$

Combine eq 1 with 2, then substitute eq 16

$$d[\text{R-OBs}]/dt = -[k_2 + k_1k_c/(k_{-1} + k_c)][\text{R-OBs}] \tag{17}$$

Integration gives

$$\ln [\text{R-OBs}] = -k_t t + C$$

where $k_t = k_2 + k_1k_c/(k_{-1} + k_c)$ and C is an integration constant. At $t = 0$

$$C = \ln [\text{R*-OBs}]_0$$

Therefore

$$[\text{R-OBs}] = [\text{R*-OBs}]_0 e^{-k_t t} \tag{18}$$

Equations 4 and 16 give

$$d[\text{OBs}]/dt = k_1k_c/(k_{-1} + k_c)[\text{R-OBs}] + k_2[\text{R-OBs}] = k_t[\text{R-OBs}] \tag{19}$$

From eq 18 and 19

$$d[\text{OBs}] = k_t[\text{R*-OBs}]_0 e^{-k_t t} dt$$

Integration gives

$$[\text{OBs}] = -[\text{R*-OBs}]_0 e^{-k_t t} + C$$

At $t = 0$, $C = [\text{R*-OBs}]_0$. Therefore

$$[\text{OBs}] = [\text{R*-OBs}]_0[1 - e^{-k_t t}]$$

The logarithmic form of this equation is eq 8. From eq 1

$$[\text{R*-OBs}] = [\text{R*-OBs}]_0 e^{-(k_1 + k_2)t} \tag{20}$$

Insert (20) into (5)

$$d[\text{R*-OAc}]/dt = k_2[\text{R*-OBs}]_0 e^{-(k_1 + k_2)t}$$

Therefore

$$[\text{R*-OAc}] = k_2/(k_1 + k_2)[\text{R*-OBs}]_0[1 - e^{-(k_1 + k_2)t}] \tag{21}$$

Combination of eq 7, 20, and 21 gives eq 9.

Formation of R_2-OAc from R′-OBs

$$d[\text{R}_2\text{-OAc}]/dt = k_2[\text{R}'\text{-OBs}] = k_2[\text{R-OBs}] - k_2[\text{R*-OBs}]$$

After introduction of eq 18 and 20

$$d[\text{R}_2\text{-OAc}]/dt = k_2[\text{R*-OBs}]_0[e^{-k_t t} - e^{-(k_1 + k_2)t}]$$

Since $[\text{R*-OBs}]_0 = 1$, integration gives

$$[\text{R}_2\text{-OAc}] = -k_2/k_t e^{-k_t t} + k_2/(k_1 + k_2)e^{-(k_1 + k_2)t} + C$$

Since $[\text{R}_2\text{-OAc}] = 0$ at $t = 0$, $C = (k_2/k_t) - k_2/(k_1 + k_2)$. Equation 13 is obtained by introduction of this constant.

Products from I

$$d[\text{R}_1\text{-OAc}]dt = k_c[\mathrm{I}] = k_1k_c/(k_{-1} + k_c)[\text{R-OBs}] = k_1k_c/(k_{-1} + k_c)[\text{R*-OBs}]e^{-k}$$

Integration gives

$$[\text{R}_1\text{-OAc}] = -k_1k_c/k_t(k_{-1} + k_c)e^{-k_t t} + C$$

Since $[\text{R}_1\text{-OAc}] = 0$ at $t = 0$, $C = k_1k_c/k_t(k_{-1} + k_c)$. From this, eq 15 is derived.