Substituent Effects on *exo*-2-Benzonorbornenyl Brosylate Acetolyses. Evidence for the Existence of Little Participation

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The existence of π participation in the acetolysis of 7-norbornenyl derivatives has been most clearly demonstrated by our previous studies with substituted 9-benzonorbornenyl brosylates.[1] The basic principle employed in these studies is that introduction of substituents into the benzene moiety can cause a variation of participation effect, while maintaining the steric requirements constant. As a part of the studies of carbonium ion reactions in the bridged benzocyclene systems, this report deals with the effect of 5,8-dimethoxy substituents in acetolysis of 2-benzonorbornenyl brosylates.[2]

5,8-Dimethoxybenzonorbornen-2(*exo*)-ol (II) was obtained by hydroboration of the suitable diene I.[3] Purification of II was successful *via* the *p*-nitrobenzoate ester. The Oppenauer oxidation followed by lithium aluminum hydride reduction yielded predominantly the *endo* alcohol IV (Scheme I). The orientations of hydroxyl groups in II and IV are established by comparison of the infrared spectra; IV showed an association with π-hydrogen bonding, whereas II did not (see Experimental Section). The corresponding brosylates, II-OBs and IV-OBs, were prepared by treatment with *p*-bromobenzenesulfonyl chloride in pyridine. The rates of acetolysis were determined by standard procedures and in each case the theoretical infinity titer was obtained. The rates are summarized in Table I with those of the relevant compounds. The acetolyses of both the brosylates (0.1 *M* solution containing equivalent sodium acetate) afforded the *exo* acetate II-OAc (roughly, in 95% yield). No other products were observed by vpc analysis.

SCHEME I

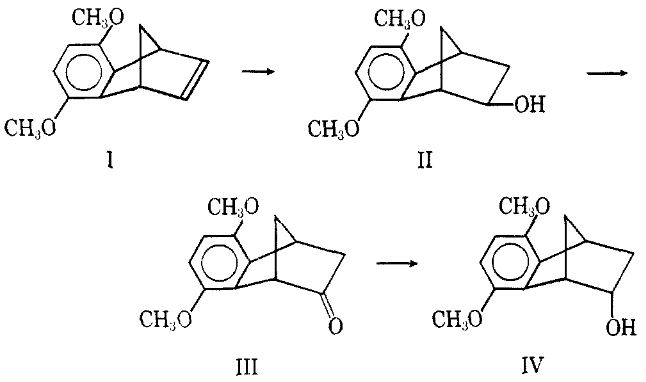
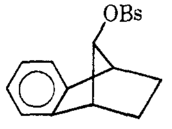


TABLE I
ACETOLYSIS RATES OF 2-BENZONORBORNENYL BROSYLATES[a]

Compounds	Temp,[b] °C	k_1, sec^{-1}	Rate ratio at 25°, *exo/endo*
5,8-$(CH_3O)_2$-*exo*-2	25.1	1.21×10^{-4}	152,000
5,8-$(CH_3O)_2$-*endo*-2	85.0	2.66×10^{-6}	
	120.0	9.54×10^{-5}	
	25.0[c]	7.97×10^{-10}	
exo-2[d]	·25.0	7.47×10^{-6}	15,000
endo-2[d,e]	25.0	5.1×10^{-10}	

[a] Carried out in glacial acetic acid containing equivalent amounts of sodium acetate and 1% of acetic anhydride. [b] Controlled to ±0.03° in the present work. [c] Calculated from the data for other temperatures. [d] See ref 4. [e] The originally obtained value of Bartlett and Gidding,[4] 1×10^{-9} sec^{-1}, was corrected to this value by H. C. Brown and G. L. Tritle and, independently, by us.

Compared to the rates of unsubstituted *exo*- and *endo*-2-benzonorbornenyl brosylates,[4] the rate enhancement of the 5,8-dimethoxy substituents in the *exo* series is shown as a factor of 16.2,[5] while no enhancement is seen in the *endo* series. Furthermore, the *exo/endo* rate ratios are obtained as 152,000 for the dimethoxyl and 15,000 for the unsubstituted. These results clearly indicate the existence of π participation. However, the effect of 6,7-dimethoxy substituents in *anti*-9-benzonorbornenyl brosylate acetolyses has been reported as a factor of 3000 at 77.6°[1c] and the *anti/syn* rate ratio is estimated as 1,360,000 from available data.[1c,d] Therefore, even if the positional difference of the substituents between both the systems must be considered, there exists clearly a large difference between participation in the 2 and 9 positions. This is consistent with our recent observation that, among the bicyclo[2.2.1]heptene, -[2.2.2]octene, and -[2.2.2]octadiene systems, the efficiency of an unsaturation for participation is the least in the most rigid bicyclo[2.2.1]-heptene.[6-9]



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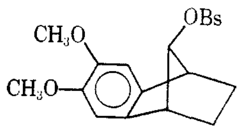

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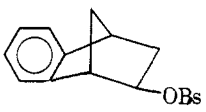

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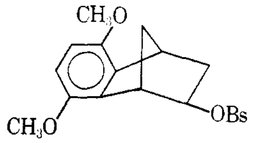

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[1] (a) H. Tanida, *J. Am. Chem. Soc.*, **85**, 1703 (1963); (b) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (c) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966); (d) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*,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

[2] It should be pointed out that this work was preliminarily carried out by G. A. Wiley, reported in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 389–391. We thank Professor Wiley for his silent permission in this publication.

[3] J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).

[4] P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

[5] The factor of 27 in Streitwieser's book should be corrected.

[6] H. Tanida, K. Tori, and K. Kitahonoki, *J. Am. Chem. Soc.*, **89**, 3212 (1967).

[7] Regarding the double-bond participation in the dehydronorbornyl system, a significant contrast has been recorded between the results of Winstein, *et al.*, on acetolysis of the brosylates (presence of participation)[8] and those of Roberts, *et al.*, on solvolysis in 80% aqueous alcohol of the halides (absence of participation).[9] Such little participation as demonstrated here could be dependent upon the leaving groups and the reaction conditions.

[8] S. Winstein, H. M. Walborsky, and K. Schreider, *ibid.*, **72**, 5795 (1950).

[9] J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

Experimental Section[10]

Kinetic Measurements.—The acetolysis conditions and procedure were the same as previously reported.[2b,6]

Materials.—5,8-Dimethoxybenzonorborandiene (I) was prepared according to the procedure of Meinwald and Wiley.[3]

5,8-Dimethoxybenzonorbornen-2(*exo*)-ol (II).—To a suspension of 9.8 g of I and 1.83 g of sodium borohydride in 150 ml of tetrahydrofuran there was added a solution of 9.15 g of boron trifluoride etherate in 20 ml of tetrahydrofuran at ~0° with stirring under nitrogen atmosphere; this was allowed to stand overnight at room temperature. Oxidation with 3 *N* sodium hydroxide and 30% hydrogen peroxide gave a crude alcohol which was, for purification, converted into the *p*-nitrobenzoate, mp 146–147° (from ethyl acetate). Hydrolysis of the ester with sodium bicarbonate in aqueous dioxane gave 4 g of the pure II: bp 128° (0.07 mm); $\nu_{\max}^{\mathrm{CCl_4}}$ 3618 (OH) cm^{-1}. Its brosylate was a viscous oil.

Anal. Calcd for $C_{13}H_{16}O_3$ (alcohol): C, 70.89; H, 7.32. Found: C, 70.82; H, 7.40.

Anal. Calcd for $C_{20}H_{19}O_6N$ (*p*-nitrobenzoate): C, 65.03; H, 5.19; N, 3.79. Found: C, 65.15; H, 5.30; N, 3.86.

5,8-Dimethoxybenzonorbornen-2-one (III).—The Oppenauer oxidation of II (4.0 g) with aluminum tri-*t*-butoxide (8.95 g) and *p*-benzoquinone (2.11 g) in benzene (230 ml) afforded a crude ketone (4.2 g). Recrystallization from ether gave the pure material, mp 93–94°. The infrared spectrum (in CCl_4) showed $\nu_{\mathrm{O=C}}$ 1760 and 1748 cm^{-1} (a little stronger).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.62; H, 6.60.

5,8-Dimethoxybenzonorbornen-2(*endo*)-ol (IV).—Treatment of III with 4 equiv of lithium aluminum hydride in ether followed by the usual work-up yielded II and IV in an approximate ratio of 9:1. Elution chromatography over standard alumina gave pure IV: mp 91.5–92.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 3612 (free OH) and 3582 (associated OH . . . π). The retention time of the *endo*-acetate on vpc (in a 1-m column of SE-30, 200°, and 2.0 kg of He) was 12 min, while that of the *exo* acetate was 14 min.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.60; H, 7.14.

The brosylate had mp 95.5–96.5° (from *n*-hexane).

Anal. Calcd for $C_{19}H_{19}O_5BrS$: C, 51.94; H, 4.36. Found: C, 52.13; H, 4.47.

Registry No.—II, 14123-80-9; *p*-nitrobenzoate of II, 14123-81-0; II-OBs, 14123-82-1; III, 14123-83-2; IV, 14123-84-3; IV-OBs, 14123-85-4.

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[10] Melting points were taken by capillary and are corrected. Infrared spectra were recorded on a Nippon Bunko DS-201-B spectrometer, except for the measurement of an internal interaction between a hydroxyl group and π electrons which was carried out by a Nippon Bunko DS-402-G (grating).

Partial Acetolysis of Neopentyl Tosylate-sulfonyl-^{18}O. An Attempt to Trap Neopentyl Cation

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Opposing views have been expressed on the timing of the ionization and rearrangement steps in reactions of neopentyl substrates which give derivatives of *t*-amyl cation. In a recent study,[1] which includes a critical review of the previous literature, the rates of several solvolyses of 1-adamantylcarbinyl arenesulfonates were found to be essentially the same as those of the corresponding neopentyl compounds, indicating the slow step in each case to be simple ionization to the primary carbonium ion. More recently, Kirmse and Horn[2] have isolated substantial to predominant yields of neopentyl products from reactions of diazoneopentane with acetic acid, trifluoroacetic acid, and thiophenol. These results strongly suggest the formation of neopentyl cations in tight ion pairs, which collapse to products at rates comparable to those of methyl migration. On the other hand, Saunders and co-workers have preferred an interpretation in terms of concerted ionization–rearrangement for the rates and migration aptitudes found in solvolysis of a series of *p*-substituted *β*-benzylisobutyl tosylates[3] and of neopentyl brosylate and its *γ*-methylated analogs.[4] In addition, Sanderson and Mosher[5] have concluded that the deoxidation of optically active neopentyl-1-*d* alcohol does not involve a free neopentyl cation, since methyl migration was found to take place with inversion of configuration at C-1 highly stereoselectively.

A sensitive method for detecting the formation of carbonium ions from ionization of appropriate carboxylic[6] or sulfonic[7] esters is the use of specifically ^{18}O-labeled substrates and analysis for rearrangement of the label in reactant recovered after partial solvolysis. In such an experiment scrambling of the label is clear evidence for an intermediate carbonium ion, although nonscrambling does not lead to a unique interpretation.

We have used this approach in an attempt to demonstrate the possible intermediacy of neopentyl cation in the acetolysis of neopentyl tosylate. The mechanistic possibilities, starting with sulfonyl-labeled neopentyl tosylate **1a**, are outlined in Scheme I. Evidence for the formation of neopentyl cation would be the conversion of **1a** to **1b**, *i.e.*, the incorporation of label into the ethereal oxygen position.

p-Toluenesulfonyl chloride enriched with ^{18}O to the extent of *ca.* 6% was prepared by the method of Oae and co-workers[8] from *p*-toluenethiol, labeled water, and chlorine. Reaction with neopentyl alcohol in pyridine gave tosylate **1a**, which was shown by mass spectrometry[9] to contain 4.1 (+0.1)% total ^{18}O *i.e.*, 3.9% above natural isotopic abundance,[10] corresponding to 5.8% excess ^{18}O in the sulfonyl oxygens. (Oxygen scrambling has been found not to occur during the preparation of an arenesulfonate more reactive than the present one.)[7c] Tosylate **1a** was solvolyzed in boiling buffered acetic acid[11] (118°) to 67% completion and the unreacted substrate was recovered and cleaved at the chain O–S linkage by reaction

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[1] J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966).

[2] W. Kirmse and K. Horn, *Tetrahedron Letters*, 1827 (1967).

[3] J. R. Owen and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **88**, 5809 (1966).

[4] R. L. Heidke and W. H. Saunders, Jr., *ibid.*, **88**, 5816 (1966).

[5] W. A. Sanderson and H. S. Mosher, *ibid.*, **88**, 4185 (1966).

[6] H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964), and references therein.

[7] (a) H. L. Goering and R. W. Thies, 152nd National Meeting of the American Chemical Society, Sept 1966, p S38; (b) D. B. Denney and E. J. Kupchik, *J. Am. Chem. Soc.*, **82**, 859 (1960); (c) D. B. Denney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

[8] S. Oae, T. Kitao, and Y. Kitaoka, *Tetrahedron*, 827 (1963).

[9] The mass spectra were measured by Morgan-Schaffer Corp., Montreal 26, Quebec, Canada.

[10] The natural abundance of ^{18}O is 0.20%. K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., p 60.

[11] Ion-pair return phenomena are particularly prominent in this medium. See S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109.