for 6 h and analyzed by GLC (SE-52). The major product was the thiophene **14**. No **16** was found.[19]

Photolysis of 11. A solution of 3.75 g of **11** dissolved in 600 mL of *n*-pentane was irradiated for 4 h. Solvent was removed with the aspirator and the reaction was analyzed by GLC (OV-225) with tetralin as internal standard. About 20% of the ester **11** had disappeared. The only product was *β-tert*-butylvinyl disulfide (**19**, 70%). Samples of **19** for analysis and spectral data were collected from gas chromatography: IR (film) 3018 (w), 2980 (s), 1706 (w), 1608 (w), 1465 (m), 1453 (m), 1383 (m), 1355 (m), 1293 (w), 1255 (m), 1230 (m), 1028 (w), 948 (m), 914 (w), 822 (w), 802 (w), 778 (w), and 620 cm^{-1} (w); UV (cyclohexane) 214 nm (ε 675); NMR (neat) δ 1.0 (s), 1.4 (9, s), and 5.9 (2, m); mass spectrum *m/e* (rel intensity) 230 (49), 215 (15), 174 (8), 116 (11), 115 (15), 113 (10), 103 (11), 101 (32), 100 (8), 99 (89), 85 (13), 83 (100), 81 (30), 79 (10), 73 (12), 67 (22), 65 (12), 61 (11), 59 (52), 57 (47), 55 (63), 53 (18), 47 (10), 45 (50), 44 (71), 43 (40), 41 (93), and 39 (37).

Anal. Calcd for $C_{12}H_{22}S$: C, 62.54; H, 9.62; S, 27.82. Found: C, 62.27; H, 9.63; S, 27.61.

Registry No.—**1a**, 15786-82-0; **1b**, 16214-69-0; **2a**, 15869-74-6; **2b**, 4427-74-1; *trans*-**3**, 61363-79-9; *cis*-**3**, 61363-80-2; *trans*-**4**, 61363-81-3; *cis*-**4**, 61363-82-4; *cis*-**10**, 27675-80-5; *trans*-**10**, 61363-83-5; **11**, 61363-84-6; **12**, 61363-85-7; **13**, 61363-86-8; **14**, 16939-13-2; **15**, 7715-02-8; **17**, 61363-87-9; **18**, 61363-88-0; *trans,trans*-**19**, 61363-89-1; *cis,trans*-**19**, 61363-90-4; thiolacetic acid, 507-09-5; phenylacetylene, 536-74-3; *tert*-butylacetylene, 917-92-0; 1-acetylcyclohexene, 932-66-1; 1-acetylcyclopentene, 16112-10-0; 3-phenyl-3-buten-2-one, 32123-84-5; sodium thiolacetate, 34832-35-4; 3-chloro-4-phenyl-2-butanone, 20849-77-8.

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Ionic Reactions in Bicyclic Systems. 10. The Effect of 6,7-Dimethoxy Substituents on Rates of Solvolysis in Secondary and Tertiary 2-Benzonorbornenyl Systems

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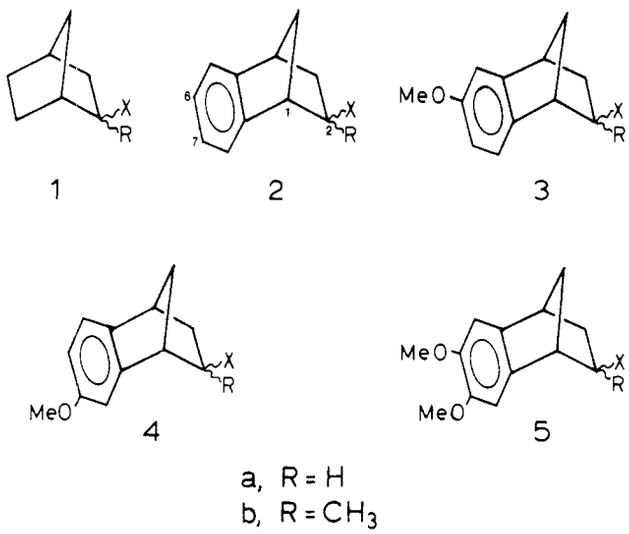
The effect of 6,7-dimethoxy substituents in *exo*- and *endo*-2-benzonorbornenyl *p*-bromobenzenesulfonate (**5a**-OBs) and 2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-**5b**-OPNB) on rates of solvolysis has been determined. The effect of the two substituents is essentially the same as that reported for a single methoxyl group at C-6 (homo-para position). At 25 °C the rate of acetolysis of *exo*-**5a**-OBs is 204 times larger than that of unsubstituted *exo*-2-benzonorbornyl *p*-bromobenzenesulfonate (*exo*-**2a**-OBs). The rate of solvolysis of *exo*-**5b**-OPNB in 90% aqueous acetone at 100 °C is 17 times larger than that for the unsubstituted tertiary system, *exo*-**2b**-OPNB. Moreover, ion-pair return (determined by the rate of carboxyl oxygen equilibration) is more important for *exo*-**5b**-OPNB than for *exo*-**2b**-OPNB, which means that ionization rates differ by a larger factor (~40) than solvolysis rates (16.6). Acetolysis rates for *endo*-2-norbornyl *p*-bromobenzenesulfonate (*endo*-**1a**-OBs), *endo*-**5a**-OBs, and *endo*-**2a**-OBs span a range of >260 at 100 °C. However, the stereochemistry for solvolysis of the optically active endo brosylates is very similar. In each case pure exo acetate is formed with from 96% (*endo*-**5a**-OBs) to 94% (*endo*-**1a**-OBs) loss of optical activity

It is clear from the effect of substituents in the aromatic ring that solvolytic reactions of *exo*-2-benzonorbornenyl derivatives (*exo*-**2a**) involve assisted ionization.[1a] A 6-methoxy substituent (homo-para) has a large rate-accelerating effect and a 7-methoxy substituent (homo-meta) a negligible effect.[1-3] In connection with other work[4] it was necessary to determine if the effect of 6,7-dimethoxy substituents in secondary (**5a**) and tertiary (**5b**) 2-benzonorbornenyl systems is comparable to that of a single 6-methoxyl substituent. That work involved optically active systems, and active 6,7-dimethoxy-2-benzonorbornenyl compounds (**5**) can be readily prepared by asymmetric hydroboration of the symmetrical 6,7-dimethoxybenzonorbornadiene.[5] On the other hand, preparation of optically active 6-methoxy derivatives (**3**) appears to be much more complicated.

This paper reports a comparison of 6,7-dimethoxy (**5**), 6-methoxy (**3**), and 7-methoxy (**4**) substituent effects on rates of solvolysis of secondary and tertiary (2-methyl) 2-benzonorbornenyl derivatives. We also have examined the effect of 6,7-dimethoxy substituents on (a) the stereochemistry of acetolysis of the optically active secondary *endo*-*p*-bromobenzenesulfonates (*endo*-**2a**-OBs and *endo*-**5a**-OBs) and (b) the magnitude of ion-pair return associated with solvolysis of the tertiary *exo*-*p*-nitrobenzoates (*exo*-**2b**-OPNB and *exo*-**5b**-OPNB).

Rates and relative rates of acetolysis of *exo*-2-norbornyl (*exo*-**1a**-OBs), *exo*-2-benzonorbornenyl (*exo*-**2a**-OBs), and methoxy substituted *exo*-2-benzonorbornenyl *p*-bromobenzenesulfonates are presented in Table I. This reaction was chosen because data were available for *exo*-**1a**-OBs,[6] *exo*-



2a-OBS, *exo*-3a-OBs, and *exo*-4a-OBs.[1a] 6,7-Dimethoxy-*exo*-2-benzonorbornenyl *p*-bromobenzenesulfonate (*exo*-5a-OBs) was prepared from the corresponding alcohol.[5] Relative rates are presented for 25 °C because most measurements were made at or near this temperature and only small extrapolations are required.

The data in Table I show that *exo*-5a-OBs is slightly more reactive than *exo*-3a-OBs. There is some scatter in reported rate constants for *exo*-3a-OBs;[1a,2a,7] however, regardless of which is used the *exo*-5a-OBs/*exo*-2a-OBs rate ratio is larger than that (150)[8] for *exo*-3a-OBs/*exo*-2a-OBs. Thus 6,7-dimethoxy substituents are at least as effective as a single 6-methoxy substituent for increasing π-assisted ionization (k_Δ).

Substituent effects on unassisted ionization (k_c) can be determined with the endo isomers because in this case assisted ionization is precluded. Table II shows the rates and relative rates of acetolysis of the endo *p*-bromobenzenesulfonates. In this series comparisons are made at 77.6 °C to take advantage of reported data[2b] and to minimize extrapolations. These data show that the substituent effect for 6,7-dimethoxy groups is small as would be expected, and similar to that for a single 6-methoxy substituent. Thus for both exo (assisted ionization, k_Δ) and endo (unassisted ionization, k_c) secondary 2-benzonorbornenyl derivatives, 6,7-dimethoxy substituents have about the same effect on ionization rates as a single 6-methoxy substituent.

Comparisons of 2-norbornyl (1) and 2-benzonorbornenyl (2) *p*-bromobenzenesulfonates in Tables I and II show that the rate-retarding effect of the benzene ring is 19 times larger in the endo isomer than in the exo isomer. This results from phenyl participation in the exo isomer which offsets part of the retarding inductive effect of the aromatic ring.[7] It should be noted that in *exo*-2a-OBs, participation increases the rate considerably more than 19-fold. This means that the electron-withdrawing effect of the aromatic ring retards unassisted ionization (k_c) more in the exo isomer than in the endo isomer. The reason for this is not clear but may have to do with through-space field effects[9] that vary with the alignment of the C–X bond and the plane of the ring.

That substantial anchimeric acceleration is involved in acetolysis of *exo*-2-OBs is clear from the magnitude of the rate retardation by nitro substituents.[2,3] 6,7-Dinitro substituents lower the rate by factors of 10^5 for the exo isomer[2a] and 10^2 for the endo isomer.[2b] This indicates that phenyl participation elevates the rate of acetolysis of *exo*-2a-OBs > 10^3-fold. This is a lower limit for k_Δ/k_c because the dinitro substituents evidently do not eliminate assisted ionization.[2a] Also, dinitro substituents probably retard unassisted ionization (k_c) more in the exo than in the endo isomer for the same reason that in 2a-OBs, the electron-withdrawing effect of the ring lowers k_c more for the exo isomer than for the endo isomer. This estimate for k_Δ/k_c is in good agreement with that ($\gtrsim$1500) determined from comparison of exo/endo rate ratios for 2a-OBs and 3-spirocyclopropylbenzonorbornen-2-yl *p*-toluenesulfonate.[10]

Table I. Rates and Relative Rates of Acetolysis of *exo*-2-Norbornyl and Benzonorbornenyl *p*-Bromobenzenesulfonate

Compd	Temp, °C	$10^5 k$, sec^{-1}	Rel rate, 25 °C
exo-1a-OBs[a]	25.0	8.84	14
exo-2a-OBs[b]	25.0	0.619[c]	1
exo-3a-OBs[b]	25.0	93.0	150
exo-4a-OBs[b]	25.0	0.403	0.65
exo-5a-OBs	25.0	126[d]	204
	19.99	69.7 ± 1.5[e]	
	30.00	225 ± 1[e]	

[a] Data taken from ref 6. [b] Data taken from ref 1a. [c] Refererence 2a reported 6.69×10^{-6} s^{-1}; ref 7 reports 7.47×10^{-6} s^{-1}. [d] Calculated from data below. [e] Average (and average deviation) of two independent determinations. Solvent contained 0.0450 M sodium acetate; [ROTs] ~ 0.008 M.

Table II. Rates and Relative Rates of Acetolysis of *endo*-2-Norbornyl and Benzonorbornenyl *p*-Bromobenzenesulfonate

Compd	Temp, °C	$10^6 k$, s^{-1}	Rel rate, 77.6 °C
endo-1a-Obs	77.6	215[a]	262
endo-2a-OBs	77.6[b]	0.814	1
	100.07	12.1 ± 0.2	
endo-3a-OBs[b]	77.6	2.8	2.7
endo-4a-OBs[b]	77.6	0.957	1.2
endo-5a-OBs	77.6	2.96[c]	3.6
	78.70	3.36 ± 0.03[d]	
	99.86	33.4 ± 0.8[d]	

[a] Extrapolated from data for 49.96 and 74.57 °C in ref 6. [b] Data taken from ref 2b. [c] Calculated from data below. [d] Solvent contained 0.1 M sodium acetate, [ROTs] = 0.095 M.

We also have compared the stereochemistry of acetolysis of optically active *endo*-2a-OBs and *endo*-5a-OBs. In earlier work[11] it was found that acetolysis of optically active *endo*-1a-OBs gives pure exo acetate with ~7% retention of the original optical activity. Similar results were reported for *endo*-2a-OBs (6% retention of optical activity).[12]

Optically active *exo*-2a-OAc, $[\alpha]^{25}_D$ 32.2° (ethanol), was prepared and converted to *endo*-2a-OH, $[\alpha]^{25}_D$ 42.6°,[13] as described earlier.[14] This sequence presumably does not alter optical purity and involves (+)-*exo*-2a-OAc → (+)-*exo*-2a-OH → (+)-2-benzonorbornenone → (+)-*endo*-2a-OH. Absolute configurations and rotations were established previously.[14a] Relative rotations were in good agreement with those reported earlier.[14a] The (+)-*endo*-2a-OH was converted to (+)-*endo*-2a-OBs, $[\alpha]^{25}_D$ 20.4°,[13] by a method designed to give complete conversion without change of optical purity.

Optically active (+)-*endo*-5a-OBs was prepared in a similar manner. In this case (+)-*exo*-5a-OAc, $[\alpha]^{25}_D$ 31.5°, gave (+)-*endo*-5a-OH, $[\alpha]^{25}_D$ 44.1°, which was converted to (+)-*endo*-5a-OBs, $[\alpha]^{25}_D$ 60.5°.[13] Absolute configurations and rotations have also been established for this system [5]

Results of the stereochemical study are summarized in Table III. In each experiment the reaction time was 8 half-lives

Table III. Acetolysis of (+)-*endo*-2a-OBs and (+)-*endo*-5a-OBs[a]

Compd	[ROBS], M	[NaOAc], M	Temp, °C	% activity[b]
endo-**2a**-OBs	0.092	0.11	100.07	4.8[c]
endo-**2a**-OBs	0.091	0.21	100.07	5.0
endo-**2a**-OBs	0.031	0.03	100.07	4.7
endo-**5a**-OBs	0.106	0.107	99.86	4.1[c]
endo-**5a**-OBs	0.102	0.213	99.86	4.0

[a] Reaction time 8 half-lives for all experiments. [b] In all cases acetate shown to be pure exo isomer by capillary GC. [c] Control experiments showed active exo acetate optically stable under these conditions.

and the acetate fraction was shown to be the pure exo isomer by capillary GC. That the exo acetates are optically stable under these conditions was shown by solvolyzing racemic *p*-bromobenzenesulfonate with active exo acetate added at the outset. In each case activity was fully preserved.

These data are in good agreement with the earlier results for *endo*-**2a**-OBs[12] and show that the stereochemistry is essentially the same for *endo*-**5a**-OBs and *endo*-**2a**-OBs. Moreover, the results are similar to those for acetolysis of optically active *endo*-**1a**-OBs (7% activity retained)[11] which, as shown in Table II, is 262 times more reactive than *endo*-**2a**-OBs. This clearly shows that the small fraction of optical activity that is retained does not result from S_N2-type solvent participation. This is also indicated by the fact that the amount of retained activity is independent of acetate ion concentration up to 0.2 M. Rather it seems that, as originally proposed for *endo*-**1a**-OBs,[11,1] in each case ionization gives the classical ion and this is partitioned between (a) isomerization to the symmetrical bridged ion which leads to racemic exo acetate and (b) solvent capture with inversion which leads to active exo product. Presumably the barrier separating the classical and nonclassical species involves relocation of solvating molecules (and the counterion in an ion-pair intermediate) and it seems reasonable that the relative barriers for isomerization and solvent capture should be similar for **1a, 2a,** and **5a.**

Data for the tertiary 2-methyl-*exo*-2-benzonorbornenyl system are presented in Table IV. Dirlam and Winstein[1b] concluded from substituent effects that solvolysis of 2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-**2b**-OPNB) involves anchimeric assistance. The present work shows that the effect of 6,7-dimethoxy substituents in *exo*-**5b**-OPNB[5] is about the same as that of the 6-methoxy substituent in *exo*-**3b**-OPNB.

The rate increase of 17 clearly results from aryl participation in the methoxy substituted compounds. It is not clear, however, if there is participation in the parent unsubstituted compound, *exo*-**2b**-OBs. From substituent effects it has been concluded[10] that phenyl participation and steric factors contribute about equally to the exo/endo rate ratio of 6500[6] for solvolysis of **2b**-OPNB in aqueous acetone. A comparison of 2-methyl-*exo*-2-norbornyl (*exo*-**1b**-OPNB)[17] and *exo*-**2b**-OPNB is included in Table IV. The rate ratio of 63 for solvolysis in 80% acetone also suggests participation in *exo*-**2b**-OPNB because the benzo ring would be expected to retard unassisted ionization (k_c) somewhat more than this amount.

Estimates of anchimeric acceleration from relative rates of solvolysis involves the assumption that relative rates of solvolysis correspond to relative rates of ionization. This is valid only if the amount of ion-pair return (if any) remains constant. In the present work we have examined ion-pair return associated with solvolysis of *exo*-**2b**-OPNB and *exo*-**5b**-OPNB

Table IV. Rates and Relative Rates of Solvolysis of Tertiary *exo*-2-Norbornyl and Benzonorbornenyl *p*-Nitrobenzoate in Aqueous Acetone

Compd	Temp, °C	$10^6 k$, s^{-1}	Rel rate, 100 °C
	A. 50% Aqueous Acetone[a]		
exo-**2b**-OPNB	100	19	1[b]
exo-**3b**-OPNB	100	320	17[b]
exo-**4b**-OPNB	100	13	0.7[b]
	B. 80% Aqueous Acetone		
exo-**1b**-OPNB	120.09	607[c]	63[d]
exo-**2b**-OPNB	120.09	9.59 ± 0.04	1[d]
	C. 90% Aqueous Acetone		
exo-**2b**-OPNB	100	0.239[e]	1[f]
	99.52	0.226	
	120.10	2.26 ± 0.3	
	120.81	2.35	
exo-**5b**-OPNB	100	3.97[e]	16.6[f]
	99.60	3.83 ± 0.06	
	79.94	0.566	

[a] Data taken from ref 1b. [b] Relative rates for 50% aqueous acetone. [c] Extrapolated from data for 75 and 100 °C in ref 17. [d] Relative rates for 80% aqueous acetone. [e] Extrapolated from data below, in all cases [ROPNB] = 0.02 M. [f] Relative rates for 90% acetone.

by the carboxyl oxygen equilibration method.[18] This involves determining the rate of randomization of the carboxyl oxygen atoms in the unsolvolyzed ester starting with discretely ^{18}O-labeled *p*-nitrobenzoate (eq 1).

$$ROC^{18}OAr \xrightarrow{k_{eq}} R\text{-}^{18}OC^{18}OAr \quad (1)$$

The carboxyl oxygen atoms in ion-pair intermediates are not always equivalent,[19] and thus k_{eq} is a lower limit for ion pair return. However, it seems that the fraction of total return detected by this method should be similar for *exo*-**2b**-OPNB and *exo*-**5b**-OPNB.

The rate constant for solvolysis (k_t) is related to that for ionization k_i as shown by eq 2, in which the last term corresponds to ion-pair return. In this equation f corrects for incomplete oxygen equilibration in the re-formed ester and is unity if equilibration is complete. In an earlier study of a similar system, 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate,[19] it was found that k_{eq} corresponds to only about 20% of total return (i.e., $f = 5$).

$$k_i = k_t + fk_{eq} \quad (2)$$

For solvolysis of *exo*-**2b**-OPNB in 90% acetone at 121 °C the k_t/k_{eq} ratio is ~4. The k_t/k_{eq} ratio for solvolysis of *exo*-**5b**-OPNB at 99.52 °C is 1.1. Thus ion pair return is more important for *exo*-**5b**-OPNB than for *exo*-**2b**-OPNB, which means that ionization rates differ by a larger factor than solvolysis rates (16.6). The difference for ionization rates determined from eq 2 and a value of 5 for f is ~40. In any case, the increase in aryl participation in going from *exo*-**2b**-OPNB to *exo*-**5b**-OPNB is partly obscured by an increase in ion-pair return.

Experimental Section

Materials. Anhydrous acetic acid containing about 0.3% acetic anhydride and aqueous acetone were prepared as described earlier.[20] Racemic *endo*-2-benzonorbornenyl *p*-bromobenzenesulfonate (*endo*-**2a**-OBs), mp 134–135 °C (lit.[7] 135–136 °C), was prepared by a published procedure.[7] 2-Methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-**2b**-OPNB), mp 111–112 °C (lit.[1b] 111–113 °C), and

6,7-dimethoxy-2-methyl-*exo*-2-benzonorbornenyl *p*-nitrobenzoate (*exo*-**5b**-OPNB), mp 146–147 °C (lit.[5] mp 146–147 °C), were prepared as described in the indicated references.

(+)-*endo*-2-Benzonorbornenyl *p*-Bromobenzenesulfonate [(+)-*endo*-2a-OBs].[21] Asymmetric hydroboration[14] of benzonorbornadiene[7] with tetraisopinocamphenyldiborane derived from (+)-α-pinene, $[\alpha]^{25}_D$ 44.6° (neat), gave a mixture of (+)-*exo*-**2a**-OAc and isopinocamphenyl acetate. Compositions could be determined by capillary GC (100-ft UCON, 150 °C) which gave baseline resolution. A homogeneous sample of (+)-*exo*-**2a**-OAc, $[\alpha]^{25}_D$ 32.2° (*c* 6.2, ethanol), was obtained by vacuum (0.25 mm) fractionation. The above acetate was converted[14a] to (+)-*exo*-**2a**-OH, $[\alpha]^{25}_D$ 15.6° (*c* 4),[13] by reduction with lithium aluminum hydride. The solid exo alcohol was purified by sublimation (60 °C, 2 mm). Oxidation (quinone and aluminum *tert*-butoxide)[7] gave (+)-2-benzonorbornenone, $[\alpha]^{25}_D$ 286° (*c* 2, isooctane), which was isolated by vacuum distillation (105 °C, 0.05 mm). Reduction of the above ketone with lithium aluminum hydride gave (+)-*endo*-**2a**-OH, $[\alpha]^{25}_D$ 43.13° (*c* 4),[13] which was contaminated with 6.5% of the exo isomer (capillary GC, 100 ft UCON, 150 °C). To avoid optical fractionation this material was converted[7] directly to (+)-*endo*-**2a**-OBs. To assure complete esterification the crude brosylate was treated with a second portion of *p*-bromobenzenesulfonyl chloride in anhydrous pyridine. Final dried ether extracts showed no evidence (GC, IR) of unreacted alcohol. The residual (+)-*endo*-**2a**-OBs had mp 122–125 °C, $[\alpha]^{25}_D$ 20.4° (*c* 6).

Anal. Calcd for $C_{17}H_{15}O_3SBr$: C, 53.83; H, 3.96; Br, 21.14; S, 8.47. Found: C, 53.97; H, 3.89; Br, 21.16; S, 8.33.

This material has the same enantiomeric composition as the (+)-*exo*-**2a**-OAc, $[\alpha]^{25}_D$ 32.2° (ethanol) (~47% optically pure),[14a] from which it was derived. The isomeric composition is the same as that of the alcohol from which it was prepared (94.5% endo, 5.5% exo).

6,7-Dimethoxy-*exo*-2-benzonorbornenyl *p*-Bromobenzenesulfonate (*exo*-5a-OBs). 6,7-Dimethoxy-*exo*-2-benzonorbornenol (*exo*-**5a**-OH) was prepared in another study[5] by hydroboration of 6,7-dimethoxybenzonorbornadiene. The sample of *exo*-**5a**-OH used in the present work was purified by recrystallization from ether–pentane followed by sublimation (1 mm) and had mp 88–89 °C; NMR ($CDCl_3$) δ 3.78 (s, 6 H), 6.78 (d, 2 H).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.84; H, 7.24.

The above *exo*-**5a**-OH was converted to the *p*-bromobenzenesulfonate derivative by a standard procedure.[7] After recrystallization from ether the *dl*-*exo*-**5a**-OBs had mp 105 °C dec with prior softening; NMR ($CDCl_3$) δ 1.60–2.04 (m, 4 H), 3.13–3.52 (m, 2 H), 3.79–3.82 (q, 6 H), 4.40–4.70 (m, 1 H), 6.75–6.82 (d, 2 H), 7.68–7.78 (q, 4 H).

Anal. Calcd for $C_{19}H_{19}O_5SBr$: C, 51.95; H, 4.33; S, 7.29; Br, 18.20. Found: C, 52.09; H, 4.49; S, 7.12; Br 18.38.

(+)-6,7-Dimethyl-*exo*-2-benzonorbornenyl Acetate [(+)-*exo*-5a-OAc].[21] Asymmetric hydroboration[14] of 6,7-dimethoxybenzonorbornadiene[5] with tetraisopinocamphenyldiborane derived from (+)-α-pinene, $[\alpha]^{25}_D$ 44.6° (neat), by a procedure reported earlier[14a] gave a mixture of (+)-*exo*-**5a**-OAc and isopinocamphenyl acetate. Fractionation under reduced pressure (0.3 mm) removed most of the isopinocamphenyl acetate. The acetate fraction was chromatographed with silica gel (100–200 mesh, 75-cm column) with dry benzene as solvent and eluent. The pure exo isomer was obtained and separated by sublimation (0.1 mm). The homogeneous (+)-*exo*-**5a**-OAc had mp 70–73 °C; $[\alpha]^{25}_D$ 31.5° (*c* 3);[13] NMR ($CDCl_3$) δ 1.60–2.37 (m, 4 H), 2.07 (s, 3 H), 3.17–3.43 (m, 2 H), 2.87 (s, 6 H), 4.59–4.83 (m, 1 H), 6.74–6.99 (d, 2 H).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.75; H, 6.87. Found: C, 68.99; H, 7.09.

Racemic and (+)-6,7-Dimethoxy-*endo*-2-benzonorbornenyl *p*-Bromobenzenesulfonate (*endo*-5a-OBs).[21] Lithium aluminum hydride reduction[14] of 6,7-dimethoxy-2-benzonorbornenone[5] gave crude *endo*-**5a**-OH, which was acylated with acetic anhydride in dry pyridine. Pure *endo*-**5a**-OAc, mp 63.5–65.5 °C, was obtained by preparative GC (10-ft UCON 550-X on firebrick, 190 °C) followed by recrystallization from ether–heptane: NMR ($CDCl_3$) δ 0.78–1.15 (m, 1 H), 1.56–1.98 (m, 2 H), 1.75 (s, 3 H), 2.16–2.52 (septet, 1 H), 3.08–3.65 (m, 2 H), 2.75–3.78 (d, 6 H), 5.12–5.46 (m, 1 H), 6.72–6.90 (d, 2 H).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.75; H, 6.89. Found: C, 68.74; H, 6.72.

Lithium aluminum hydride reduction of the above acetate gave *endo*-**5a**-OH: mp 63–70 °C; NMR ($CDCl_3$) δ 0.58–0.96 (t of d, 1 H), 1.17–2.03 (m, 2 H), 2.06–2.53 (septet, 1 H), 3.07–3.41 (m, 2 H), 3.82–3.88 (d, 6 H), 4.31–4.71 (m, 1 H), 6.87–6.92 (d, 2 H).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.85; H, 7.33.

The above *endo*-**5a**-OH was converted to the *p*-bromobenzenesulfonate derivative by a standard procedure.[7] After recrystallization from ether, *endo*-**5a**-OBs, mp 122.5–124.5 °C, was obtained: NMR ($CDCl_3$) δ 0.82–1.23 (t of d, 1 H), 1.42–1.81 (m, 2 H), 1.98–2.49 (septet, 1 H), 3.08–3.63 (m, 2 H), 3.79 (s, 6 H), 5.11–5.45 (m, 1 H), 6.65–6.84 (m, 2 H), 7.46–7.80 (m, 4 H).

Anal. Calcd for $C_{19}H_{19}O_5SBr$: C, 51.95; H, 4.33; S, 7.29; Br, 18.20. Found: C, 51.81; H, 4.42; S, 7.08; Br, 18.34.

The above (+)-*exo*-**5a**-OAc, $[\alpha]^{25}_D$ 31.5°,[13] was converted to (+)-*exo*-**5a**-OH, mp 93–98.5 °C, $[\alpha]^{25}_D$ 14.6° (*c* 5), by the procedure outlined above for racemic compounds.[21] Oxidation (aluminum *tert*-butoxide–benzoquinone in benzene)[7] gave **(+)-6,7-dimethoxy-2-benzonorbornenone,** which after purification by sublimation had mp 93.6–96 °C, $[\alpha]^{25}_D$ 394° (*c* 3.8). This corresponds to 67% optical purity.[5]

Lithium aluminum hydride reduction of the above ketone gave (+)-*endo*-**5a**-OH, $[\alpha]^{25}_D$ 44° (*c* 6), as a white, viscous liquid. Capillary GC showed that this material contained 4.4% of the exo isomer.

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.86; H, 7.41.

To avoid optical fractionation the above alcohol was converted directly to (+)-*endo*-**5a**-OBs, $[\alpha]^{25}_D$ 60.5° (*c* 4.3), mp 98–104 °C, by the method outlined above for the unsubstituted system (**2a**).

Anal. Calcd for $C_{19}H_{19}O_5SBr$: C, 51.95; H, 4.33; S, 7.29; Br, 18.20. Found: C, 51.81; H, 4.42; S, 7.08; Br, 18.34.

This material has the same enantiomeric composition as the (+)-*exo*-**2a**-OAc, $[\alpha]^{25}_D$ 31.5°, from which it was derived. Correlation with (+)-6,7-dimethoxy-2-benzonorbornenone[5] shows the acetate (and rest of the series) to be 67% optically pure. The isomeric composition of the *endo*-**5a**-OBs is the same as that of the alcohol from which it was prepared (95.6% endo, 4.4% exo).

Kinetic Experiments. A. Acetolysis of *p*-Bromobenzenesulfonates. Rates of acetolysis of *endo*-**2a**-OBs, *exo*-**5a**-OBs, and *endo*-**5a**-OBs were determined by methods described earlier.[1,20] Reactions were followed to >50% completion and in all cases good first-order behavior was observed. Pertinent data regarding concentrations are included in footnotes in Tables I and II.

B. Solvolysis of *p*-Nitrobenzoates in Aqueous Acetone. Rates of solvolysis of *exo*-**5b**-OPNB and *endo*-**5b**-OPNB were determined by a standard ampule technique.[19] Reactions were followed to >75% completion and in all cases good first-order behavior was observed. Concentrations are indicated in a footnote in Table IV.

C. Carboxyl–Oxygen Equilibration. *exo*-**2b**-OPNB-*carbonyl-*^{18}O, mp 111–112 °C, 2.071% excess ^{18}O, and *exo*-**5b**-OPNB-*carbonyl-*^{18}O, mp 146–147 °C, 2.353% excess ^{18}O, were prepared from the pure tertiary alcohols and *p*-nitrobenzoyl-*carbonyl-*^{18}O chloride in the usual manner.[22] Control experiments of the type described elsewhere[19] showed the above esters to be discretely labeled in the carbonyl position. Rate constants for equilibration of the carbonyl oxygen atoms were determined as reported previously.[19] In each case concentrations were the same (0.02 M) as for the solvolysis rate studies reported in Table IV.

For solvolysis of *exo*-**2a**-OPNB-*carbonyl-*^{18}O in 90% acetone at 120.81 °C, k_{eq}[19] = 5.7 × 10^{-7} s^{-1}. Thus, $k_t/k_{eq} \sim 4$. For *exo*-**5a**-OPNB-*carbonyl-*^{18}O in 90% acetone at 99.6 °C, k_{eq} = 3.4 × 10^{-6} s^{-1}. In this case $k_t/k_{eq} \sim 1.1$.

Product Studies. Results of product studies of acetolysis of (+)-*endo*-**2a**-OBs and (+)-*endo*-**5a**-OBs are summarized in Table III. As noted above, these samples contained some exo isomer and were not purified to avoid optical fractionation. However, the exo content is known and harmless as the exo esters solvolyze much more rapidly and give only racemic exo acetate.[12] The data in the last column of Table III have been corrected for the small amount of exo brosylate although the correction is probably less than experimental error.

Acetolysis products were isolated as described earlier for similar experiments.[20]

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Registry No.—*endo*-**1a**-OBs, 61076-43-5; *exo*-**1b**-OPNB, 61076-44-6; (+)-*exo*-**2a**-OH, 21159-75-1; (+)-*endo*-**2a**-OH, 21159-76-2; (+)-*exo*-**2a**-OAc, 21159-74-0; *endo*-**2a**-OBs, 61117-22-4; (+)-*endo*-**2a**-OBs, 25273-19-2; (+)-*exo*-**2a**-OBs, 25328-74-9; *exo*-**2b**-OPNB, 61117-23-5; *endo*-**5a**-OH, 61076-45-7; *exo*-**5a**-OH, 61117-24-6; (+)-*endo*-**5a**-OH, 61117-25-7; +-*exo*-**5a**-OH, 61117-26-8; *endo*-**5a**-OAc, 61076-46-8; (+)-*exo*-**5a**-OAc, 61117-27-9; *exo*-**5a**-OBs, 61138-75-8; (+)-*exo*-**5a**-OBs, 61138-76-9; *endo*-**5a**-OBs, 61138-77-0; (+)-*endo*-**5a**-OBS, 61138-78-1; *exo*-**5b**-OPNB, 54576-24-8; *endo*-

5b-OPNB, 61117-28-0; benzonorbornadiene, 4453-90-1; (+)-2-benzonorbornenone, 21159-73-9; p-bromobenzenesulfonyl chloride, 98-58-8; 6,7-dimethoxybenzonorbornadiene, 54576-19-1; 6,7-dimethoxy-2-benzonorbornenone, 54576-22-6; (+)-6,7-dimethoxy-2-benzonorbornenone, 54630-83-0.

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Preparation and Spectral Properties of the 3-*p*-Tolylsulfenyl- and 3-*p*-Tolylsulfonyl-2-norbornanols

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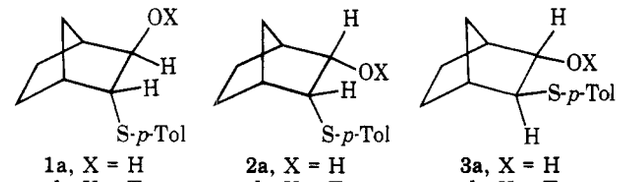
The synthetic routes to the four 3-*p*-tolylsulfenyl-2-norbornanols and the four 3-*p*-tolylsulfonyl-2-norbornanols are described. The key reaction is that between the *p*-methylthiophenoxide ion and *exo*-norbornene oxide. The NMR spectra of these alcohols and their tosylate derivatives in the region of the C-2 and C-3 protons are discussed. Infrared studies were carried out on all cis alcohols to determine the extent of intramolecular H bonding in these compounds.

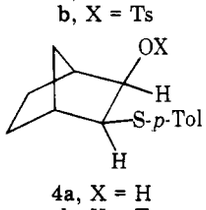
The tosylate derivatives of the four isomeric 3-*p*-tolylsulfenyl-2-norbornanols (**1a–4a**) and the four isomeric 3-*p*-tolylsulfonyl-2-norbornanols (**5a–8a**) were required for two separate mechanistic studies. The 3-*p*-tolylsulfenyl-2-norbornyl tosylates (**1b–4b**) were desired for investigation of neighboring group participation by sulfur in the norbornyl system,[1] whereas the 3-*p*-tolylsulfonyl-2-norbornyl tosylates (**5b–8b**) were desired for investigation of the E1cB mechanism.[2] Because NMR and IR data on these compounds should serve as good models for eclipsed effects of the sulfur and SO_2 groups on vicinal hydrogen, hydroxyl, and tosylate functions, we are reporting their preparations and spectral properties at this time.



1a, X = H
b, X = Ts

2a, X = H
b, X = Ts

3a, X = H
b, X = Ts



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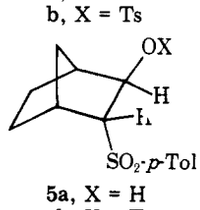
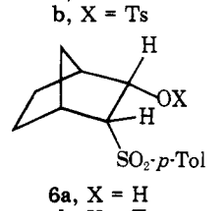
b, X = Ts



5a, X = H
b, X = Ts



6a, X = H
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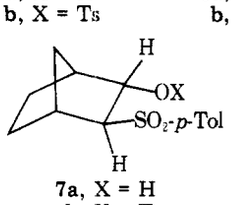
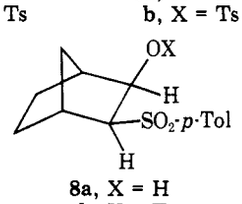


7a, X = H
b, X = Ts



8a, X = H
b, X = Ts

Scheme I illustrates the preparative routes to the 3-*p*-tolylsulfenyl-2-norbornanols. The key reaction in their preparation and the subsequent preparation of the 3-*p*-tolylsulfonyl-2-norbornanols was that of *exo*-norbornene oxide with the sodium salt of *p*-methylthiophenol to give the trans product, **1a**. Most oxirane ring openings of *exo*-norbornene oxide involving Brønsted–Lowry and Lewis acids proceed to give rearrangement products.[3] However, because the reaction with *p*-methylthiophenoxide ion is done in a basic medium, only one product, that of nucleophilic attack from the endo side of the norbornyl system, is obtained.

Attempts to secure 3-*endo*-*p*-tolylsulfenyl-2-norbornanone (**9**) from **1a** by conventional oxidation procedures, e.g., chromic acid, proved unsuccessful because the sulfide is oxidized to the sulfone more readily than the alcohol to the ketone. Consequently, the oxidation of both groups resulted.[4] The reagent mixture that selectively oxidized the alcohol group without affecting the sulfide was *N,N*-dicyclohexylcarbodiimide (DCC) and dimethyl sulfoxide (Me_2SO).[5] Although NMR analysis showed that **9** was formed uncontaminated with any exo isomer (**10**), dicyclohexylurea, formed as a by-