Acetolyses of 6-Substituted *syn*-9-Benzonorbornenyl and 9-Methylbenzonorbornen-9-(*anti*- and -*syn*)-yl Arenesulfonates. *anti–syn* Rate Ratios as a Test for Participation. Substituent Effects and Variation from Secondary to Tertiary Systems

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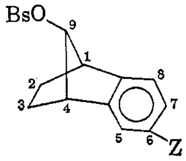
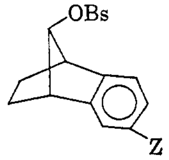
Abstract: Rates in the acetolyses of 6-substituted *syn*-9-benzonorbornenyl brosylates were determined, and their substituent effects ($k_{CH_3O}/k_{NO_2} = 43$) were compared to those of the *anti* brosylates ($k_{CH_3O}/k_{NO_2} = 386{,}000$). The factor of 43 indicates the absence of homobenzylic conjugation by the aromatic ring, as demonstrated in the *anti* series, as well as efficient transmission of polar effects by the benzene moiety. The *anti–syn* rate ratios obtained by the combination of data in both series are well correlated by the modified Hammett relationship, $\log (k/k_0) = {}^1/_2\rho(\sigma_p{}^+ + \sigma_m{}^+)$, with $\rho = -3.57$. 9-Methylbenzonorbornen-9-(*anti*- and -*syn*)-yl tosylates were prepared, and the products and rates of acetolysis were determined. Acetolysis of the tertiary *anti* tosylate led to the acetate with 98% retention and the olefin (9-methylenebenzonorbornene, 2%), while that of the *syn* led to the acetate with 67% inversion and 10% retention and the olefin (21%). The variation of *anti–syn* rate ratios from the secondary to the tertiary system is discussed in terms of participation effects.

The large effect of 6 substituents in the acetolyses of *anti*-9-benzonorbornenyl brosylates (I-OBs) (a factor of 386,000 was found between the rates of the methoxy and the nitro derivatives)[1,2] provides one of the most important evidences for the homobenzylic participation in these derivatives and also for the homoallylic participation in the norbornenyl derivatives, which were originally suggested by Bartlett[3] and Winstein,[4] respectively. Furthermore, our observation that the effects of the 6 substituent and the 7 substituent are additive indicates a symmetrical transition state (one of the most powerful supporting data for the 7-norbornenyl nonclassical ion).[2c,5] This paper deals with the rates and products in the acetolyses of 6-substituted *syn*-9-benzonorbornenyl brosylates (II-OBs) and 9-methylbenzonorbornen-9-(*anti*- and -*syn*-)-yl tosylates (III-OTs and IV-OTs). Combined treatment of these results makes the Hammett approach possible for the *anti–syn* rate ratio and provides an experimental evaluation for an important suggestion in the participation theory:[6] tertiary carbonium ions should be stable enough to require little or no participation. Both are well-defined tests for the existence of nonclassical transition states, but not direct evidence for nonclassical ions.

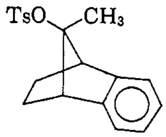
Preparations. The syntheses and properties of the various types of II-OH used in this study were already reported.[2b] Their brosylates II-OBs were prepared by standard procedures and gave satisfactory analyses. Addition of methyllithium to 9-benzonorbornenone[3,7] produced a mixture composed of 88% III-OH and 12% IV-OH. These were isolated in the pure state by a combination of recrystallization and chromatography. The structural characterization was made by comparison of the chemical shifts of the 9-methyl groups (τ 8.96 in III-OH and 8.73 in IV-OH) and also by the presence of an internal interaction between the hydroxyl group and the π electrons of the benzene ring in the infrared spectrum of IV-OH. Since the *p*-nitrobenzoates of the tertiary III-OH and IV-OH were found



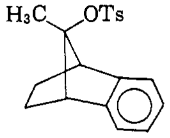
Ia-OBs, Z = H
b-OBs, Z = CH_3O
c-OBs, Z = CH_3
d-OBs, Z = Cl
e-OBs, Z = NO_2



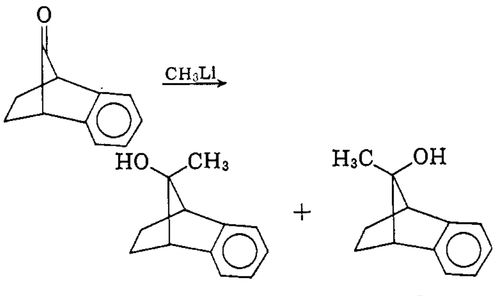
IIa-OBs, Z = H
b-OBs, Z = CH_3O
c-OBs, Z = CH_3
d-OBs, Z = Cl
e-OBs, Z = NO_2



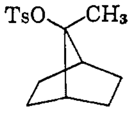
III-OTs



IV-OTs



III-OH IV-OH



V-OTs

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[1] The numbering used in the papers of this series is shown in the charts.

[2] (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).

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

[4] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955), and the subsequent papers.

[5] Footnote 12 in M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

[6] (a) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 135–136; *Chem. Rev.*, **56**, 707 (1956); (b) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 62; (c) refer to H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **86**, 1246, 5006 (1964); P. von R. Schleyer, *et al.*, *ibid.*, **86**, 2722 (1964), and references cited therein.

[7] H. Tanida, H. Miyazaki, and H. Ishitobi, *Can. J. Chem.*, **44**, 98 (1966).

Table I. Acetolyses of *syn*-9-Benzonorbornenol Brosylates[a]

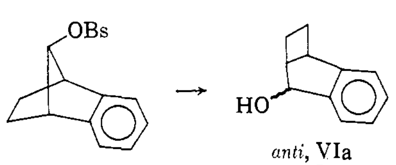
			Calcd at 77.60°				k_1, sec^{-1} (77.6°),	
6-Subst	Temp, °C[b]	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal/deg	k_1, sec^{-1}	Rel rate	of *anti* brosylates[c]	Rate ratio, *anti*:*syn*
CH_3O	170.0	3.05×10^{-4}	31.4	−4.5	2.07×10^{-8}	1.6	8.08×10^{-4}	3.9×10^{4}
	135.0	1.32×10^{-5}						
CH_3	170.1	3.03×10^{-4}	31.4	−4.6	2.04×10^{-8}	1.6	8.44×10^{-5}	4.1×10^{3}
	135.0	1.32×10^{-5}						
H	170.0	2.01×10^{-4}	31.6	−4.8	1.28×10^{-8}	1	1.49×10^{-5}	1.2×10^{3}
	161.5	9.85×10^{-5}						
	135.0	8.62×10^{-6}						
Cl	170.1	6.81×10^{-5}	31.9	−6.3	3.89×10^{-9}	0.31	6.63×10^{-7}	1.7×10^{2}
	135.0	2.82×10^{-6}						
NO_2	170.1	1.43×10^{-5}	33.8	−5.3	4.73×10^{-10}	0.037	2.07×10^{-9}	4.4
	149.9	2.23×10^{-6}						
7-Norbornyl brosylate[d]	187.3	8.10×10^{-5}	34.6	−2.9	4.49×10^{-10}	0.035		
	172.2	2.00×10^{-5}						
	150.2	2.70×10^{-6}						

[a] Carried out in glacial acetic acid containing equivalent amounts of sodium acetate. [b] Controlled to ±0.05° for runs below 150° and to ±0.08° for runs from 160 to 190°. [c] Cited from ref 2b. [d] For the tosylate, S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, 77, 4183 (1955), have reported k_1 (205°) = 8.40×10^{-5} sec^{-1}, $\Delta H^{\ddagger}$ = 35.7 kcal, $\Delta S^{\ddagger}$ = −3.5 cal/deg. With the ratio ROBs:ROTs = 2.90, k_1 of the brosylate at 77.6° is calculated as 1.86×10^{-10} sec^{-1}.

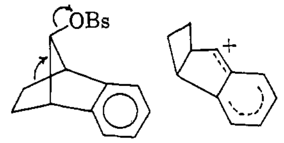
to be very inert under solvolysis conditions, the syntheses of their tosylates were undertaken. Reactions of tosyl chloride with the lithium salts of III-OH and IV-OH in tetrahydrofuran (prepared by treatment with *n*-butyllithium) were successful for this purpose. As a reference compound, 7-methylnorborn-7-yl tosylate (V-OTs) was similarly prepared from 7-methylnorbornan-7-ol.[8]

Solvolysis of *syn*-9-Benzonorbornenyl Brosylates and Substituent Effects on the *anti–syn* Rate Ratios. The rates of acetolysis were determined by standard procedures, and in each case the theoretical infinity titer was obtained. Table I summarizes the rates from the acetolyses of IIa–e-OBs and, for comparison, the rates at 77.60° calculated by Arrhenius plots, the rates of Ia–e-OBs, and the *anti–syn* rate ratios.

Solvolysis of II-OBs leads to completely rearranged, but nonstereospecific, products. The reaction in a water–acetone (40:60 vol. %) with added $NaHCO_3$ at 120° for 1 week yielded a mixture consisting of 98.6% *anti*-2-benzo[3,4]bicyclo[3.2.0]heptenol (VIa) and 1.4% of its *syn* isomer VIb. The structural determination of these products and their acid-catalyzed rearrangements were separately reported.[9] However, since a control experiment showed that VIb epimerized slowly to the sterically less hindered VIa[10] under the hydrolysis conditions, it is not clear whether the above product ratio represents complete kinetic control. It is theoretically significant that, despite the absence of rate enhancement (a factor of 1.05 relative to 7-norbornyl brosylate), the acetolysis of IIe-OBs showed predominant rearrangement; a rough vpc showed the absence of the retention product. In contrast, acetolysis of 7-norbornyl brosylate yields a mixture containing 91% unrearranged acetate, 7% *anti*-2-bicyclo[3.2.0]heptanol, and 2% bicyclo[3.2.0]hept-2-ene.[11] Therefore, it should be considered that the formation of a stabilized benzylic carbonium ion, probably with participation of the 1,2-carbon bond,[12] provides a strong driving force for the rearrangement in the reaction of IIa–e-OBs.



anti, VIa
syn, VIb



Compared to a factor of 386,000 in the I series, the rate range from the methoxy to the nitro in the II series was only 43. This substantiates the fact that significant participation (homobenzylic conjugation) such as in the acetolysis of I is absent in that of II. However, the factor of 43 is too large for a simple electrostatic interaction. An example of similar reactions involving only inductive effects is the acetolysis of 5-substituted 2-indanyl brosylates. These materials were synthesized[13] and solvolyzed. The rate constants are listed in Table II. The corresponding rate factor is only 8. This value is normal, because the inductive effect should decrease rapidly when going through saturated bonds.[14] Therefore, it may be argued by the factor of 43 (the *syn* effect) that polar effects of the benzene ring are transmitted with considerable efficiency by the π cloud to the reaction center. Consequently, the rate change in the I series involves two factors: participation by the aromatic π system and this *syn* effect. By eliminating

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[8] R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[9] H. Tanida, Y. Hata, and H. Ishitobi, *Tetrahedron Letters*, 361 (1967).

[10] The $LiAlH_4$ reduction of 2-benzo[3,4]bicyclo[3.2.0]heptenone yields a 1:9 mixture of VIa and VIb.

[11] S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958).

[12] A referee pointed out the possibility of this effect. We appreciate his comment and infer on this basis that, if the difference in steric factors between II-OBs and 7-norbornyl-OBs could be neglected in controlling the departure of the brosyl groups, the absence of the participation would result in a rate of IIe-OBs considerably slower than that of 7-norbornyl-OBs because of polar effects by the nitrobenzene moiety in IIe-OBs.

[13] Syntheses and properties will be reported in N. Inamoto, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, in press.

[14] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 1.

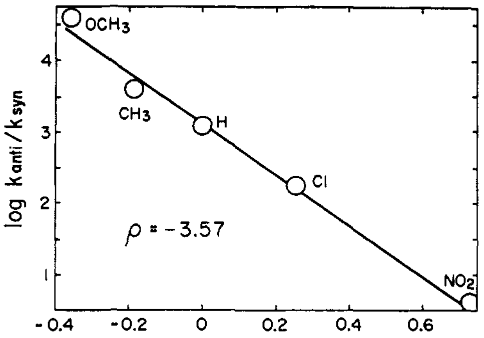
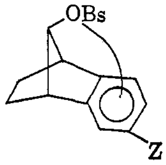


Figure 1. The ρ–σ treatment of *anti–syn* rate ratios in acetolyses of 9-benzonorbornenyl brosylates.

this effect, the *anti–syn* rate ratio should represent the rate change due only to the participation. Table I shows that the ratio changes from a factor of 3.9×10^{-4} for the methoxyl derivative to 4.4 for the nitro

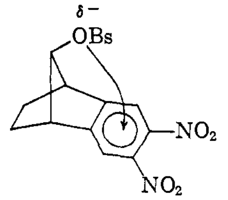


derivative. The plots of log (k_{anti}/k_{syn}) *vs.* $^1/_2(\sigma_p{}^+ + \sigma_m{}^+)$ yield a reasonably good correlation with $\rho = -3.57$ (Figure 1). This is similar to the correlation of log k_{anti} by $^1/_2(\sigma_p{}^+ + \sigma_m{}^+)$ where $\rho = -5.10$.[2b,c] By simple σ^+ plots the chloro and nitro derivatives are distinctly below the line defined by the methoxy, methyl, and hydrogen points. Other Hammett plots attempted in a previous paper[2b] provided unsatisfactory correlations. The large negative ρ value (-3.57) thus obtained indicates unequivocally that the amount of participation and the magnitude of the *anti-syn* rate ratio increase as activating substituents are introduced into the aromatic ring, whereas they reverse by introducing deactivating substituents. Figure 1 also suggests that, with a more positive σ^+ value than the nitro, the rate of a *syn* derivative would be greater than that of the corresponding *anti*. This was proven by the rates of 6,7-dinitro derivatives where $k_{anti} = 1.40 \times 10^{-5}$ and $k_{syn} = 9.21 \times 10^{-5}$ sec^{-1} at 198.5 ± 0.4° in a water–acetic acid (20:80 vol. %) mixture. It is conceivable that the highly electron-deficient group (dinitrobenzene) electrostatically attracts the leaving sulfonyloxy anion on the same side.

Table II. Acetolyses of 5-Substituted 2-Indanyl Brosylates

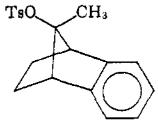
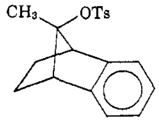
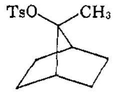
Subst	Temp, °C[a]	k_1, sec^{-1}	Rel rate at 77.60°
C_2H_5	77.60	1.51×10^{-4}	1.4
CH_3O	77.60	1.39×10^{-4}	1.3
H[b]	92.87	5.28×10^{-4}	
	77.60	1.09×10^{-4}	1
	75.81	9.35×10^{-5}	
	62.78	2.06×10^{-5}	
CH_3CO	100.02	3.68×10^{-4}	0.36
	77.60	3.89×10^{-5}	
NO_2	100.02	1.31×10^{-4}	0.15
	77.60	1.63×10^{-5}	

[a] Controlled to ±0.03°. [b] The product is quantitatively 2-indanol acetate.



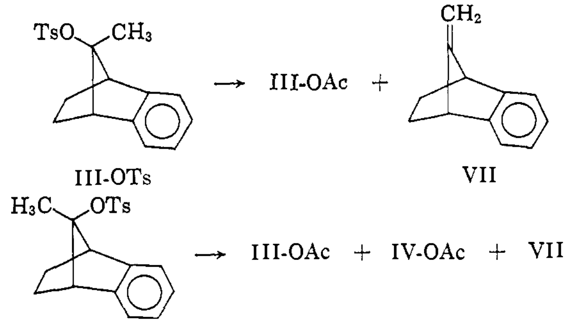
Acetolysis of 9-Methylbenzonorbornen-9-(*anti*- and -*syn*)-yl Tosylates (III-OTs and IV-OTs) and Variation of the *anti–syn* Rate Ratios from Secondary to Tertiary Systems. Table III lists the rates from acetolysis of III-OTs, IV-OTs, and V-OTs, with other pertinent data.

Table III. Rates of Acetolysis and *anti–syn* Rate Ratios for Secondary and Tertiary 9-Benzonorbornenyl Arenesulfonates

Compd	Temp, °C[a]	k_1, sec^{-1}	Rate ratio at 50° *anti*:*syn*	Rate ratio at 50° Me:H[b]
	18.7 37.3 50.0	4.97×10^{-5} 6.39×10^{-4} 3.12×10^{-3}[c]	493	18,000
	50.0	6.33×10^{-6}		86,700
	37.3 50.0	2.05×10^{-5} 1.15×10^{-4}		5.1×10^7
7-Norbornyl-OBs	50.0	6.48×10^{-12}[d]		
anti-9-Benzonorbornenyl-OBs	50.0	5.01×10^{-7}[e]	2400	
syn-9-Benzonorbornenyl-OBs	50.0	2.12×10^{-10}[d]		

[a] Controlled to ±0.03°. [b] Calculated with the rate ratio ROBs: ROTs = 2.90. [c] Calculated by Arrhenius plots. [d] Calculated from the observed rates in Table I. [e] Calculated from the observed rates in ref 2b.

The acetolysis of III-OTs resulted in a mixture consisting of 98% III-OAc and 2% 9-methylenebenzonorbornene (VII). In contrast, the reaction with IV-OTs



III-OTs

VII

IV-OTs

yielded a mixture consisting of 67% III-OAc, 10% IV-OAc, and 21% VII. These products were recovered unchanged under the reaction conditions and were verified to be the products of kinetically controlled solvolyses. Absence of the IV-OAc (inversion product) from III-OTs was demonstrated by vpc in amounts greater than 0.3% yield. It should be noted that this absence and the formation of VII less than that from IV-OTs, with the *anti–syn* rate ratio by a factor of 493, indicate some amounts of participation in the acetolysis of III-OTs.

Without firm experimental supporting evidence, it has been widely suggested that,[6,15–18] as a cationic center is made more and more stable by changing a secondary system into a tertiary system, both the amount of participation and the magnitude of the *anti–syn* (or *exo–endo*) rate ratio in the norbornyl derivatives, which has been attributed to carbon participation,[19] should be expected to drop. Following this suggestion, Brown and his associates extensively studied the solvolysis rates of the secondary and tertiary esters or halides in the 2-norbornyl[15a–c] and 2-benzonorbornenyl[17] systems and observed no significant changes in the *exo–endo* rate ratios between the secondary and tertiary derivatives. These results have been interpreted in an alternative way as the absence of significant carbon participation (Brown[15,17,20]), or a fortuitous cancellation ofin creasing steric assistance in the tertiary systems with decreasing carbon participation Schleyer[21]). Since participation of the π electrons in *anti*-7-norbornenyl and *anti*-9-benzonorbornenyl systems is the greatest on record and its existence is accepted by even nonclassical nonsupporters,[20b] the present rate results should help to clarify this problem.

As shown in Table III, the *anti–syn* rate ratios changed from a factor of 2400 to 493 with the transformation from the secondary to the tertiary system. This change in the rate ratio would be predicted for a major decrease in carbon participation accompanied by increasing stability of the cationic center. However, the change between both systems is only a factor of 4.9. Accordingly, it should be concluded that, even though theoretically sound, the above suggestion is too insensitive as a test of participation when compared with the study of substituent effects as mentioned above.

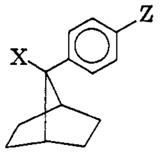
A methyl group at a carbonium center stabilizes the electron-deficient species because of its ability to supply electrons to the electron-deficient center. The greater the electron deficiency, the greater the contribution of the substituent. Brown has observed a relatively constant factor of 55,000 for the effect of CH$_3$:H (the contribution of methyl) in many representative isopropyl and *t*-butyl systems

$$(CH_3)_3CX:(CH_3)_2CHX = 55{,}000 \text{ at } 25^\circ$$

$$C_6H_5(CH_3)_2CX:C_6H_5(CH_3)CHX = 1800$$

and a factor of 1800 in *t*-cumyl chloride and α-phenylethyl chloride. This indicates that the methyl substituent is making a much smaller contribution to the resonance-stabilized α-phenylethyl transition state than to the less stable isopropyl transition state.[15d,22] Therefore, the small CH$_3$:H factor of 18,000 relative to 86,700 (Table III) is in line with the presence of participation of the *anti* series (I and III), but the difference is, here again, too small to demonstrate this procedure as a competent test for participation.

The CH$_3$:H factor of 5.1 × 10^7 for the 7-norbornyl cation is very large. This reveals that the cation makes an enormous demand on substituents for further stabilization. The existence of great participation in this system is consistent with this finding. We are currently investigating the substituent effects on the solvolysis of 7-phenylnorborn-7-yl derivatives, with the expectation that an extraordinarily large ρ value will be obtained as a semiquantitative expression of the enormous electron demand.



Experimental Section[23]

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

9-Methylbenzonorbornen-9-(*anti*- and -*syn*)-ol (III-OH and IV-OH). A. Methyl iodide (8.52 g) in 20 ml of ether under a nitrogen atmosphere was added to a suspension of 830 mg of lithium metal in 30 ml of boiling ether. After stirring for 1 hr, a solution of 6.32 g of 9-benzonorbornenone in 40 ml of benzene was added and the mixture refluxed for 1 hr. The mixture was poured into a saturated NH$_4$Cl solution, extracted with ether, and dried. Evaporation of the ether gave 6.93 g of a 88:12 mixture of III-OH and IV-OH. Recrystallization from *n*-hexane yielded pure III-OH with mp 108–108.5°. Elution chromatography of the mother liquor on Florisil gave a second yield of III-OH as well as IV-OH with mp 92 2–93.2°. The yields were 4.67 g of III-OH and 0.62 g of IV-OH.

Anal. Calcd for C$_{12}$H$_{14}$O: C, 82.72; H, 8.10. Found for III-OH: C, 82.62; H, 8.05. For IV-OH: C, 82.59; H, 8.08.

B. Treatment of 9-benzonorbornenone with methylmagnesium iodide in ether resulted in the exclusive formation of III-OH. The yield was 88%.

Tosylates of III-OH and IV-OH. A. III-OTs. To a solution of 1.05 g of III-OH in 30 ml of tetrahydrofuran, a solution of 4.4 ml of 15% *n*-butyllithium–*n*-hexane solution was added dropwise at 5–10° under a nitrogen atmosphere. After stirring for 30 min, a solution of 1.34 g of tosyl chloride in 10 ml of tetrahydrofuran was added at 5–7° and the mixture stirred for 3 hr. The tetrahydrofuran was evaporated; the residual syrup was dissolved in ether, washed with water, dried, and evaporated. The crystals obtained were recrystallized from *n*-hexane to yield 1.57 g (80%) of III-OTs with mp 90–91°.

Anal. Calcd for C$_{19}$H$_{20}$O$_3$S: C, 69.48; H, 6.14. Found: C, 69.27; H, 6.35.

B. IV-OTs, mp 74.8–75.8°, was similarly obtained.

Anal. Found: C, 69.56; H, 6.15.

7-Methylnorborn-7-yl tosylate, mp 48–49°, was similarly prepared from 7-methylnorbornan-7-ol, mp 98–99° (lit.[8] 97–98°).

Anal. Calcd for C$_{15}$H$_{20}$O$_3$S: C, 64.25; H, 7.19. Found: C, 64.44; H, 7.21.

9-Methylenebenzonorbornene. Methyltriphenylphosphonium bromide (7.14 g) was added to a stirred solution of 12.6 ml of 15% *n*-butyllithium–*n*-hexane in 60 ml of ether at approximately 23° over a 15-min interval. The mixture was stirred for an additional

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[15] (a) H. C. Brown, F. J. Chloupek, and M-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246, 1247, 1248 (1964); (b) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964); (c) H. C. Brown and H. M. Bell, *ibid.*, 5006 (1964); (d) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964).

[16] References cited in ref 15.

[17] H. C. Brown and G. L. Tritle, *J. Am. Chem. Soc.*, **88**, 1320 (1966).

[18] G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

[19] S. Winstein, A. H. Lewin, and K. C. Pande, *J. Am. Chem. Soc.*, **85**, 2324 (1963); S. Winstein, *et al.*, *ibid.*, **87**, 376, 378, 379, 381 (1965), and references cited therein.

[20] (a) M-H. Rei and H. C. Brown, *ibid.*, **88**, 5335 (1966); (b) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).

[21] See footnote 2 in ref 20a.

[22] A private communication from Professor H. C. Brown.

[23] Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Infrared spectra were determined with a Nippon Bunko IR-S spectrometer in carbon tetrachloride and carbon disulfide; nmr spectra were determined at 60 Mc with a Varian A-60 spectrometer using tetramethylsilane as an internal standard.

2 hr until a dark orange solution was obtained. To this a solution of 3.16 g of 9-benzonorbornenone in 50 ml of tetrahydrofuran was added and the mixture refluxed for 10 hr. The tetrahydrofuran was evaporated; the residue was extracted with ether, washed with water, dried, and evaporated, leaving an oil. Distillation of the oil followed by elution chromatography over Florisil yielded 1.1 g (35%) of 9-methylenebenzonorbornene, bp 76–78° (5 mm), $n^{25}\text{D}$ 1.5680.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.44; H, 7.88.

6,7-Dinitrobenzonorbornen-9-*anti*-ol. To a solution of 656 mg of 6-nitrobenzonorbornen-9-*anti*-ol acetate[2b] in 8 g of 98% H_2SO_4 was added a mixture containing 225 mg of fuming HNO_3 (*d* 1.5) and 450 mg of 98% H_2SO_4 at about 0°. The usual work-up gave 480 mg of the crude dinitro acetate. This compound was hydrolyzed by heating for 4 hr on a steam bath in a solvent composed of 70 ml of 20% H_2SO_4 and 30 ml of dioxane. The work-up yielded 6,7-dinitrobenzonorbornen-9-*anti*-ol, mp 130–131°.

Anal. Calcd for $C_{11}H_{10}O_5N_2$: C, 52.80; H, 4.03; N, 11.20. Found: C, 52.96; H, 4.26; N, 10.81.

The brosylate was prepared by the standard procedure and had mp 195°.

Anal. Calcd for $C_{17}H_{13}O_7SBrN_2$: C, 43.51; H, 2.79; N, 5.97. Found: C, 43.54; H, 2.85; N, 6.03.

6,7-Dinitrobenzonorbornen-9-*syn*-ol, mp 148–149°, was similarly prepared by the nitration of 6-nitrobenzonorbornen-9-*syn*-ol acetate,[2b] followed by hydrolysis.

Anal. Calcd for $C_{11}H_{10}O_5N_2$: C, 52.80; H, 4.03; N, 11.20. Found: C, 52.88; H, 4.09; N, 11.03.

The acetate had mp 216–217°.

Anal. Calcd for $C_{13}H_{12}O_6N_2$: C, 53.43; H, 4.14. Found: C, 53.42; H, 4.02.

The brosylate had mp 204–205°.

Anal. Calcd for $C_{17}H_{13}O_7SBrN_2$: C, 43.51; H, 2.79. Found: C, 43.46; H, 2.84.

Vpc analyses of solvolysis products were carried out on a Hitachi gas chromatograph Model F-6, equipped with a 1 × 3 mm stainless steel column packed with 10% SE 30 on 60–80 mesh Chromosorb W. Helium was used at a pressure of 1 kg/cm^2 as a carrier gas. Retention times of *anti*- and *syn*-2-benzo[3,4]bicyclo[3.2.0]heptenol at 150° were 20.2 and 23.1 min, respectively. Those of 9-methylenebenzonorbornene, III-OAc, and IV-OAc at 120° were 9.5, 38.4, and 35.3 min, respectively.

Proximity Effects. XLVI. Stereospecific Synthesis of *cis*- and *trans*-4-Phenylcyclooctanol[1]

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Abstract: The stereospecific synthesis of *cis*- and *trans*-4-phenylcyclooctanol *via* transannular reactions involving oxygen-bridged ring precursors is described. A number of alternative paths involving cyclizations with lead tetraacetate, mercuric acetate, and mercuric oxide and iodine have been investigated and several products have been identified. An improved synthesis of *cis*-5-phenylcyclooctanol is described.

Previous papers in this series describe the synthesis of cyclooctane derivatives as part of a general study of proximity effects and transannular reactions in medium-ring compounds.[4] Our interest in such systems includes the use of transannular reactions to develop convenient stereospecific routes to the less accessible phenylcyclooctanols. The general approach was to synthesize cyclooctyl compounds with suitably constituted oxygen bridges which could subsequently be severed by hydrogenolysis. Thus, in principle, bridge scission[5] of 1-phenyl-9-oxabicyclo[4.2.1]nonane (**1a**) and 1-phenyl-9-oxabicyclo[3.3.1]nonane (**1b**) at the benzylic carbon–oxygen bonds would give rise to 4-phenylcyclooctanol and 5-phenylcyclooctanol, respectively. The utility of this approach depends on the hydrogenolysis occurring exclusively at the benzylic position and on the ring-opening process being stereospecific. There was ample evidence that the former condition would hold; the latter condition appeared less certain. As an initial exploration of this idea this paper describes the synthesis and hydrogenolysis of the cyclic ethers **1a** and **b**.

Many examples of the formation of cyclic ethers on treatment of steroidal alcohols with lead tetraacetate have been reported.[6] The reaction has been extended to saturated acyclic,[7] unsaturated acyclic,[8] and saturated bicyclic[9] alcohol systems. The cyclic ethers formed usually have been five membered rather than six membered although in some cases mixtures of the two have been isolated. For example, treatment of cyclooctanol with lead tetraacetate in benzene gave 9-oxabicyclo[4.2.1]nonane; no detectable amount of the 1,5 isomer could be found in the product.[10] Under similar conditions, 1-methylcyclooctanol gave a mixture (1:3) of 1-methyl-9-oxabicyclo[4.2.1]nonane and 1-methyl-9-oxabicyclo[3.3.1]nonane.[10] Thus, introduction of a methyl group may alter the conformation of the cyclooctane ring so as to favor the formation of the 1,5 over

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[4] For a general discussion see A. C. Cope, M. M. Martin, and M. A. McKervey *Quart. Rev.* (London), **20**, 119 (1966).

[5] Removal of the carbonyl bridge in compounds containing the bicyclo[3.3.1]nonan-9-one system offers a promising method for the synthesis of a variety of substituted cyclooctanes and cyclooctapolyenes. See A. C. Cope, F. S. Fawcett, and G. Munn, *J. Am. Chem. Soc.*, **72**, 3399 (1950); A. C. Cope, E. S. Graham, and D. J. Marshall, *ibid.*, **76**, 6159 (1954); A. C. Cope and D. M. Gale, *ibid.*, **85**, 3743 (1963); G. L. Buchanan, M. McKillop, and R. A. Raphael, *J. Chem. Soc.*, 833 (1965).

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