

major advantages for the anti-Markovnikov opening of such trisubstituted epoxides.

The following procedure is representative. A dry 100-ml flask, fitted with a rubber syringe cap and a magnetic stirring bar, was placed in an ice bath and flushed with dry nitrogen and then maintained under a static atmosphere of the gas. There was then introduced into the flask 10 mmoles of borane (4.4 ml of a 2.28 *M* solution in THF), 10 mmoles of lithium borohydride (5.6 ml of a 1.79 *M* solution in THF), and 20 ml of THF. The reaction was initiated by the injection of 10 mmoles of 1-methylcyclopentene oxide (0.981 g) in 10 ml of THF at 0°. After 24 hr at 0°, the reaction mixture was hydrolyzed with 10 ml of a 1:1 mixture of 1.0 *M* sulfuric acid and THF; 10 mmoles of cyclohexanol (10 ml of a 1.00 *M* solution in THF) was added as an internal standard. Potassium carbonate was added to saturate the aqueous phase, and the THF phase was separated, dried over anhydrous magnesium sulfate, and analyzed by glpc. The analysis revealed an 88.3% yield of alcohols (27.6% 1-methylcyclopentanol and 72.4% *cis*-2-methylcyclopentanol). No trace of the *trans* isomer was detected.

The hydroboration-oxidation of 1-substituted cycloalkenes provides a highly satisfactory route to the pure *trans*-2-substituted cycloalkanols.¹ The present development now provides a convenient route to the isomeric *cis* derivatives.

(7) Graduate assistant on Research Grant DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office, Durham.

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Received March 1, 1968

Solvolyses of 6- and 7-Methoxybenzonorbornen-2-yl Derivatives. Directing Effects of a Methoxy Substituent for Participation

Sir:

Studies of substituent effects such as carried out by us in the solvolysis of benzonorbornenyl brosylates¹ have been evaluated as a decisive test for π -participation effects.² We now report the directing effects of a methoxy substituent in the solvolyses of 6- and 7-methoxybenzonorbornen-2-yl derivatives I and II, evidencing the presence of large participation in solvolysis of these compounds.

The hydrochlorination of benzonorbornadiene was reported to give solely *exo*-2-chlorobenzonorbornadiene.³ The reaction with 6-methoxybenzonorbornadiene⁴ gave a 7:3 mixture of *homo-para* and *homo-*

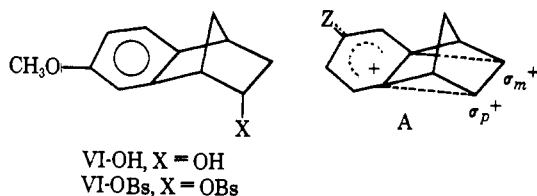
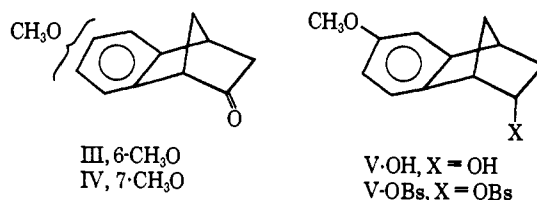
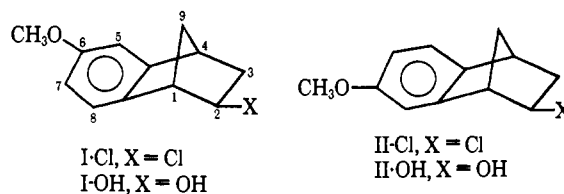
(1) (a) H. Tanida, *J. Am. Chem. Soc.*, **85**, 1703 (1963); (b) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964); (c) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966); (d) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

(2) (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) N. Brookhart, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3135 (1966), ref 12; (c) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5336 (1966).

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

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

meta chlorides I-Cl and II-Cl, respectively. On hydrolysis of the mixture in 70% aqueous acetone in the presence of 1 equiv of NaHCO₃ for 3 hr at 75°, I-Cl was converted into the *homo-para-*exo**-alcohol I-OH, mp 51–52°,⁵ whereas II-Cl remained unreacted; I-OH and II-Cl were separated by chromatography. When the reaction with the separated II-Cl was carried out once again for 6 hr, II-Cl was isolated in a pure state, *n*²⁵_D 1.5670. Treatment of I-OH with thionyl chloride led to I-Cl, bp 115° (1 mm), *n*²⁵_D



1.5672. Solvolysis of II-Cl in boiling 70% aqueous acetic acid for 1 day followed by treatment of thus-formed acetate-alcohol mixture with LiAlH₄ afforded the *homo-meta-*exo**-alcohol II-OH, bp 120° (1 mm), *n*²³_D 1.5684. Oxidation of I-OH and II-OH gave the *homo-para* ketone III, bp 110° (bath temperature, 1 mm), *n*²⁰_D 1.5689, and the *homo-meta* IV, *n*²³_D 1.5664, respectively. By comparison of the characteristic ¹L_a bands in the ultraviolet spectra of III (λ_{\max} 238 μ (ϵ 8660)) and IV (shoulder at 228 μ (ϵ ~5620)), the *homo-para* and *homo-meta* assignments were confirmed.^{6,7} Lithium aluminum hydride re-

(5) All new compounds gave spectral and microanalytical data consistent with the proposed structure.

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

(7) The Diels-Alder reaction of β -naphthol with maleic anhydride is a good method for synthesis of benzobicyclo[2.2.2]octen-2-one derivatives: K. Takeda, S. Nagakura, and K. Kitahonoki, *Pharm. Bull. Japan*, **1**, 135 (1953). According to a private communication from Dr. Takeda, the reactions with 2,6- and 2,7-dihydroxynaphthalenes lead to 6- and 7-hydroxybenzobicyclo[2.2.2]octen-2-one-9,10-dicarboxylic acid anhydrides, respectively. The ¹L_a bands in 6- and 7-methoxybenzobicyclo[2.2.2]octen-2-ones, prepared from the anhydrides, correspond to those in III and IV, respectively. We thank Dr. Takeda for his informing us of the results prior to publication.

Table I. Summary of Rates in Solvolysis

Compd ^a	Solvent ^b	Temp, °C	k_1 , sec ⁻¹	Calcd at 77.6°		<i>exo:endo</i> rate ratio
				k_1 , sec ⁻¹	Rel reactivity	
I-Cl (<i>homo-para</i>)	70% aqueous acetone	75.0	2.64×10^{-4}	3.36×10^{-4}	178	3.2×10^5
		50.0	2.16×10^{-6}			
II-Cl (<i>homo-meta</i>)	70% aqueous acetone	145.0	3.17×10^{-4}	7.63×10^{-7}	0.40	1600
		120.4	4.46×10^{-6}			
V-OBs (<i>homo-para</i>)	Acetic acid	120.5	1.93×10^{-4}	2.18×10^{-6}	5.6×10^{-4}	
		77.6	2.18×10^{-6}			
VI-OBs (<i>homo-meta</i>)	Acetic acid	120.5	8.75×10^{-6}	9.57×10^{-7}	2.5×10^{-4}	
		77.6	9.57×10^{-7}			
<i>exo</i> -2-Benzonorbornenyl chloride	70% aqueous acetone	145.0	5.36×10^{-4}	1.89×10^{-6}	1	4200
		120.0	8.27×10^{-6}			
<i>exo</i> -2-Benzonorbornenyl brosylate	Acetic acid	50.0	1.88×10^{-4} ^c	3.87×10^{-3}		
		25.0	7.47×10^{-6} ^c			
<i>endo</i> -2-Benzonorbornenyl brosylate	Acetic acid	114.8	5.49×10^{-6} ^c	9.35×10^{-7}	2.4×10^{-4}	
		95.8	7.60×10^{-6} ^c			

^a In the present runs, [RX] = 0.019 M. ^b The aqueous acetone is volume per cent and the acetic acid contained 0.02 M NaOAc and 1% acetic anhydride. ^c P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

duction of III and IV led to the respective *endo*-alcohols V-OH, mp 54.5–55°, brosylate mp 97–98°, and VI-OH, mp 63–63.5°, brosylate mp 111–112°. Rates of solvolysis of the chlorides and brosylates and their conditions are summarized in Table I.

In the *exo* series, the *homo-para*-methoxy substituent increases the rate by a factor of 178 and the *homo-meta*-methoxy depresses it slightly (0.4). The small increasing effect (2.3) is noted in the rate of the *homo-para endo*, while almost no effect on the *homo-meta endo* is noted. The results in the *exo* series are those to be expected on the basis of the methoxy substituent effects on electrophilic aromatic reactions and also, consistent with our previous suggestion, the rates at the *homo-para* position would be correlated with σ_p^+ and those at the *homo-meta* position with σ_m^+ (formula A).^{1a} The high *exo:endo* rate ratio exhibited by 2-benzonorbornenyl brosylate, with the high stereospecificity in product, was originally attributed by Bartlett and Giddings⁸ to the ability of the benzene ring to assist ionization. An alternative explanation based on the unusual steric requirements of the rigid bicyclic system has been proposed.⁹ In accord with the former proposal, the present results indicate that the amount of participation and the magnitude of the *exo:endo* rate ratio increase greatly by introducing an activating substituent, while maintaining the steric requirements constant. In acetolyses of 9-benzonorbornenyl brosylates, we have found a linear Hammett correlation for the *anti:syn* rate ratio and that introduction of a nitro group reduces the ratio near unity and two nitro groups reverse the *anti* and the *syn* rates.^{1d} Increments of the *exo:endo* rate ratio in the present system from 4200 (at 77.6°) for the unsubstituted to 3.2×10^5 for the *homo-para* methoxyl correspond to a ρ of -2.4 in a $\rho\sigma^+$ treatment. Therefore, if introduction of a deactivating substituent(s) having σ^+ of >1.5 results in equality of both the *exo* and *endo* rates (or reverses them), it be-

comes clear that the steric requirements have no effect on the *exo:endo* rate ratio.¹⁰

(10) NOTE ADDED IN PROOF. After submitting this communication, we were informed by Professors Winstein and Brown of similar independent results on the same topics. We thank them for showing us their communications: D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1901 (1968); H. C. Brown and G. Tritle, *ibid.*, **90**, 2689 (1968).

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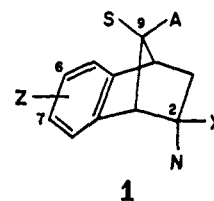
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Received March 1, 1968

π Participation and *exo:endo* Rate Ratios in the Solvolysis of Methoxy- and Nitro-Substituted Benzonorbornen-2-yl Derivatives

Sir:

The benzonorbornadiene system **1** offers many advantages for the study of the importance of π partici-



ipation in a rigid system.¹ It is possible to introduce both activating² and deactivating substituents into the aromatic ring and observe the effect on the *anti:syn* rate ratio at the 9 position³ or the *exo:endo* rate ratio

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

(2) The first application of this technique appears to have been made by G. A. Wiley for the 5,8-dimethoxy derivative, as reported in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 389–391.

(3) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964); (b) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

(8) See Table I, footnote c.

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