tallization from ethanol–water(lit.[9] 84°). Like III the n.m.r. spectrum of IV shows only the tolyl methyl resonance at 7.67 τ (intensity, 3) in the region 4–10 τ. There was a series of resonances attributed to the aromatic protons (τ, 2.4–3.0; intensity, 14) and a sharp singlet at 3.3 τ (intensity, 1). The ultraviolet spectrum in 95% ethanol had a maximum at 310 mμ (ϵ 24,000).

[CONTRIBUTION FROM THE SHIONOGI RESEARCH LABORATORY, SHIONOGI & CO., LTD., FUKUSHIMA-KU, OSAKA, JAPAN]

Substituent Effects and Homobenzylic Conjugation in *anti*-7-Benzonorbornenyl *p*-Bromobenzenesulfonate Solvolyses[1-4]

BY HIROSHI TANIDA, TERUJI TSUJI, AND HIROYUKI ISHITOBI

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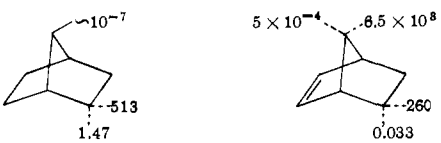
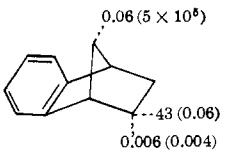
A series of 4′-substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates was prepared and the acetolysis of these sulfonates proceeds with retention of configuration. The relative rates of CH_3O, CH_3, H, Cl, Br, and NO_2 derivatives at 77.60° were 53.7, 5.7, 1, 0.045, 0.030, and 1.39×10^{-4}, respectively. The data indicate major participation by the aromatic ring, facilitating acetolysis. The rate data are not correlated by the Hammett relationship, $\log (k/k_0) = \rho\sigma$, or by the modified Hammett relationship, $\log (k/k_0) = \rho\sigma^+$. They are correlated with good precision by $(\sigma^+ + \sigma)$ or by $(\sigma_p^+ + \sigma_m^+)$, yielding straight lines with $\rho = -2.40$ or -2.55. The implications of this correlation in terms of the precise nature of the participation in the transition state for the acetolysis are discussed.

The solvolytic behavior of norbornyl systems have provided many well-known examples for the demonstration of anchimeric assistance to ionization. Acetolytic reactivities (at 25°, relative to cyclohexyl *p*-bromobenzenesulfonate) of 5- and 7-norbornenyl and of 7- and 2-norbornyl *p*-bromobenzenesulfonates are summarized as[5]



The most remarkable rate enhancement was observed on the 7-*anti*-norbornenyl system.[6] The mere introduction of a double bond into the saturated 7-norbornyl system accelerated the acetolysis rate by a factor of 10^{11}. This large rate enhancement indicates participation by the double bond, facilitating ionization of the sulfonate group.

The solvolyses of 2- and 7-benzonorbornenyl derivatives were found by Bartlett and Giddings[7] to parallel qualitatively the results in the analogous norbornenyl system. In the case of *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonate, the acetolysis rate was faster than that of 7-norbornyl *p*-bromobenzenesulfonate by a factor of 5×10^5, in contrast to the much larger factor of 10^{11} provided by the double bond of the *anti*-7-norbornenyl derivative. The acetolysis rates of benzonorbornenyl *p*-bromobenzenesulfonates relative to cyclohexyl and the corresponding norbornyl *p*-bromobenzenesulfonate (shown in parentheses) at 25° are summarized[5,7a]



In spite of the smaller factor exerted by the aromatic ring in the *anti*-7-benzonorbornenyl derivatives, it is evident that participation must be quite important in accounting for the enhanced rates observed in these derivatives.

At the present time there is considerable discussion as to the precise nature of the participation in the solvolysis of derivatives of this kind, and of the precise structure of the carbonium ions produced in the ionization stage.[6b,8] It appeared to us that some light might be thrown on this interesting question by examining the effect of substituents in *anti*-7-benzonorbornenyl derivatives on the rate of acetolysis. Accordingly, we undertook the synthesis of a number of 4′-substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates and a study of their rates of acetolysis.[9]

Results

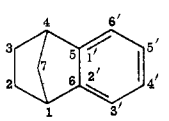
Preparations.—Most of the 4′-substituted benzonorbornadienes (I, II, III, IV, and V), which were required in the present study as the starting materials, were prepared in high yields by our modification[10] of Wittig's procedure.[11] The introduction of a benzoyloxy group into the *anti*-7-position of the above dienes was achieved

(1) Paper V of a series on Bicyclic Systems; Paper IV: H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

(2) Some of the results of this paper appeared in preliminary form: H. Tanida, *J. Am. Chem. Soc.*, **85**, 1703 (1963).

(3) Presented, in part, at the 14th Organic Reaction Mechanism Symposium of the Chemical Society of Japan in Fukuoka, Oct., 1963.

(4) The ring system of benzonorbornadiene and its numbering are shown as



(5) For a recent review, see J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(6) (a) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963), and references therein.

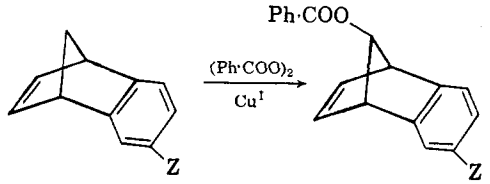
(7) (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

(8) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963), and references therein.

(9) It should be pointed out that the effect of methoxy substituents in the 3′- and 6′-positions of *anti*-7-benzonorbornenyl system was previously examined by G. A. Wiley, and that in the mid-course of this work we learned Professor Streitwieser's prediction based on molecular orbital theory for a part of our results. Refer to A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 389.

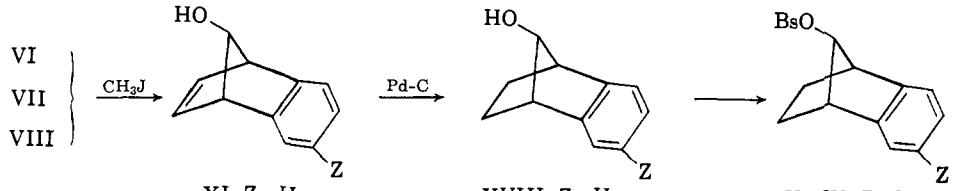
(10) H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, **37**, 40 (1964).

(11) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).



I, Z = H
II, Z = CH_3O
III, Z = CH_3
IV, Z = Cl
V, Z = Br

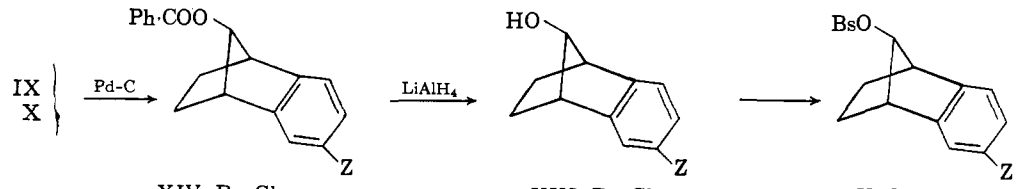
VI, Z = H
VII, Z = CH_3O
VIII, Z = CH_3
IX, Z = Cl
X, Z = Br, *p*-ClPhCOO instead of PhCOO



XI, Z = H
XII, Z = CH_3O
XIII, Z = CH_3

XVIII, Z = H
XIX, Z = CH_3O
XX, Z = CH_3

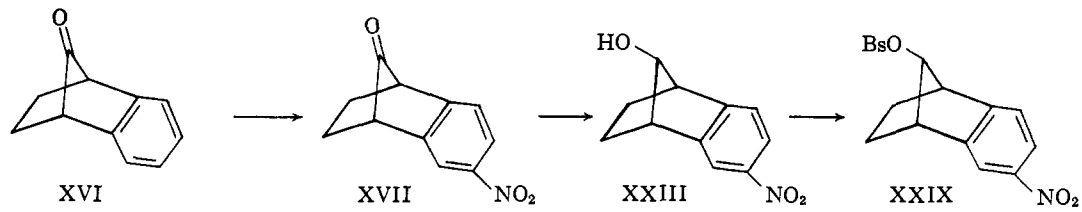
XXIV, Z = H
XXV, Z = CH_3O
XXVI, Z = CH_3

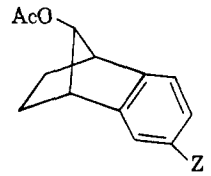


XIV, R = Cl
XV, R = Br
p-ClPhCOO instead of PhCOO

XXI, R = Cl
XXII, R = Br

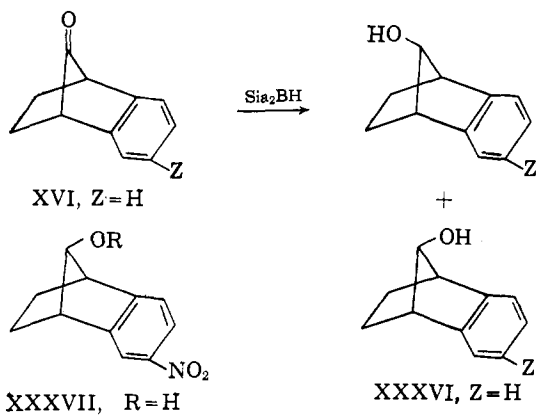
XXVII, Z = Cl
XXVIII, Z = Br





XXX, Z = H
XXXI, Z = CH_3O
XXXII, Z = CH_3

XXXIII, Z = Cl
XXXIV, Z = Br
XXXV, Z = NO_2



XXXVII, R = H
XXXVIII, R = CH_3CO

XXXVI, Z = H

by our method[12,13] yielding *anti*-7-benzoyloxybenzonorbornadiene (VI) and its 4′-methoxyl, 4′-methyl, and 4′-chloro derivatives (VII, VIII, and IX, respectively), and *anti*-7-*p*-chlorobenzoyloxy-4′-bromobenzonorbornadiene (X). Reactions of VI, VII, and VIII with methylmagnesium iodide gave *anti*-7-benzonorbornadienol (XI), *anti*-4′-methoxybenzonorbornadien-7-ol (XII), and *anti*-4′-methylbenzonorbornadien-7-ol (XIII), respectively, which on catalytic reduction over palladium–charcoal afforded the corresponding monoenols XVIII, XIX, and XX. Catalytic reduction of IX and X gave *anti*-7-benzoyloxy-4′-chlorobenzonorbornene (XIV) and *anti*-7-*p*-chlorobenzoyloxy-4′-bromobenzonorbornene (XV), respectively, which were transformed by lithium aluminum hydride into *anti*-4′-chlorobenzonorbornen-7-ol (XXI) and its 4′-bromo analog XXII. Our benzoyloxylation employed here gave only *anti* products, with no evidence of the epimers, in an agreement with the prediction based on the reaction mechanism.[13] Gas chromatographic analyses using authentic *syn* isomers confirmed these observations. Their orientations were established by comparison of the infrared spectra of

(12) H. Tanida and T. Tsuji, *Chem. Ind.* (London), 211 (1963).
(13) H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

TABLE I

ACETOLYSIS RATES OF *anti*-7 BENZONORBORNENOL BROSYLATES

4′-Substituent	Temp., °C.	$k\psi$, sec.$^{-1}$	Calculated at 77.60° ΔH^*, kcal.	ΔS^*, cal./deg.	$k\psi$,[c] sec.$^{-1}$	Rel. rate[c]
CH_3O	77.65 ± 0.03	8.27×10^{-4}	28.9	9.3	8.08×10^{-4}	53.7
	77.65 ± .03	8.00×10^{-4}				
	64.41 ± .03	1.56×10^{-4}				
	64.40 ± .02	1.52×10^{-4}				
	59.85 ± .02	8.44×10^{-5}				
CH_3	90.18 ± .03	3.38×10^{-4}	27.4	0.5	8.44×10^{-5}	5.7
	77.60 ± .03	8.60×10^{-5}				
	72.81 ± .03	4.77×10^{-5}				
H	97.75 ± .03	1.34×10^{-4}	27.7	−2.1	1.49×10^{-5}	1
	95.75 ± .05	1.058×10^{-4}[b]				
	77.65 ± .03	1.50×10^{-5}				
	74.79 ± .05	1.022×10^{-5}[b]				
Cl	120.55 ± .07	1.134×10^{-4}	32.2	4.7	6.63×10^{-7}	0.045
	103.55 ± .04	2.11×10^{-5}				
	93.85 ± .03	4.72×10^{-6}				
	77.65 ± .03	6.95×10^{-7}				
Br	104.28 ± .04	1.25×10^{-5}	. .	. . .		0.030[d]
NO_2	168.50 ± .20	4.62×10^{-5}	33.2	−3.9	2.07×10^{-9}	1.39×10^{-4}
	152.75 ± .15	1.107×10^{-5}				
7-Norbornyl brosylate[a]			35.7	−3.5	1.86×10^{-10}	1.25×10^{-5}

[a] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955), and ROBs/ROTs rate ratio assumed to be 2.90. [b] Cited from ref. 7a. [c] Calculated from the least-square slopes of the Arrhenius plots. [d] Calculated on the assumption of that the slope of the Arrhenius plots is equal to that of the Cl compound.

XVIII, XIX, XX, XXI, and XXII with XI, XII, and XIII; the latter showed clearly an internal interaction between the hydroxyl group and the π-electrons of the double bond,[14] the ν_{OH} absorptions of XVIII, XIX, XX, XXI, and XXII appearing at 2.75–2.76 μ,[15] whereas those of XI, XII, and XIII were at 2.81 μ.[16]

The preparation of *anti*-4′-nitrobenzonorbornen-7-ol (XXIII) began with the nitration of benzonorbornen-7-one (XVI), which was available from XVIII by the Oppenauer oxidation.[7a] The nitration gave exclusively 4′-nitrobenzonorbornen-7-one (XVII),[17] which was led by sodium borohydride to the predominant formation of *anti*-4′-nitrobenzonorbornen-7-ol (XXIII).[18] The n.m.r. spectrum of XVII and the formation of 2-nitronaphthalene in high yield by dehydrogenation of XVII over palladium–charcoal unequivocally established that the position of the nitro group was originally 4′. The *anti* configuration of XXIII was confirmed by comparison of the infrared band of hydroxyl and the n.m.r. signal of C-7 hydrogen with those of an authentic sample of *syn*-4′-nitrobenzonorbornen-7-ol (XXXVII) described below.

The preparation of authentic *syn*-alcohols will be needed for the investigation of stereochemistry of the solvolysis products. Disiamylborane reduction[19] of XVI yielded approximately equal amounts of *anti*- and *syn*-7-benzonorborneol (XVIII and XXXVI). The pure *syn*-alcohol was isolated by careful elution chromatography and its structure was confirmed by infrared and n.m.r. spectra (see Experimental). Gas chromatography of XXXVI recorded a distinguishable peak at shorter retention time than XVIII in line with expectation for the shielding effect of the benzo grouping on the hydroxyl group.[20] This observation was also obtained in the case of all but one of our 4′-substituted compounds which were prepared from the respective ketones.

The one exception was the 4′-nitro compound. The hard volatility of XXIII and XXXVII made it difficult for us to perform quantitative gas chromatographic analysis. Therefore, authentic samples of XXXVII and of XXXVII-acetate were prepared by nitration of XXXVI and XXXVI-acetate, and the positions of their nitro groups were determined by the n.m.r. spectra.

All of the *p*-bromobenzenesulfonates of the above-mentioned *anti*-alcohols were prepared by standard procedures. The properties of the new compounds described here are summarized in Tables II, III, and IV (Experimental).

Solvolysis Rates.—The rates of acetolyses were carried out in the usual manner.[21] The solvolysis rates are summarized in Table I, together with the derived activation parameters. For comparison, the rate constants at 77.60° were calculated, using least square slopes derived from Arrhenius plots. The plots were good straight lines (Experimental).

The methoxy substituent in the 4′-position increases the rate by a factor of 53.7. A methyl group is effec-

(14) *Cf.* P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306 (1959).

(15) The measurements were carried out using a Perkin–Elmer Model 12C, LiF prism, 20-mm. cell, in carbon tetrachloride solution.

(16) Further support was obtained by behavior of the hydrogen at the 7-position in the n.m.r. spectra, attributed to diamagnetic anisotropy effects of the double bond: K. Tori, T. Muneyuki, T. Tsuji, Y. Hata, and H. Tanida, to be published (presented at the 16th Annual Meeting of the Chemical Society of Japan in Tokyo, April, 1963). Hydrogenation of the double bond causes an upfield shift of the *anti*-7-hydrogen of about 0.15–0.25 p.p.m. Also, *cf.* R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(17) For the remarkable orientation effect of benzonorbornenes observed on aromatic substitution reactions, see H. Tanida 3nd R. Muneyuki, *Tetrahedron Letters*, **No. 38**, 2787 (1964).

(18) It was previously noted by Bartlett and Giddings (ref. 7a) that the reduction of benzonorbornen-7-one by lithium aluminum hydride yields only the *anti* isomer. This marked stereospecificity of this reduction to yield the *anti* isomer favorably is unexpected and is being investigated in this laboratory.

(19) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 486 (1961); H. C. Brown and D. B. Bigley, *ibid.*, **83**, 3166 (1961).

(20) It was also noted that the *syn*-acetate exhibits shorter retention time than the *anti*-acetate, but this difference is much less than that of the alcohol.

(21) *E.g.*, S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

tive, causing an increase in rate of 5.7 over the parent compound. The chloro and bromo substituents result in a rate that is slower than the parent compound by factors of 0.045 and 0.030, respectively. Finally, the nitro substituent results in a rate that is very slow, 1.39×10^{-4} that of the parent compound.

Solvolysis Products.—In order to determine the products of the acetolysis, we carried out the solvolysis of each of the *p*-bromobenzenesulfonates in glacial acetic acid containing an equivalent quantity of sodium acetate.[21] In each case we isolated quantitatively an acetate whose infrared spectrum and other properties agreed with those of the authentic *anti*-acetate. These acetates were reduced to alcohols with lithium aluminum hydride. Careful gas chromatographic analyses carried out on the acetates and on the derived alcohols indicated only one product at the same retention times as those of the *anti* compounds. A quantitative experiment with authentic *anti* and *syn* epimeric alcohols XVIII and XXXVI demonstrated the absence of *syn* compound in the solvolysis product of XXIV in amounts greater than 0.3%.[22] The same demonstration was established on the solvolysis products of all our 4′-substituted compounds, except for the nitro compound. Since we could not find an effective gas chromatographic technique for the separation of the epimers of alcohols XXIII and XXXVII and acetates XXXV and XXXVIII, the analysis of the acetolysis product of XXIX was carried out by infrared spectrum. The infrared spectrum of the acetolysis product was consistent with that of XXXV, but quite different from that of XXXVIII. Quantitative estimation by the characteristic absorptions of XXXVIII at 1150 and 1645 cm.$^{-1}$ proved the absence of XXXVIII in the acetolysis product in amounts greater than 5%.

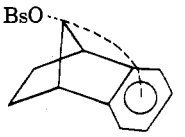
Discussion

Rates of Acetolysis.[23]—The effect of substituents on the rates of acetolysis of the *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonate is very large, far larger than can be accounted for in terms of a simple inductive effect. There can be little doubt that the acetolysis reaction involves participation by the aromatic ring, and that the substituents markedly affect the contribution of the aromatic ring to facilitate the ionization of the sulfonate substituent.

Certainly, the huge range of reactivity of 386,000 from 4′-methoxy to 4′-nitro appears not to be compatible with any simple electrostatic influence of the substituent. It is of the same order of magnitude as the range of reactivity observed by Brown and Okamoto[24] in the solvolysis of the substituted *t*-cumyl chlorides where direct resonance interaction of the substituent with the carbonium carbon occurs.

In the case of the 4′-nitro substituent, the rate is very slow and it might be questioned whether participation is important here. However, the 4′-nitro derivative undergoes solvolysis 11 times faster than 7-norbornyl *p*-bromobenzenesulfonate itself, in spite of the rate-retarding inductive influence of the nitrobenzo grouping. This points strongly to participation even in the case of the nitro derivative.[25]

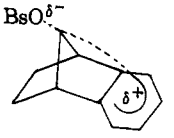
These results clearly indicate that the transition state must involve participation of some kind by the aromatic ring.



Solvolysis Products.—The synthetic methods used to produce the 7-hydroxy derivatives yielded the *anti*-7-alcohols. By comparison of infrared and n.m.r. spectra with those of authentic *syn* isomers, the stereochemistry of the *anti*-7-alcohols were unequivocally established.

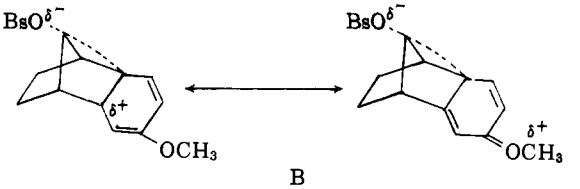
Solvolysis of the brosylates of these alcohols yielded acetates which were reduced to alcohols. Quantitative experiments by gas chromatography using authentic *syn*-alcohols demonstrated that the acetolysis of all but one of these brosylates proceeded with over-all retention of configuration. As the only exception, there may remain some questions for the case of the 4′-nitrobrosylate, because of the nonavailability of a precise analytical method. However, in this case also, we can say the acetolysis proceeds with retention of configuration within a limitation of about 95%. Consequently, these results strongly argue for participation by the aromatic ring.[26]

Correlation of Rate Data.—It is of considerable interest to know the precise nature of the participation of the aromatic ring in facilitating the ionization of the 7-sulfonate ester substituent. It is possible to conceive that this participation involves only interaction of the π-electron cloud, as indicated by the structure



A

Alternatively, the transition state may resemble the σ-complex which is usually proposed for typical aromatic substitution reactions.



B

Although the precise nature of the intermediate formed following ionization would be of interest, it is

(22) Bartlett and Giddings[7a] reported that the solvolysis of XXIV yielded pure *anti*-7-acetate. By the availability of the *syn*-alcohol, we confirmed their result.

(23) It has been shown that internal return may be an important factor to be considered in acetolyses. Refer to (a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1011 (1960); (b) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958). However, the absence of data bearing on the point in the present system makes it necessary to base the present discussion on solvolytic rates.

(24) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957), and references therein.

(25) This conclusion is supported by our observation that the 4′,5′-dinitro-*anti*-7-benzonorbornenyl *p*-bromobenzenesulfonate undergoes acetolysis at a rate much slower even than that of the 4′-nitro derivative.

(26) We noticed the formation of a small amount of the *syn*-alcohol XXXVI in the solvolysis of XXIV, when a more nucleophilic solvent, such as aqueous Cellosolve, rather than acetic acid was used. This observation also argues for participation in acetolysis. The relation between the stereochemistry of solvolysis product and the kind of solvent is being studied in this laboratory.

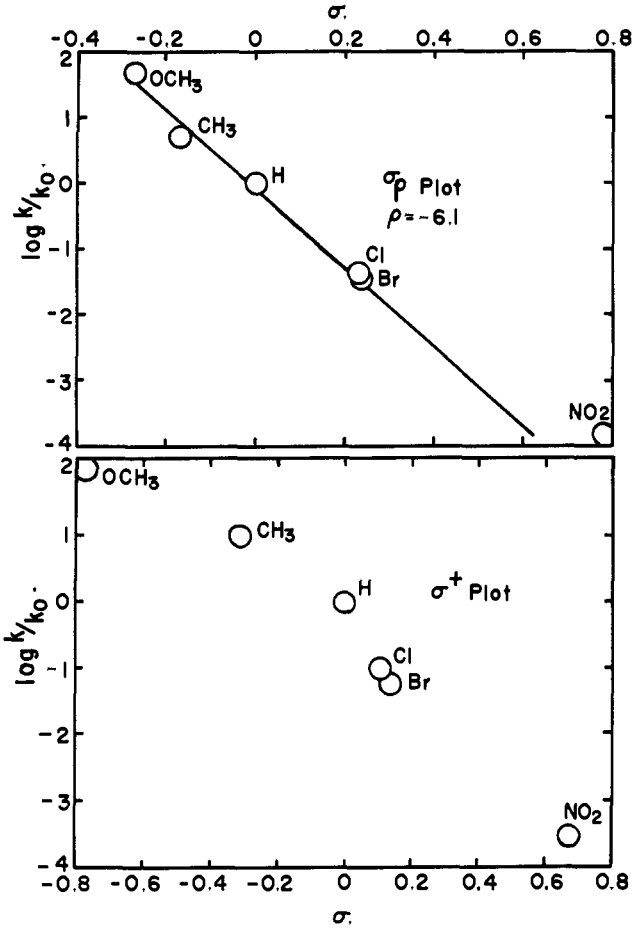


Fig. 1.—A (upper): the ρ–σ treatment of the relative acetolysis rates. B (lower): the ρ–σ^+ treatment of the relative acetolysis rates.

evident that the rate data can give information only with regard to the transition state, and not with respect to the intermediate formed subsequently.

It appeared that it might be possible to obtain information as to the precise nature of the interaction in the transition state by establishing whether the rate data are correlated by the Hammett σ-constant[27] or the Brown–Okamoto σ^+-constants.[28]

A plot of the relative rates of acetolysis (Table I) *vs.* the σ-constants yields a reasonable good correlation (Fig. 1A). However, the 4′-nitro derivative is distinctly above the line defined by the other points. That is to say, the nitro derivative appears to be considerably more reactive than would be predicted from the other data. We were originally concerned over the question whether the observed slow rate of the nitro compound established participation in this derivative. A point below the line might have been considered as evidence that participation is incomplete in this derivative. However, there appears to be no simple explanation for a point which is above the line. Moreover, the calculated value for the reaction constant, ρ, is -6.1, a value far larger than that observed for any reaction which is correlated satisfactorily by σ.

A simple plot of the rate data *vs.* σ_p^+ likewise provides an unsatisfactory correlation (Fig. 1B).[29] The

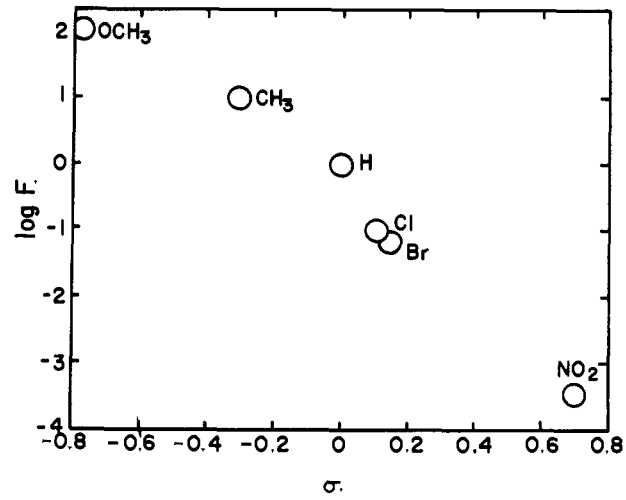
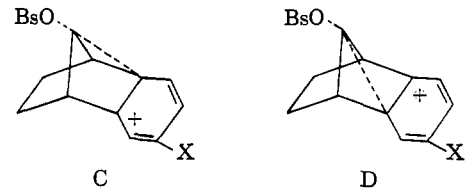


Fig. 2.—The ρ–σ^+ treatment of the partial rate factors.

methoxy, methyl, and hydrogen points are correlated reasonably well, but the halo and nitro points are far below the line defined by the first-named points.

We considered the possibility that solvolysis might be proceeding through two concurrent reactions, involving participation at the points *meta* and *para* to the substituent.



Accordingly, we calculated partial rate factors by use of the relationships

$$\text{obsd. relative rate} = F_{p-x} + F_{m-x}$$

$$\frac{\log F_{p-x}}{\log F_{m-x}} = \frac{\sigma_p{}^+{}_{-x}}{\sigma_m{}^+{}_{-x}}$$

However, this did not improve the correlation significantly (Fig. 2).

It is evident from the plots that the use of σ places the nitro derivative above the line, whereas the use of σ^+ places it below the line. Consequently, we considered the possibility that the use of the sum of σ^+ and σ might provide a satisfactory correlation. Accordingly, we plotted the rates relative to one-half the rate of the parent compound *vs.* $(\sigma^+ + \sigma_p)$, in which σ^+ was employed according to the manner described in ref. 26 (Fig. 3A). A reasonably good correlation was realized.

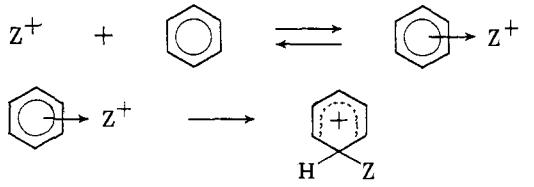
There are theoretical reasons why such a correlation might be anticipated. The mechanism of aromatic substitution is believed to involve the formation of a π-complex, followed by its transformation into a σ-complex.[30]

(27) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; (b) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(28) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(29) It was considered that bonding would occur predominantly *para* to the methoxy, methyl, and halo groups, but predominantly *meta* to the nitro group. Consequently, $\sigma_p{}^+$ was used for the first four substituents and $\sigma_m{}^+$ for the nitro group. Since there are two equivalent positions in the parent compound, we used one-half the observed rate for the hydrogen compound.

(30) For example, see L. M. Stock and H. C. Brown, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1963, Chapter 2.



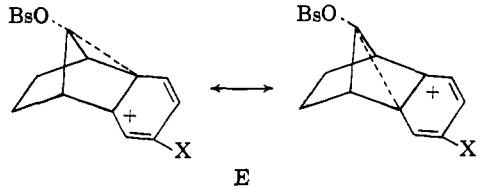
The reaction rate should then depend on the stabilities of both the π- and σ-complexes.

$$\text{rate} = K_\pi k_\sigma [\text{ArH}][Z^+]$$

It is customary to ignore the contribution of the π-complex in favor of the much larger factor introduced by the σ-complex.[31]

According to this interpretation, the transition state for the acetolysis would be somewhere between the π-complex participation, indicated in A, and the σ-complex participation, indicated in B.

The data can also be correlated by $(\sigma_p^+ + \sigma_m^+)$ (Fig. 3B). In this case it can be argued that the participation involves contributions from both the *meta* and *para* positions simultaneously, so that both σ_p^+ and σ_m^+ contribute to the stability of the transition state.

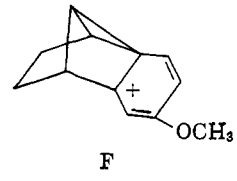


E

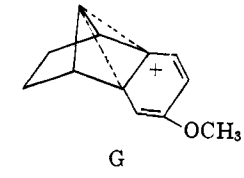
Unfortunately, there does not appear to be any simple means for selecting between these alternative correlations and interpretation at the present time.

Rate data for 4',5'-disubstituted derivatives may make it possible to select between these alternative possibilities, and we are currently investigating this question.

The Nature of the Carbonium Ion Intermediate.—The question remains as to the nature of the intermediate produced following the departure of the leaving group. Does it have the classical structure F, or the nonclassical structure G?



F



G

Unfortunately, the present data do not appear to provide any basis for selecting between these two alternative possibilities. Moreover, both intermediates would predict solvolysis with over-all retention, so that the observed stereochemistry of substitution does not permit a choice to be made. The results with the symmetrically substituted derivative now under study may indicate better whether the reaction proceeds through the formation of a symmetrical or an unsymmetrical transition state and thereby provide some evidence as to whether a classical or a nonclassical intermediate is formed in the ionization stage.

(31) There have been some examples recently where the evidence indicates that this simplification is not satisfactory. Thus Benkeser[32] and Eaborn[33] have noted reactions in which the rates of substitution are better correlated by σ than by σ^+ constants.

(32) R. A. Benkeser, T. V. Liston, and G. M. Stanton, *Tetrahedron Letters*, No. **16**, 1 (1960).

(33) (a) C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 542 (1961); (b) R. W. Bott, C. Eaborn, and J. A. Waters, *ibid.*, 681 (1963); (c) C. Eaborn and K. C. Pande, *ibid.*, 1566 (1960).

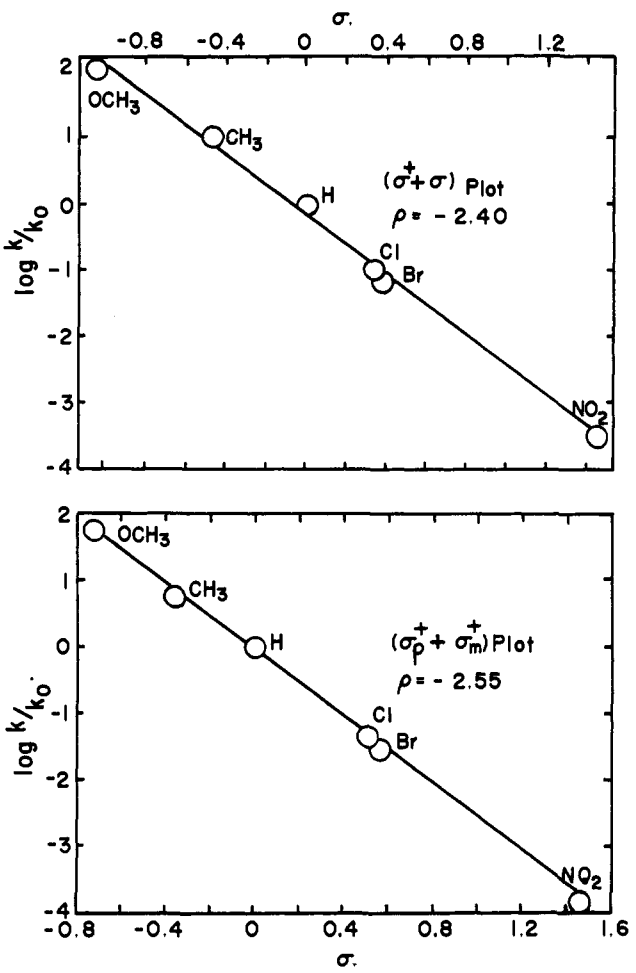


Fig. 3.—A (upper): the $(\sigma^+ + \sigma)$ plots of the relative acetolysis rates. B (lower): the $(\sigma^+ + \sigma^+)$ plots of the relative acetolysis rates.

Experimental[34]

Properties and analyses of the new compounds prepared in the present study are summarized in Tables II, III, and IV.

Materials.—All of 4'-substituted benzonorbornadienes, which were used as starting compounds for the syntheses of the desired compounds, were obtained in good yields by our modification[10] of Wittig's procedure[11] for the addition of benzyne to cyclopentadiene. 4'-Methoxybenzonorbornadiene, b.p. 99–100° (4 mm.), n^{23}D 1.5642; 4'-methylbenzonorbornadiene, b.p. 110–112° (22 mm.), n^{24}D 1.5541; 4'-chlorobenzonorbornadiene, b.p. 112–112.5° (10 mm.), n^{21}D 1.5763; 4'-bromobenzonorbornadiene, b.p. 127–129° (10 mm.), n^{29}D 1.5191, were used.

An Example of Benzoyloxylation of the 7-Position of Benzonorbornadienes. *anti*-7-Benzoyloxy-4'-methoxybenzonorbornadiene (VII).—To a stirred mixture of 76.8 g. (0.446 mole) of 4'-methoxybenzonorbornadiene (II) and 357 mg. of freshly prepared cuprous bromide in 250 ml. of chlorobenzene there was added under a nitrogen atmosphere a solution of 30 g. (0.124 mole) of benzoyl peroxide in 140 ml. of chlorobenzene over a period of 3 hr. at about 80°. After the addition was completed, the reaction temperature was raised to 100° and stirred for 10 hr. Qualitative analysis by potassium iodide–starch paper indicated that no benzoyl peroxide remained after this period. During the course of the reaction, the color of the solution changed

(34) Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Unless stated otherwise, infrared spectra were determined with a Nippon Bunko IR-S spectrometer in carbon tetrachloride and carbon disulfide; n.m.r. spectra were determined at 60 Mc. with a Varian A-60 spectrometer using tetramethylsilane as internal standard in deuteriochloroform.

TABLE II

4′-SUBSTITUTED *anti*-7-BENZONORBORNENOL DERIVATIVES

4′-Subst.	7-Subst.[a]	M.p. or b.p. (mm.), °C.	Recrystn. solvent[e] or n_D (t, °C.)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3O	HO	79	E	$C_{12}H_{14}O_2$	75.76	76.02	7.42	7.41
	AcO	115 (b.t.) (0.02)[b]	1.5382 (22)	$C_{14}H_{16}O_3$	72.39	72.22	6.94	6.95
	BsO	93.5–94.5	H	$C_{18}H_{17}BrO_4S$	52.81	52.97	4.19	4.30
CH_3	HO	95–96		$C_{12}H_{14}O$	82.72	82.44	8.10	8.14
	AcO	67.5–68.5	E	$C_{14}H_{16}O_2$	77.75	77.82	7.46	7.62
	BsO	97–98	E	$C_{18}H_{17}BrO_3S$	54.97	55.18	4.36	4.38
H	HO	105–106[c]						
	AcO	78–79 (0.3)	1.5333 (25)	$C_{13}H_{14}O_2$	77.20	76.91	6.98	6.72
	BzO	112–112.5	H	$C_{18}H_{16}O_2$	81.79	82.07	6.10	6.22
	BsO	135.4–136.4[d]	E					
Cl	HO	115	H	$C_{11}H_{11}ClO$[f]	67.87	68.00	5.70	5.70
	AcO	110–112 (b.t.)[b] (0.05)	1.5459 (23)	$C_{13}H_{13}ClO_2$	65.97	66.16	5.54	5.58
	BzO	127–127.3	H	$C_{18}H_{15}ClO_2$[g]	72.36	72.59	5.06	5.20
	BsO	91–92	E	$C_{17}H_{14}BrClO_3S$	49.35	49.51	3.41	3.43
Br	HO	125–126	HE	$C_{11}H_{11}BrO$	55.25	55.32	4.64	4.71
	BsO	83.5–84.5	HE	$C_{17}H_{14}Br_2O_3S$	44.56	44.86	3.08	3.18
NO_2	HO	114.5–115	C	$C_{11}H_{11}NO_3$[h]	64.38	64.37	5.40	5.60
	AcO	94	HE	$C_{13}H_{13}NO_4$[i]	63.15	63.45	5.30	5.50
	BsO	134.5	E	$C_{17}H_{14}BrNO_5S$[j]	48.13	48.28	3.33	3.33

[a] Substituent: AcO = acetoxy, BsO = *p*-bromobenzenesulfonyloxy, Bz = benzoyloxy. [b] Bath temperature. [c] Lit.[7a] m.p. 104.1–105.7°. [d] Lit.[7a] m.p. 132.5–135°. [e] Solvent: E = ether, H = *n*-hexane, C = carbon tetrachloride, HE = a mixed solvent of *n*-hexane and ether. [f] Calcd.: O, 8.22. Found: O, 8.43. [g] Calcd.: O, 10.71. Found: O, 10.69. [h] Calcd.: N, 6.83. Found: N, 6.75. [i] Calcd.: N, 5.67. Found: N, 5.47. [j] Calcd.: Br, 18.83. Found: Br, 18.97.

TABLE III

4′-SUBSTITUTED *anti*-7-BENZONORBORNADIENOL DERIVATIVES

4′-Subst.	7-Subst.[a]	M.p. or b.p. (mm.), °C.	Recrystn. solvent[b] or n_D (t, °C.)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3O	HO	69.5–70.5	HE	$C_{12}H_{12}O_2$	76.57	76.55	6.43	6.39
	BzO[a]	91–91.5	H	$C_{19}H_{16}O_3$	78.06	77.95	5.52	5.57
CH_3	HO	109–110 (3)	1.5712 (27.5)					
	BzO[a]	90.5	H	$C_{19}H_{16}O_2$	82.58	82.56	5.84	5.92
Cl	BzO[a]	124.5–125	HE	$C_{18}H_{13}ClO_2$[c]	72.85	72.83	4.42	4.51
Br	*p*-ClBzO	137.3–137.8	HB	$C_{18}H_{12}BrClO_2$	57.55	57.29	3.22	3.29

[a] Substituent: Bz = benzoyloxy, *p*-ClBzO = *p*-chlorobenzoyloxy. [b] Solvent: H = *n*-hexane, HE = a mixed solvent of *n*-hexane and ether, HB = a mixed solvent of *n*-hexane and benzene. [c] Calcd.: Cl, 11.95. Found: Cl, 11.75.

TABLE IV

4′-SUBSTITUTED *syn*-7-BENZONORBORNEOL DERIVATIVES

4′-Subst.	7-Subst.[a]	M.p. or b.p. (mm.), °C.	Recrystn. solvent[d] or n_D (t, °C.)	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3O	HO	64.5–66	c	$C_{12}H_{14}O_2$	75.76	75.72	7.42	7.42
H	HO	117–118	H	$C_{11}H_{12}O$	82.46	82.59	7.55	7.44
	AcO	125 (b.t.)[b] (3)	1.5377 (26)	$C_{13}H_{14}O_2$	77.20	77.42	6.98	7.01
Cl	HO	123–124	HE	$C_{11}H_{11}ClO$	67.87	67.70	5.70	5.90
Br	HO	123–124	HE	$C_{11}H_{11}BrO$	55.25	55.41	4.64	4.50
NO_2	HO	127–128.5	HE	$C_{11}H_{11}NO_3$	64.38	64.39	5.40	5.49
	AcO	95.5–96.5	HE	$C_{13}H_{13}NO_4$	63.15	63.25	5.30	5.36

[a] Substituent: AcO = acetoxy. [b] Bath temperature. [c] Purified by sublimation. [d] Solvent: H = *n*-hexane, HE = a mixed solvent of *n*-hexane and ether.

gradually from blue to brown. After cooling to room temperature, the reaction mixture was extracted with 10% aqueous sodium carbonate to remove benzoic acid, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, 51 g. of crude II was recovered by vacuum distillation, leaving a viscous residue. High vacuum distillation of this residue gave 17 g. of crude VII, b.p. 167–171° (0.045 mm.), and left 24.4 g. of viscous high molecular products. Crude VII was purified by recrystallization from hexane to yield 11 g. (30.4%) of pure VII as colorless needles.

The benzoyloxy esters VI, VIII, IX, and X were prepared in a similar manner.

anti-**4′-Methoxybenzonorbornadien-7-ol (XII).**—To a solution of methylmagnesium iodide in ether, which was prepared from 23.4 g. of methyl iodide and 3.91 g. of magnesium turnings in 140 ml. of anhydrous ether, there was added dropwise a solution of 9.38 g. of VII in 270 ml. of anhydrous ether under nitrogen atmosphere. After heating for 2 hr. under reflux, the mixture was poured into a concentrated aqueous solution of ammonium chloride. The separated ether layer was washed with 10% aqueous sodium thiosulfate and water, and dried over anhydrous sodium sulfate. A by-product, phenyldimethylcarbinol, was removed by vacuum distillation at about 110–120° (5 mm.). The residue (6.2 g.) was recrystallized from a mixed solvent of *n*-hexane and ether to give 5.44 g. (90%) of colorless prisms of XII.

anti-**7-Benzonorbornadienol (XI)** and *anti*-**4′-methylbenzonorbornadien-7-ol (XIII)** were similarly prepared from VI and VIII, respectively.

anti-**4′-Methoxybenzonorbornen-7-ol (XIX).**—Catalytic reduction of XII with palladium-on-charcoal yielded colorless prisms of XIX almost quantitatively.

Similarly, XVIII and XX were prepared from XI and XIII, respectively.

anti-**7-Benzoyloxy-4′-chlorobenzonorbornene (XIV)** and *anti*-**7-*p*-chlorobenzoyloxy-4′-bromobenzonorbornene (XV)** were obtained in quantitative yield by catalytic reduction of IX and X,

respectively, with palladium-on-charcoal in ethanol. Both are colorless crystals.

anti-4′-**Chlorobenzonorbornen-7-ol** (**XXI**).—To a suspension of 1.14 g. of lithium aluminum hydride in 120 ml. of anhydrous ether was added over 1.5 hr. a solution of 7.94 g. of the benzoyl ester XIV in 340 ml. of ether at such a rate as to maintain gentle reflux. After an additional 2.5 hr. of reflux, the mixture was treated cautiously with wet ether and then with water. It was poured into chilled water, and 10% hydrochloric acid was added until the inorganic precipitate was dissolved. The layers were separated and the aqueous layer was extracted twice with 100-ml. portions of ether. The combined ether layers were dried, evaporated, and a by-product, benzyl alcohol, was removed under vacuum. Recrystallization of the residue from *n*-hexane yielded 3.63 g. (75%) of XXI.

anti-4′-Bromobenzonorbornen-7-ol (**XXII**) was similarly obtained.

4′-Nitrobenzonorbornen-7-one (**XVII**).—To a solution of 1.0 g. of benzonorbornen-7-one (XVI) in 3 g. of 80% sulfuric acid 671 mg. of powdered potassium nitrate was slowly added at 40°. After stirring for 2 hr., the reaction mixture was poured onto ice and extracted with ether. The ether solution was washed with water and aqueous sodium bicarbonate, dried, and evaporated. The residue was recrystallized from ether to give 825 mg. of XVII (64.3%) as colorless prisms, m.p. 126–126.5°; n.m.r. (in $CDCl_3$): two aromatic H at 1.8–1.9 τ,[35a] one aromatic H at 2.5–2.7,[35b] two bridgehead H at 6.5 τ.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.46; N, 6.89. Found: C, 65.08; H, 4.75; N, 7.06.

Dehydrogenation of XVII.—The mixture of 100 mg. of the ketone XVII with 50 mg. of 20% palladium-on-charcoal was heated at 330–350° for 2 hr. An evolution of gas was noticed. The reaction mixture was extracted with ether, washed with water, dried over sodium sulfate, and evaporated. Treatment of the residue with Merck alumina in pentane followed by recrystallization from alcohol gave 24 mg. of 2-nitronaphthalene, m.p. 78.5–79°, which was identified with an authentic sample.

anti-4′-**Nitrobenzonorbornen-7-ol** (**XXIII**).—To a solution of 1.81 g. of XVII in 100 ml. of anhydrous methanol was slowly added a powder of 0.84 g. of sodium borohydride. After stirring for 3 hr. at room temperature and then for 1 hr. under reflux, the mixture was treated with water to decompose the excess of sodium borohydride, the methanol was removed, and water was added to yield an oil, which was extracted with ether. The ether extract was washed with water and aqueous sodium bicarbonate, dried over sodium sulfate, and evaporated. Recrystallization of the residue gave 1.30 g. (70%) of XXIII as colorless needles; infrared: ν_{OH} 2.76 μ (LiF prism, 20-mm. cell, in CCl_4 solution); n.m.r. (in $CDCl_3$): two aromatic H at 1.8–2.0,[35a] one aromatic H at 2.6–2.8 τ,[35b] C–H at 6.15 (multiplet), two bridgehead H at 6.75 τ (quartet).

The acetate of XXIII (**XXXV**) showed the following n.m.r. (in $CDCl_3$): two aromatic H at 1.8–2.0,[35a] one aromatic H at 2.6–2.8,[35b] C_7–H at 5.4 (multiplet), two bridgehead H at 6.53 τ (quartet).

anti-4′-**Methoxybenzonorbornen-7-ol** *p*-**Bromobenzenesulfonate** (**XXV**).—To 3.31 g. of 4′-methoxybenzonorbornen-7-ol in 8.5 ml. of anhydrous pyridine was added 4.44 g. of *p*-bromobenzenesulfonyl chloride. The solution was left in a refrigerator for over a week. Upon addition of the mixture to ice and water, an oil was isolated and extracted with ether. The ether solution was washed twice with 5% aqueous acetic acid and aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. After evaporation of ether, the residue was kept in a refrigerator for completion of crystallization. The crystals which formed were recrystallized from ether to give colorless needles. The yield was 5.57 g. All other *p*-bromobenzenesulfonates were obtained in a similar way.

anti-**Benzonorbornen-7-ol Acetate** (**XXX**).—To 0.20 g. of *anti*-7-benzonorbornenol in 0.6 ml. of anhydrous pyridine was added 0.13 g. of acetic anhydride and the mixture allowed to stand for a few days in a refrigerator with a calcium tube. The mixture was poured onto ice and extracted with ether. The ether solution was washed with 1% hydrochloric acid and aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. Evaporation of the ether gave crude acetate in quantitative yield and distillation at 78–79° (0.3 mm.) gave the pure product.

(35) (a) An AB part (multiplet) of an ABK system; (b) a K part (second-order doublet) of an ABK system.

The other acetates were prepared in the same way.

syn-**7-Benzonorbornenol** (**XXXVI**).—2-Methylbut-2-ene (18.2 g.) was dissolved in a solution of 3.54 g. of sodium borohydride in 70 ml. of diglyme and the mixture, cooled to 0°, was treated with 17.6 g. of boron trifluoride etherate to form disiamylborane. To the reagent at 0° was added 7.9 g. of benzonorbornen-7-one (XVI) in 20 ml. of diglyme and the reaction mixture maintained at 0° for 3 hr. with stirring, then left overnight at room temperature. Oxidation at room temperature with 100 ml. of 3 *N* sodium hydroxide followed by 80 ml. of 30% hydrogen peroxide produced 7.9 g. (98%) of the mixture of *anti*- and *syn*-7-benzonorbornenol (XVIII and XXXVI). Analysis by gas chromatography (polyethylene glycol succinate column at 180°) showed 46% *anti*-, 54% *syn*-alcohol. The *syn*-alcohol XXXVI was isolated by elution chromatography on Florisil with a mixed solvent of petroleum ether and ether; infrared, ν_{OH} 2.79 μ (LiF prism, 20-mm. cell, in CCl_4 solution).

The n.m.r. of XXXVI (in $CDCl_3$): C_7–H at 5.96 (triplet), two bridgehead H at 6.81 τ (quartet). For reference, the n.m.r. of XVIII (in $CDCl_3$): C–H at 6.15 τ (multiplet), two bridgehead H at 6.84 τ (quartet).

syn-**Benzonorbornen-7-ol acetate** was prepared in a manner similar to that used for XXX; n.m.r. (in $CDCl_3$): C_7–H at 5.16 τ (triplet), two bridgehead H at 6.62 τ (quartet). For reference, the n.m.r. of XXX (in $CDCl_3$): C_7–H at 5.46 (multiplet), two bridgehead H at 6.66 τ (quartet).

syn-4′-**Methoxybenzonorbornen-7-ol**, *syn*-4′-**chlorobenzonorbornen-7-ol**, **and** *syn*-4′-**bromobenzonorbornen-7-ol** were prepared by the Oppenauer oxidation of the corresponding *anti*-alcohols followed by disiamylborane reduction. The isolation of these *syn*-alcohols was achieved in a manner similar to that used for XXXVI. The Oppenauer oxidation was carried out according to the method which Bartlett and Giddings[7a] used for the preparation of XVI.

syn-4′-**Nitrobenzonorbornen-7-ol** (**XXXVII**).—To a solution of 30 mg. of XXXVI in 1 ml. of nitromethane, a solution of 20 mg. of concentrated nitric acid (*d* 1.38) in 67 mg. of 98% sulfuric acid was slowly added at 0°. After stirring for 2 hr., the reaction mixture was worked up in a manner similar to that used for XVII. The yield was 13 mg.; n.m.r. (in $CDCl_3$): two aromatic H at 1.8–2.0,[35a] one aromatic H at 2.5–2.7,[35b] C_7–H at 5.73 (triplet), two bridgehead H at 6.69 τ (quartet).

syn-4′-**Nitrobenzonorbornen-7-ol Acetate** (**XXXVIII**).—To a solution of 25 mg. of *syn*-benzonorbornen-7-ol acetate in 1 ml. of acetic anhydride was added 17 mg. of fuming nitric acid (*d* 1.50) at 0°. After standing at 0° for 5 hr., then at room temperature for a day, the reaction mixture was worked up in a manner similar to that used for XVII; n.m.r. (in $CDCl_3$): two aromatic H at 1.8–2.0,[35a] one aromatic H at 2.6–2.8,[35b] C_7–H at 5.1 (triplet), two bridgedhead H at 6.5 τ (quartet).

Structure of Acetolysis Products.—The acetolysis solution was allowed to remain in a constant temperature bath for more than 10 half-lives of each of the *p*-bromobenzenesulfonates, concentrated by distilling the acetic acid under slightly reduced pressure, diluted with ether, and treated with water and solid sodium bicarbonate to remove acetic acid. After drying over anhydrous sodium sulfate, the ether solution was evaporated on a steam bath and the residue was pumped for some time in a vacuum desiccator. The infrared spectrum of the residue was identical with that of each of the authentic *anti*-7-benzonorbornenyl acetates and the yield was quantitative. The residue was added dropwise to excess lithium aluminum hydride in ether, causing gentle boiling with each drop, and refluxed for a few hours. Water was added cautiously until no further reaction occurred; then 5% aqueous hydrochloric acid was added until all precipitate had dissolved. The ether layer was separated, washed with sodium carbonate solution, and dried over sodium sulfate. The residue obtained after evaporation of the ether had an infrared spectrum identical with that of each of the authentic *anti*-7-benzonorbornenols. Quantitative gas chromatographic analyses of these derived alcohols with authentic *syn*-alcohols under the following conditions demonstrated the absence in amounts greater than 0.3% of *syn* compounds in the solvolysis products. Exceptionally, the solvolysis product of the 4′-nitro compound was investigated by comparison of the infrared spectrum using the charts of authentic *anti*- and *syn*-alcohols.

Gas Chromatographic Analyses of the Solvolysis Products.—A standard column of 3 m. × 6 mm. stainless steel tubing was employed with helium as carrier gas in a Shimazu gas chromatograph Model GC-1B: the column was packed with 5% by weight

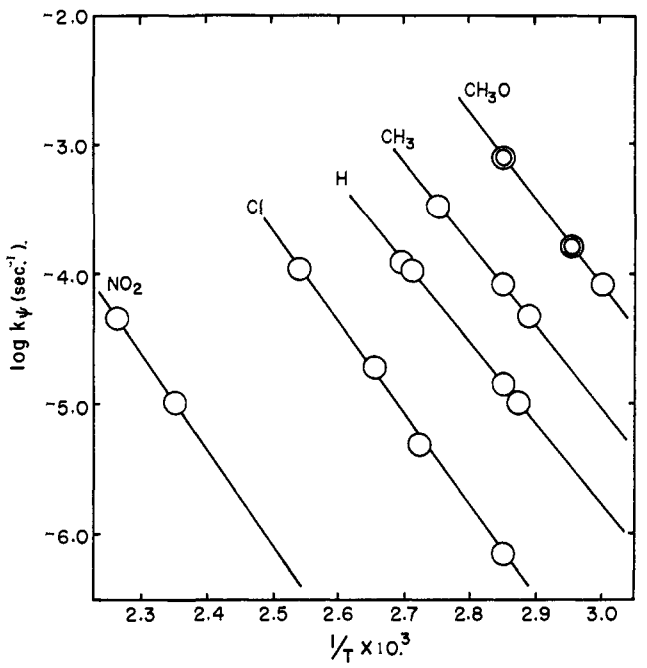


Fig. 4.—Arrhenius plots of the acetolysis rates of *p*-bromobenzenesulfonates: O, one run; ⓞ, two runs.

of diethylene glycol succinate suspended on acid-washed, 30–60 mesh Chromosorb W. Analyses were carried out under the following conditions: for XVIII and XXXVI, at 180° with a flow rate of 100 ml./min., the retention time of 5.6 min. to XXXVI and of 8.5 min. to XVIII; for XIX and its *syn* epimer, at 100° with 100 ml./min.; for XXI and its *syn* epimer, at 200° with 100 ml./min.; for XXII and its *syn* epimer, at 200° with 100 ml./min.; for XXX and its *syn* epimer, at 170° with 100 ml./min.

Kinetic Measurements.—The chosen acetolysis conditions and procedures were similar to those of Bartlett and Giddings,[7a] which in turn had been chosen to be similar to those of Winstein, *et al.*[21]

Reagent grade acetic acid was heated under reflux with about 4% potassium permanganate for 5 hr., distilled, dried over phosphorus pentoxide, and then redistilled. The distilled acid was further purified by collecting the fraction boiling at 117–118° after refluxing with 3% of acetic anhydride, and stored for use with addition of 1% acetic anhydride. Sodium acetate standard solution was made by dissolving anhydrous sodium carbonate in acetic acid and by refluxing for 5 hr. with sufficient acetic anhydride to remove the water of neutralization, and its concentration was adjusted to 0.104 *M* at room temperature. Perchloric acid standard solution was prepared by adding reagent grade 70% perchloric acid to the solution of the above acetic acid and sufficient acetic anhydride to remove the water; the concentration was approximately 0.02 *M*.

Samples of sulfonate ester were weighed into 30-ml. volumetric flasks so that solutions approximately 0.10 *M* in ester would be obtained, then filled to 30 ml. with the sodium acetate–acetic acid solution. Rate constants were determined by the infinity titer method; zero time meant that the complete solution and thermal equilibrium had been reached. Aliquots, usually eight 3-ml. portions of a reaction solution at reaction temperature, were pipetted directly from the volumetric flask into the constant temperature bath at recorded times and drained into 20 ml. of purified dioxane.[36]

(36) Refer to L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 285.

In necessary cases, aliquots were pipetted from the flask at a constant temperature into ampoules. The sealed ampoules were placed in the constant temperature bath at once and individual ampoules were removed at recorded times and plunged into ice-cold water. "Infinity" ampoules were removed after at least ten half-lives and usually two were taken for each run. The contents of each ampoule were diluted with 20 ml. of dioxane. Two drops of a saturated solution of brom phenol blue in acetic acid was added, and the residual sodium acetate was titrated with the perchloric acid solution. Disappearance of the yellow indicator color was taken as the end-point. Plots of log $(A_\infty - A_t)$ *vs.* time where A_∞ and A_t are titers at "infinity" and at any time were uniformly linear. The slopes multiplied by −2.303 gave the pseudo-first-order rate coefficients. Data from a representative run are presented in Table V.

TABLE V

ACETOLYSIS OF XXV. A TYPICAL RUN AT 64.41 ± 0.03°

Time, min.	Ml. of $HClO_4$ required	$A_t - A_\infty$	log $(A_t - A_\infty)$
10	13.16	12.50	1.0969
25	12.16	11.50	1.061
50	9.84	9.18	0.9628
70	8.42	7.76	.8899
105	6.19	5.53	.7427
130	4.99	4.33	.6365
160	3.89	3.23	.5092
210	2.63	1.97	.2945
∞	0.66		
∞	0.66		

The plot of log $(A_t - A_\infty)$ *vs.* time was linear with slope -4.055×10^{-3} min.$^{-1}$; multiplied by −2.303/60, this gave the rate coefficient, 1.56×10^{-4} sec.$^{-1}$.

Calculation of the enthalpy and entropy of activation was performed by the usual method.[37] Plots of log k_ψ *vs.* $1/T$ formed straight lines for all compounds, as shown in Fig. 4, and their slopes were calculated by the method of least squares.

An Example of Calculation of Partial Rate Factor.—For CH_3O compound

$$k_{p\text{-}OCH_3} + k_{m\text{-}OCH_3} = \text{obsd. rate constant}$$

$$\frac{k_{p\text{-}OCH_3}}{k_H/2} + \frac{k_{m\text{-}OCH_3}}{k_H/2} = \text{rel.} \times 2 = 107.4$$

$$F_{p\text{-}OCH_3} + F_{m\text{-}OCH_3} = 107.4 \qquad (1)$$

$$\frac{\log F_{p\text{-}OCH_3}}{\log F_{m\text{-}OCH_3}} = \frac{\sigma^+_{p\text{-}OCH_3}}{\sigma^+_{m\text{-}OCH_3}} = \frac{-0.778}{+0.047} = -16.5 \qquad (2)$$

from eq. 1 and 2, we obtained

$$F_{p\text{-}OCH_3} = 106.4,\ F_{m\text{-}OCH_3} = 0.76$$

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(37) Refer to J. F. Bunnett, "Technique of Organic Chemistry. Vol. VIII: Investigation of Rates and Mechanisms of Reactions. Part I," 2nd Ed., S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p. 200.