

Solvolysis Reactions of 7-Norbornenyl and Related Systems. Substituent Effects as a Diagnostic Probe for Participation

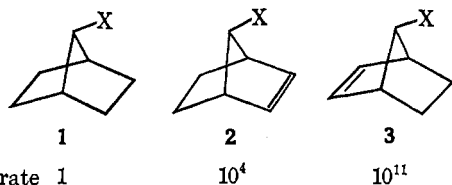
HIROSHI TANIDA

Shionogi Research Laboratory, Shionogi and Company, Ltd., Fukushima-ku, Osaka, Japan

Received March 19, 1968

The solvolysis reactions of norbornyl halides and *p*-toluenesulfonates (tosylates) and of related compounds have been widely studied in recent years. A number of striking rate effects have been observed; for example, *syn*-7-norbornenyl tosylate (**2**) solvolyzes (in acetic acid) 10^4 times faster than its saturated analog **1**, while its *anti* isomer **3** solvolyzes 10^{11} faster than **1**.¹ Some of these and other dramatic effects have been attributed to *participation* of neighboring σ - or π -bond electrons in an initial carbonium ion forming step. However, other authors have suggested that many of the unusual rate effects are of steric origin and have averred that there is no compelling evidence for participation. Indeed, this has been a subject of lively controversy.

The essential idea of participation is that electrons from a nearby σ or π bond interact covalently with the carbon from which the halide, tosylate, or other "leaving group" departs, assisting the primary bond-breaking step. Interaction occurs at the back side of carbon with respect to the leaving group, in the manner of an intramolecular S_N2 reaction.



A great many experiments have been performed in many laboratories with the objective of determining whether or not certain solvolysis rates are enhanced by participation of σ - or π -bond electrons.^{2,3} In this account, it is shown that substituent effects on solvolysis rates can, in appropriate cases, provide definitive evidence for participation.

π -Participation in the 7-Norbornenyl Systems

The saturated **1** is extraordinarily unreactive in solvolysis. Although this is a secondary alkyl system, the development of a positive charge at C_7 is resisted

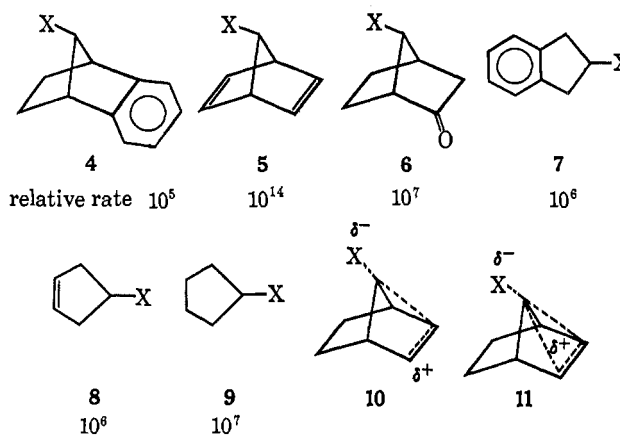
(1) (a) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957); (c) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(2) Participation by unshared electron pairs from nearby atoms is a well-recognized phenomenon in solvolysis reactions, but is not dealt with in this account. Henceforth in this article, *participation* means only participation by electrons of σ or π bonds.

(3) For recent reviews, see (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) B. Capon, *Quart. Rev. (London)*, **18**, 45 (1964); (c) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; (d) G. D. Sargent, *Quart. Rev. (London)*, **20**, 301 (1966).

even more than in ordinary primary alkyl systems. For instance, the rate of acetolysis (solvolysis in acetic acid) of 7-norbornyl *p*-bromobenzenesulfonate (brosylate)⁴ is 10,000 times slower than that for *n*-butyl brosylate. Therefore, it is predicted that the system should have an extraordinarily high sensitivity to factors promoting ionization.

The striking effects on solvolysis rate due to the introduction of a double bond into **1** were mentioned in the introduction. A fused *anti*-benzene ring is also



effective, causing an increase in rate of 10^5 .⁵ The introduction of two double bonds results in an enormous rate enhancement of 10^{14} .⁶ A carbonyl at C_2 causes an increase in rate of 10^7 , probably *via* enolization.⁷

Explanations proposed for the great acceleration by double bonds are: (a) anchimeric assistance⁸ due to homoallylic conjugation (an unsymmetrical transition state) (**10**), (b) anchimeric assistance due to symmetrical nonclassical electron delocalization (**11**),^{1a,c} or (c) widening of the C_1 - C_7 - C_4 bond angle. Introduction of the 2,3-double bond pushes C_1 and C_4 further apart (because of increased C_1 - C_2 - C_3 and C_2 - C_3 - C_4 bond angles and in spite of a shortened C_2 - C_3 bond distance), causing an increase in the C_1 - C_7 - C_4 angle which is favorable for the formation of a trigonal carbonium ion.⁵ In all studies previous to ours, these factors were not independent nor could they be estimated individually with any precision. In fact, the

(4) Factors for the inertness were suggested by W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

(5) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(6) S. Winstein and C. Ordroneau, *ibid.*, **82**, 2084 (1960).

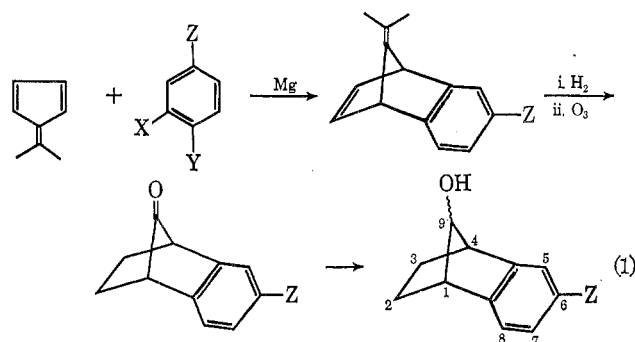
(7) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2599 (1966).

(8) The term "anchimeric assistance" denotes the driving force provided by participation by neighboring parts of a molecule: S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **75**, 147 (1953).

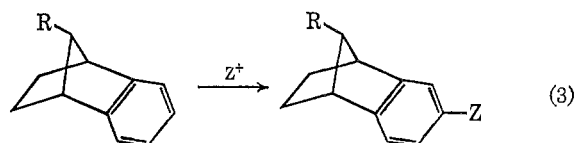
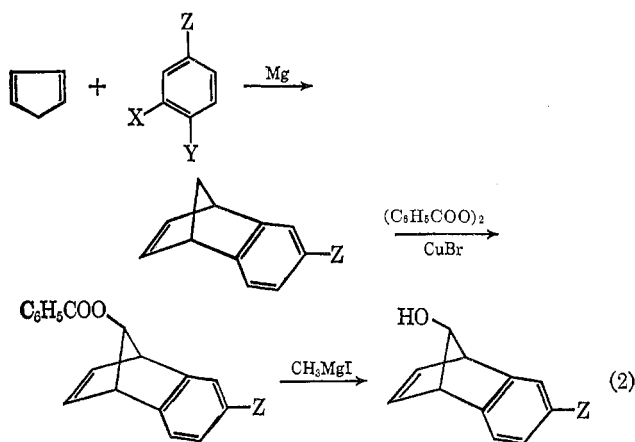
rates of acetolysis of 2-indanyl (7) and cyclopentyl brosylates (9), which have larger C₁-C₂-C₃ angles, are 10 and 100 times, respectively, greater than that of the *anti*-9-benzonorbornenyl brosylate (4), which has a smaller C₁-C₉-C₄ angle. Therefore, it might be argued that anchimeric assistance is unimportant, at least, in the case of the 4 system.

In order to get a better understanding of this situation, we undertook the synthesis of a number of 6-substituted *anti*-9-benzonorbornenyl brosylates and a study of their substituent effects on acetolysis. The basic principle employed here is that introduction of substituents into the benzene moiety can cause a variation of participation effects, while maintaining steric factors constant. In addition, it might be possible to clarify the nature of participation by an application of theory and experience well developed in aromatic chemistry.

The compounds required were most conveniently prepared by cycloaddition of benzyne to dimethylfulvene,⁹ followed by a few simple reactions (eq 1). The copper-catalyzed reaction of benzoyl peroxide with benzonorbornadiene or its aromatic-substituted de-



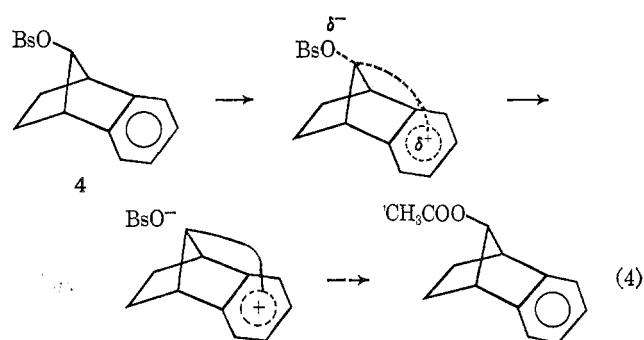
X, Y = halogens
Z = CH₃O, CH₃, H, F, Cl, Br



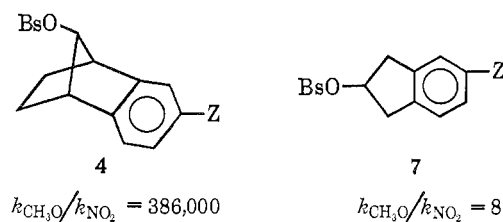
Z = NO₂, Br, CH₃CO

rivatives¹⁰ to form *anti*-9-benzoyloxybenzonorbornadiene in a stereospecific manner, although less satisfactory, was another useful method (eq 2).¹¹ Electrophilic aromatic substitution reactions of benzonorbornene (which, incidentally, show an unusually strong β orientation)¹² were a means for introducing several substituents (eq 3). By these methods, several kinds of 6-substituted *anti*-9-benzonorbornenol derivatives were synthesized.¹³

Acetolyses of all the brosylates thus prepared were strictly first order. In buffered acetolysis, the respective *anti* acetates were formed quantitatively with retention of configuration. The absence of inverted *syn* acetates was demonstrated. These results suggest over-all retention of configuration by the mechanism of eq 4.



The methoxy substituent increases the rate by a factor of 53.7. The rate increase due to methyl is 5.7. The chloro, bromo, and nitro substituents decelerate acetolysis by factors of 0.045, 0.030, and 1.4×10^{-4} , respectively. Moreover, identical rates were observed for 6-nitro-*syn*-9-benzonorbornenyl and 7-norbornyl brosylates (Table I). The extreme effect of substituents, $k_{\text{OCH}_3}:k_{\text{NO}_2}$, amounts to a factor of 386,000.¹³ These effects are far larger than can be accounted for by any simple electrostatic influence of the substituents and indicate that if the C₁-C₉-C₄ bond angle effect does exist, it must be relatively unimportant.¹⁴ On the other hand, the corresponding factor, $k_{\text{OCH}_3}:k_{\text{NO}_2}$, in



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

(11) (a) H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964); (b) M. E. Brennan and M. A. Battiste, *ibid.*, **33**, 324 (1968).

(12) (a) H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.*, **87**, 4794 (1965); (b) *Tetrahedron Letters*, 2787 (1964).

(13) (a) H. Tanida, *J. Am. Chem. Soc.*, **85**, 1703 (1963); (b) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964).

(14) Gassman also made a similar suggestion by the fact that replacement of the proton at C₇ in 2 and 3 by the anisyl group eliminates the participation of the π electrons. See P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

(9) R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1966).

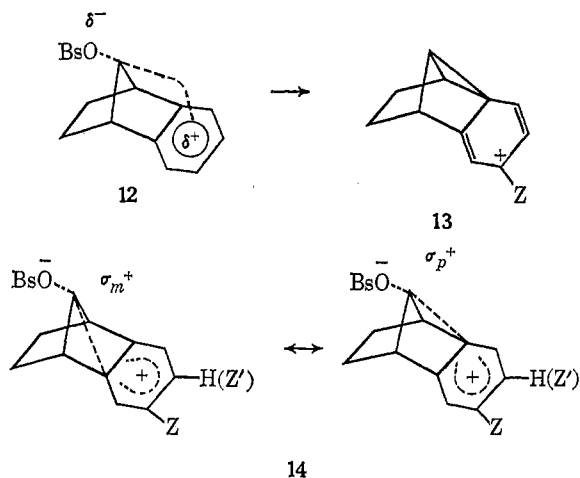
Table I
Acetolyses of 9-Benzonorbornenyl Brosylates^a

6 subst	<i>anti</i> -Brosylate		<i>syn</i> -Brosylate		<i>anti:syn</i> rate ratio	Ketone ^b $\nu_{C=O}$, cm ⁻¹
	k_1 , sec ⁻¹	Rel rate	k_1 , sec ⁻¹	Rel rate		
CH ₃ O	8.08×10^{-4}	54	2.07×10^{-8}	1.6	3.9×10^4	1788
CH ₃	8.44×10^{-5}	5.7	2.04×10^{-8}	1.6	4.1×10^3	1788
H	1.49×10^{-5}	1	1.28×10^{-8}	1	1.2×10^3	1792
Cl	6.63×10^{-7}	0.045	3.89×10^{-9}	0.31	1.7×10^2	1797
Br		0.030				1797
NO ₂	2.07×10^{-9}	1.4×10^{-4}	4.73×10^{-10}	0.037	4.4	1800
7-Norbornyl brosylate	4.49×10^{-10}	3.0×10^{-5}		0.035		
6,7-(CH ₃ O) ₂	4.47×10^{-2}	3000				1785
6,7-(CH ₃) ₂	5.35×10^{-4}	36				

^a At 77.6°. ^b Carbonyl stretching frequencies of 9-benzonorbornenones in CCl₄. Logarithms of the *anti* and *syn* rates are linearly correlated with $\nu_{C=O}$, respectively.

7 is only 8.¹⁵ This value is normal because the inductive effect should decrease rapidly when going through saturated bonds. Accordingly, the transition state in the solvolysis of 4 must involve some type of participation by the aromatic ring.

Linearity of the Hammett plot for the acetolysis may be attained by either of two devices: the use of $1/2(\sigma_p + \sigma_p^+)$ as abscissa, with a ρ of -4.80 , or the use of $1/2(\sigma_p^+ + \sigma_m^+)$, with a ρ of -5.10 . The idea behind the former method was that the reaction involves a transition state in which there is both π and σ bonding to the carbonium ion center as in 12 and 13 (unsymmetrical homobenzylic conjugation). The latter correlation would be appropriate if participation involved contribution from both the *meta* and *para* positions simultaneously, so that both σ_p^+ and σ_m^+ contribute to the stability of a symmetrical nonclassical transition state, as indicated in 14.^{13b}



Evidence for a Symmetrical Transition State

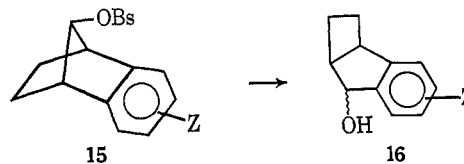
6,7-Dimethoxy- and 6,7-dimethyl-*anti*-9-benzonorbornenyl brosylates were synthesized, and it was found that the effect on the rate of introducing a second 7-methoxy or 7-methyl substituent is the same as for the introduction of the first methoxyl or methyl group

(15) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Am. Chem. Soc.*, **89**, 2928 (1967).

(Table I).¹⁶ The results correlate well with $(\sigma_p^+ + \sigma_m^+)$ (Figure 1) and strongly suggest a symmetrical transition state. Inasmuch as the transition state of this highly endothermic step probably resembles the carbonium ion produced (the Hammond postulate), the results imply that the carbonium ion is symmetrical in the same sense.

Substituent Effects on the *anti:syn* Rate Ratio

Solvolysis of *syn*-9-benzonorbornenyl brosylate (15) leads to rearranged *anti*- and *syn*-2-benzo[3,4]bicyclo[3.2.0]heptenols (16). The factor, $k_{CH_3O}:k_{NO_2}$, was 43. This indicates that there is no significant participation, such as in the *anti* acetolysis. However, the factor of 43 is too large for a simple electrostatic interaction. The rate change in the *anti* series involves two factors: participation by the aromatic π system and a *syn* effect. By eliminating this effect, the *anti:syn* rate ratio should represent the rate change due only to participation. Table I shows that the ratio changes from 3.9×10^4 for the methoxyl derivative to 4.4 for the nitro derivative. The same kind of plots as the above, $\log(k_{anti}:k_{syn})$ vs. $1/2(\sigma_p^+ + \sigma_m^+)$, yield a good correlation with $\rho = -3.57$. The large negative ρ value 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 are diminished by introducing deactivating substituents.



π -Participation in the 2-Benzonorbornenyl System

Three groups¹⁷ recently determined the effects of methoxy substituents on rates of solvolysis of *exo*-2-benzonorbornenyl derivatives (17): the 6-methoxy sub-

(16) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966).
(17) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968); (b) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); (c) H. C. Brown and G. L. Trittle, *ibid.*, **90**, 2689 (1968).

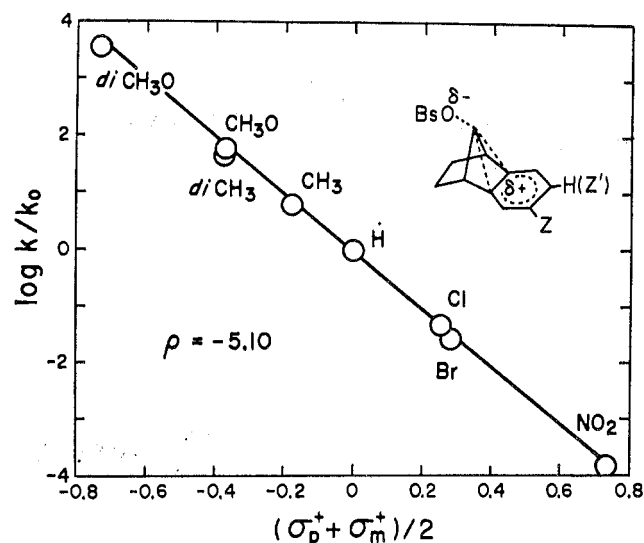
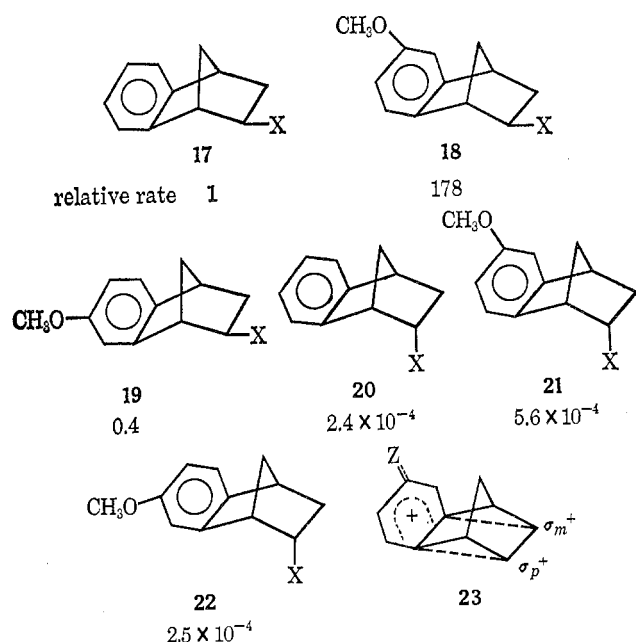


Figure 1. The ρ - σ treatment of the relative rates in acetolyses of substituted *anti*-9-benzonorbornenyl brosylates.

stituent (a *homo-para* system) (18) accelerates the rate by a factor of 178 (77.6°), whereas the *homo-meta* 7-methoxy substituent (19) depresses it by a factor of 0.4. In the *endo*-2-benzonorbornenyl series (20), the 6-methoxyl (21) increases the rate slightly (2.3), but the 7-methoxyl (22) has almost no effect. We predict that in the *exo* series the rates at the *homo-para* position will correlate with σ_p^+ and those at the *homo-meta* position with σ_m^+ , just as in electrophilic aromatic substitution reactions (23).^{13a}



Variation of Participation Effects from Secondary to Tertiary Systems

It has been suggested without firm experimental supporting evidence that, 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 *anti:syn* (or *exo:endo*) rate ratio in the norbornyl derivatives, which has been attributed to par-

Table II

Rates of Acetolysis and *anti:syn* Rate Ratios for Secondary and Tertiary 9-Benzonorbornenyl Arenesulfonates^a

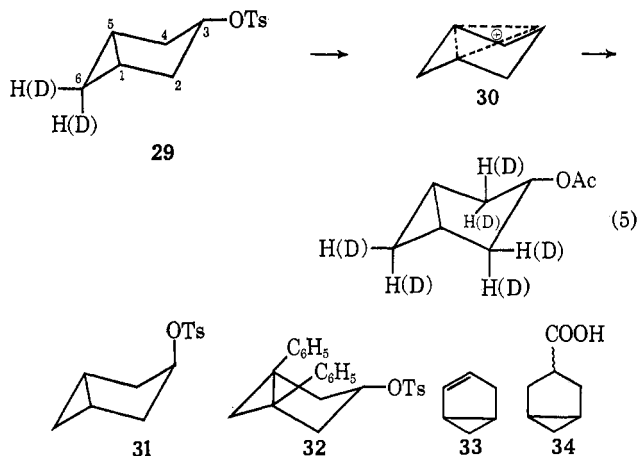
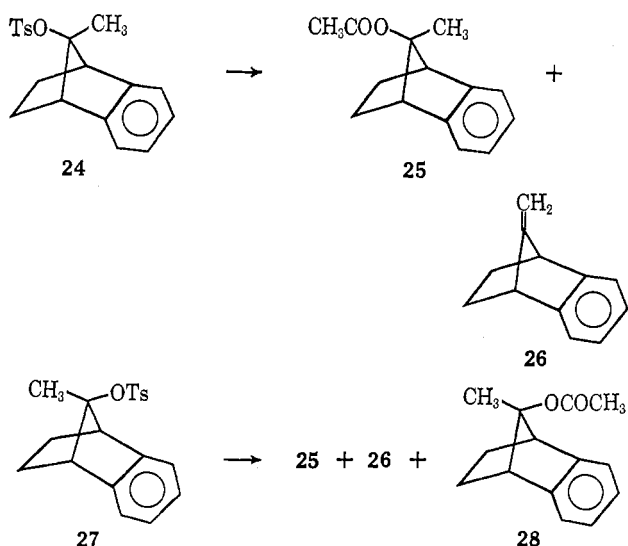
Compd	k_1 , sec ⁻¹	Rate ratio ^d	
		<i>anti:syn</i>	Me:H
9-Methyl- <i>anti</i> -9-benzonorbornenyl ^b (24)	3.12×10^{-3}	493	18,000
9-Methyl- <i>syn</i> -9-benzonorbornenyl ^b (27)	6.33×10^{-6}		86,700
<i>anti</i> -9-Benzonorbornenyl ^c (4)	5.01×10^{-7}	2400	
<i>syn</i> -9-Benzonorbornenyl ^c (15)	2.12×10^{-10}		
7-Methyl-7-norbornyl ^b	1.15×10^{-4}		5.1×10^7
7-Norbornyl ^c	6.48×10^{-12}		

^a At 50.0°. ^b *p*-Toluenesulfonate. ^c *p*-Bromobenzenesulfonate. ^d Calculated with the rate ratio *p*-bromobenzenesulfonate:*p*-toluenesulfonate = 2.9.

ticipation, should drop.¹⁸ The rates and products from acetolysis of 9-methylbenzonorbornenyl (9-*anti* and 9-*syn*)-tosylates (24 and 27) constitute a good test of this suggestion, which is a key tenet of nonclassical carbonium ion theory. Rate data for 24, 27, and some comparison compounds are set forth in Table II.¹⁵ Acetolysis of 24 afforded a mixture consisting of 98% of the *anti* acetate 25 with retention and 2% of the 9-methylene compound 26, an elimination product, while acetolysis of 27 yielded a mixture consisting of 67% 25, 21% 26, and 10% *syn* acetate 28. Absence of the inverted 28 as a product and diminished formation of 26 in the reaction of 24 indicate that participation from the secondary to the tertiary introduces various steric problems, which might lead to a fortuitous cancellation of increasing steric assistance in the tertiary systems with decreasing participation. Therefore, the attenuation of *anti:syn* rate ratios of the above kind does not faithfully reflect the amount of participation existing in the original secondary system.

Brown has observed a relatively constant CH₃:H rate ratio of 55,000 between rates of solvolysis of analogous *t*-butyl and isopropyl derivatives, and a ratio of 1800 between *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. The small CH₃:H factor of 18,000 (for 24 and 4) relative to 86,700 (for 27 and 15) is in accord with the occurrence of participation in the *anti* series, but the difference is, here again, very small. Therefore, we conclude that such a procedure, which involves transformation from

(18) Refer to (a) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 135-136; (b) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 62; and ref 3d.



a secondary to a tertiary system, is an insensitive and indirect test for participation. It was reported that, in solvolysis of the 2-norbornyl and 2-benzonorbornenyl systems, the transformation from these secondary systems to tertiary systems by introducing methyl or phenyl substituents at the reaction sites does not significantly change the *anti:syn* rate ratios.¹⁹ These results are not definitive evidence for the absence of participation in the 2-norbornyl and 2-benzonorbornenyl systems.

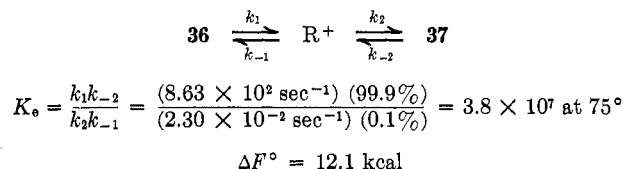
Homocyclopropyl Participation and the Trishomocyclopropenyl Ion Problem

Most of the fundamental concepts in the nonclassical ion hypothesis are involved in the trishomocyclopropenyl ion (**30**) which has been proposed by Winstein and Sonnenberg in the acetolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate (**29**).²⁰ Solvolysis of **29** proceeds some nine times more rapidly than that of the *trans* isomer **31**, shows special salt effects, and yields almost exclusively the *cis* acetate with retention (eq 5). In contrast, **31** yields a mixture of olefin and inverted *cis* acetate. When tosylates deuterated at position 6 are used, the acetate obtained from **29** has deuterium equally distributed at positions 2, 4, and 6, but in that from **31** there is little redistribution. These results were interpreted in terms of direct participation by the C₁-C₆ bonding electrons in the ionization of **29** and consequent formation of the symmetrical **30**.

However, **30** is not compatible with the observation that 3-deuterio-*cis*-3-bicyclo[3.1.0]hexylamine undergoes deamination to give a mixture of *cis* and *trans* 3-alcohols with little scrambling of the label, together with *cis* and *trans* 2-alcohols.^{21a} Phenyl substitutions at C₁ and C₆ in **29** (**32**) cause no rate enhancement.^{21b}

By these results, Corey prefers a mechanism involving a rapidly equilibrating set of classical isomeric ions.²¹ Furthermore, acid-catalyzed addition reactions to the olefin (**33**)²² and electrolytic oxidative decarboxylation of the acids (**34**)²³ did not indicate unique stability for **30**, but rather considerable stability for the 2-carbonium ion.

The acetolysis of *exo-anti*-8-tricyclo[3.2.1.0^{2,4}]octyl brosylate (**35**), in which p-like orbitals of the *exo*-cyclopropyl group are directed away from the reactive 8 position, is slower by a factor of 3 than the acetolysis of the "slow" 7-norbornyl brosylate.²⁴ In striking contrast, the solvolysis of the *endo* isomer **36**, where the cyclopropyl ring orbitals are directed toward the 8 position, proceeds with rate enhancement by a factor of 10¹⁴-10¹⁵.²⁵ Hydrolysis of the *p*-nitrobenzoate **36-O-p-NB** in buffered 70% aqueous acetone yielded a mixture of alcohols in 82.2% yield and an internally returned, less reactive *p*-nitrobenzoate (**37-O-p-NB**) in 15.2% yield. The alcohol mixture was composed of 99.9% of the rearranged *endo*-3-tricyclo[5.1.0.0^{4,8}]octanol (**37-OH**) and 0.1% of the retained **36-OH**.²⁶ The reaction with **37-OTs** proceeded, forming alcohols of the same types and composition and, therefore, *via* identical intermediate(s). The partition factor and the reactivity ratio between the **36** and **37** systems thus obtained lead to an energy profile. The ground-state



(21) (a) E. J. Corey and R. L. Dawson, *J. Am. Chem. Soc.*, **85**, 1782 (1963); (b) E. J. Corey and H. Uda, *ibid.*, **85**, 1788 (1963).

(22) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

(23) P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 2252 (1966).

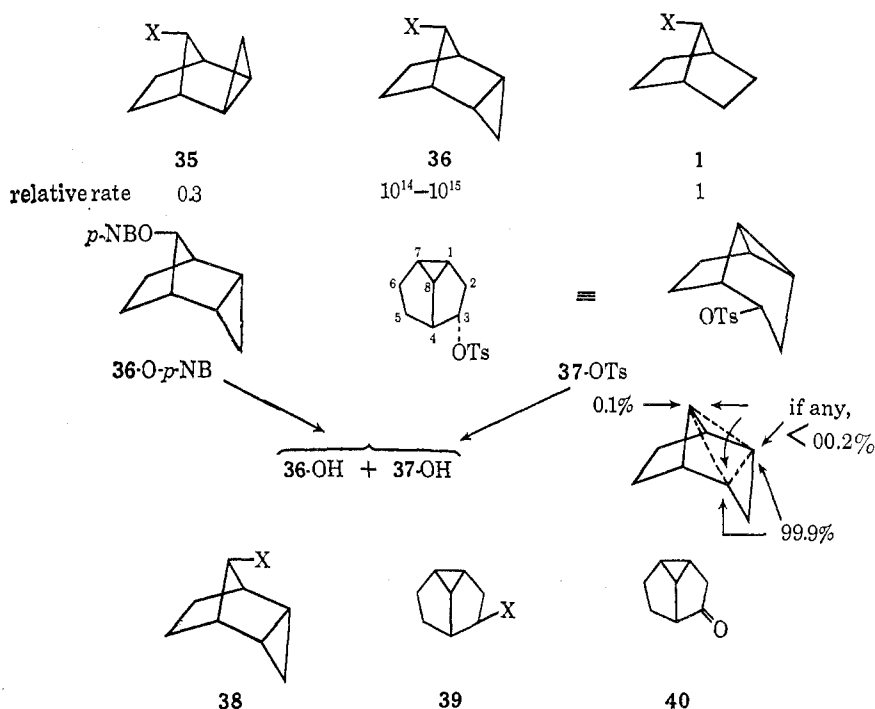
(24) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(25) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

(26) Hydrolysis in the presence of 2 equiv of NaHCO₃ gives a mixture of alcohols of the reported composition.^{25a} It has been found that the composition is sensitive to the presence of alkali.

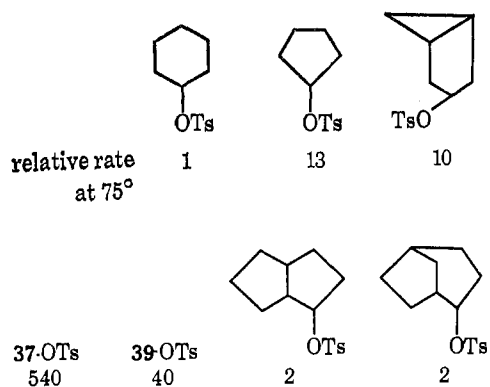
(19) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **86**, 1246, 1247, 1248, 5004, 5006 (1964); **88**, 1320 (1966).

(20) (a) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961); (b) S. Winstein, E. C. Friedrich, R. Baker, and Y.-I. Lin, *Tetrahedron Suppl.*, **8**, Part II, 621 (1966).



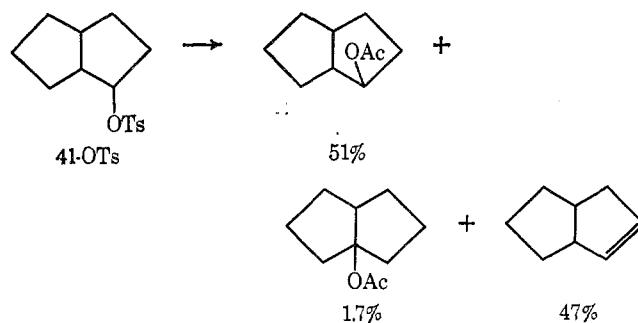
energy difference, ΔF° , suggests that the transformation of **36** to **37** involves a considerable amount of strain relief.

However, **37-OTs** is still very reactive. Comparison of its solvolysis rate with those of almost all the compounds considered by us to be appropriate is as follows.



The *exo* tosylate **39-OTs** forms mainly *endo*-3-tricyclo[2.2.2.0^{2,6}]octanol, so that its reactivity cannot be discussed on the same basis as for **37-OTs**. The stereospecificity in products from **36-O-p-NB** and **37-OTs** is remarkable; the *syn*-**38** and the *exo*-**39** derivatives were demonstrated to be absent, or at least not present in amounts greater than 0.02%. In contrast, the results from acetolysis of a model compound, *endo*-2-bicyclo[3.3.0]octyl tosylate (**41-OTs**), were as shown below.²⁷

Reductions of the ketone **40** with several kinds of complex metal hydrides led to a very predominant formation of the *endo* **37-OH**. Equilibration experiments afforded a mixture of 38% **37-OH** and 62%



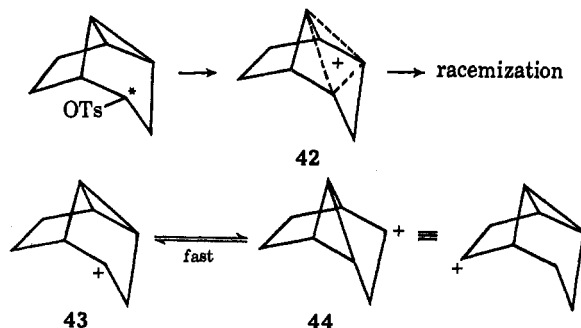
39-OH.²⁸ The carbonyl stretching band of **40** (1743 cm^{-1}) is located at a region near those for some models, 3-bicyclo[3.1.0]hexanone (1739 cm^{-1}) and 2-bicyclo[3.3.0]octanone (1738 cm^{-1}). These results indicate that (a) the solvolysis of **37-OTs** proceeds exclusively or almost exclusively with retention of configuration; (b) on the assumption of Dauben's "steric approach control," a carbonium ion intermediate(s) is collapsing by solvent attack from the *endo* direction sterically less favored than the *exo*; (c) the predominantly formed **37-OH** is not a thermodynamically favored alcohol; and (d) if one can use a ketone as a carbonium ion model, it is unreasonable to consider an unusually strained state for the cationic intermediate from **37-OTs** as compared to those from **29** and **41-OTs**. Consequently, it is very difficult to explain the high reactivity and the stereoselective product formation of **37-OTs** on the basis of steric factors. However, direct participation by the C₁-C₃ bonding electrons is not inconsistent with the facts.

An optically active sample of **37-OH** was prepared. In acetolysis of its tosylate at 25°, the rate of loss of the optical activity was 3.2 times faster than the rate of

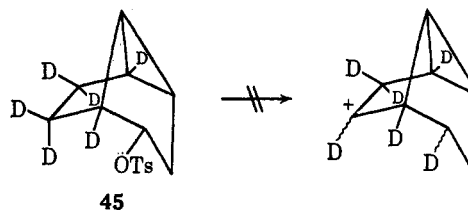
(27) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron Letters*, 6435 (1966).

(28) Almost the same composition, 39% *endo* and 61% *exo*, has been reported in an equilibration with **41-OH** by A. C. Cope, M. Brown, and H. E. Petree, *J. Am. Chem. Soc.*, **80**, 2852 (1958).

acid production (evidence for internal return). Complete racemization was observed. Our experiments showed that remaining activity, if any, was less than 2.2% in buffered acetolysis and 2.3% in buffered hydrolysis. The racemization indicates that the reaction proceeds through a symmetrical trishomocyclopropenyl cation (42), rapidly interconverting unsymmetrical cations (43 and 44), or the occurrence of the 1,3-hydride shift from C₅ to C₃. The properly polydeuterated material 45 was prepared, and its acetolysis ruled out the 1,3-hydride shift.



Our findings so far obtained are not direct evidence for the existence of the trishomocyclopropenyl ion, but



it is possible to accommodate all the results simply and economically by the formulation of the nonclassical structure. Most theories and concepts of chemistry are still built empirically by the accumulation of experimental evidence.

This paper is based on lectures given at Universität München, Università di Roma, École Nationale Supérieure de Chimie, Institut de Chimie des Substances Naturelles, Université D'Aix-Marseille, Harvard University, State University of New York at Albany, University of Ottawa, Case Western Reserve University, Michigan State University, Loyola University, University of California at Santa Cruz, and University of Alberta during the fall of 1967. The author thanks Professors R. Huisgen, G. Illuminati, M. Julia, H. Felkin, B. Waegell, P. D. Bartlett, W. D. Closson, R. R. Fraser, G. A. Olah, H. Hart, J. W. Wilt, J. F. Bunnett, and S. Masamune of the respective universities and, in addition, Professor M. Hanack of Tübingen for their invitations, hospitality, and helpful discussions. It is a pleasure to acknowledge the contribution of my coworkers, whose names are to be found in the references.

Additions and Corrections

Volume 1, 1968

Hiroshi Tanida: Solvolysis Reactions of 7-Norbornenyl and Related Systems. Substituent Effects as a Diagnostic Probe for Participation.

Page 243. In the formula at the bottom of the right column, $R^+ \rightleftharpoons \mathbf{37}$ should read $R^+ \rightleftharpoons \mathbf{37}$.

Page 244. In the upper chart, <00.2% should read <0.02%.