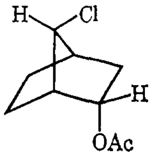
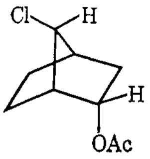
since both **3** and **4** gave the same reaction mixture it could be assumed that both **3** and **4** were yielding the same intermediate. This behavior is clearly different from that observed for 7-oxygenated norbornanes[1] but similar to that noted for the parent norbornyl system. This indicates to us that **3** and **4** may be satisfactory compounds for the generation of an electron-deficient norbornyl cation.

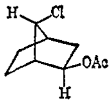
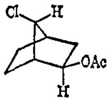
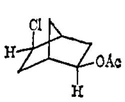
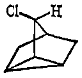


**11**



**12**

Table II. Products from the Acetolysis of 7-Chloro-2-tosyloxynorbornanes

| Starting tosylate[b] | Percentage composition of the product mixture[a]<br><br>**7** | <br>**8** | <br>**9** | <br>**10** | Other |
|---|---|---|---|---|---|
| **3**[c] | 14 | 70 | 9 | 4 | 3 |
| **4** | 11 | 69 | 8 | 7 | 5 |
| **1**[c] | 45 | 42 | 9 | 2 | 2 |
| **2** | 24 | 42 | 8 | 16 | 9 |

[a] Product analyses were carried out by vpc after *ca.* 10% reaction since considerable decomposition occurred on prolonged reaction time. [b] Structures in Table I. [c] Roberts and coworkers previously published a product study on **1** and **3**. On the basis of infrared spectra they estimated that both **1** and **3** gave a 50:50 mixture of **7** and **8** (ref 3).

In the epimeric pair **1** and **2** the chlorine was *syn* to the leaving tosylate group and might be expected to have some interaction with the leaving group. Although the rate comparison indicated very little influence of the stereochemistry of the chlorine, product studies showed that **1** and **2**, although they produced the same products, gave different product mixtures with the predominant path for **2** involving an initial hydride shift. Thus **1** and **2** are less satisfactory models than **3** and **4**.

The high *exo*/*endo* rate ratio, the formation of the same products, and the absence of *endo* products in the solvolysis of the 7-chloro-2-tosyloxynorbornanes indicate that norbornanes in which the formation of a partial positive charge in the 1 position is electronically unfavorable can still behave in a manner very similar to the parent norbornyl system. It would appear that this similarity is most consistent with the theory that there is very little delocalization of charge in the ionization of **5** and **6**.

**Acknowledgment.** This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(7) Alfred P. Sloan Research Fellow, 1967–1969.
(8) National Science Foundation Trainee, 1965–1968.

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*Received December 23, 1968*

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## Substituent Effects on the Acetolysis of *exo*- and *endo*-2-Norbornyl Tosylates

*Sir:*

A crucial point of discussion in relation to the classical–nonclassical norbornyl cation controversy has been the meaning of the *exo*/*endo* rate ratios observed in the solvolysis of 2-norbornyl arenesulfonates.[1] The classical carbonium ion school of thought suggests that *exo*-2-norbornyl tosylate (**1**) solvolyzes at a "normal" rate while *endo*-2-norbornyl tosylate (**2**) solvolyzes abnormally slow for steric reasons.[1b,2] In contrast the nonclassical theory would have **2** solvolyzing at a "normal" rate while **1** is proposed to be abnormally fast owing to neighboring group participation by the 1,6 $\sigma$ electrons.[1d] Our studies on the effect of electron-withdrawing substituents on the *exo*/*endo* rate ratio of 2-norbornyl tosylates have shown that certain 7-oxygenated *exo–endo* pairs behave anomalously, and thus have meaningless *exo*/*endo* rate ratios,[3] while the *anti*-7-chloro-2-tosyloxynorbornanes appear to solvolyze in an uncomplicated fashion and hence should have a meaningful *exo*/*endo* rate ratio.[4] In order to gain an insight into the over-all effects of substituents on the rates of solvolysis of norbornane derivatives, we have collected and correlated the rates of eight different *exo–endo* pairs of 7-substituted 2-norbornyl tosylates. We wish to report at this time on the results of this correlation and on the mechanistic implications of these results.

Table I lists the rates of acetolysis at 25° for eight 7-substituted *exo*-2-tosyloxynorbornanes.[5–9] A $\rho\sigma^*$ plot of the data is shown in Figure 1. For the eight 7-substituted *exo*-2-tosyloxynorbornanes $\rho$ was $-2.33$ (correlation coefficient $-0.979$). Considering the approximations involved, this correlation was unusually good. Although the plot covers a rate spread of *ca.* 18,000 (the rate difference between **3** and **9**), all points fall within a rate factor of 3 of being on the least-squares slope.

In contrast to the unexpectedly good correlation of the reaction rates of *exo*-2-tosyloxynorbornanes with the inductive effect of various 7-substituents, a similar correlation for the corresponding *endo* isomers listed in Table II can best be described as giving an almost

(1) For recent reviews which discuss this point, see: (a) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 111–232; (b) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); *Chem. Eng. News*, **45**, 87 (Feb 13, 1967); Special Publication No. 16, The Chemical Society, London 1962, p 140; (c) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (d) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965); (e) G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); see also P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1966.

(2) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966).

(3) P. G. Gassman and J. G. Macmillan, *J. Am. Chem. Soc.*, in press, and references contained therein.

(4) P. G. Gassman and J. M. Hornback, *ibid.*, **91**, 4280 (1969).

(5) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).

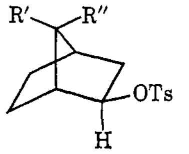
(6) S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952); S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, 74, 1127 (1952); P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965).

(7) P. J. Stang and P. von R. Schleyer, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, No. P-192. We wish to thank Professor Schleyer for providing us with the rates of 4 and 11 prior to publication.

(8) P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, 2433 (1968).

(9) P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966).

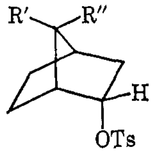
Table I. Acetolysis Rates at 25° for



| Compound R' | Compound R'' | Compound no. | Ref | Rate, sec$^{-1}$ [a] | $k_{rel}$ at 25° | $\sigma^*$ [b] |
|---|---|---|---|---|---|---|
| CH$_3$ | CH$_3$ | **3** | 5 | $2.57 \times 10^{-4}$ | 17,800 | −0.20 |
| H | H | **1** | 6 | $2.33 \times 10^{-5}$ | 1,620 | 0.00 |
| OCH$_3$ | H | **4** | 7 | $1.95 \times 10^{-6}$ | 136 | +0.52 |
| CH$_2$—<br>O | CH$_2$<br>O | **5** | 3 | $1.29 \times 10^{-7}$ | 9 | +1.04 |
| OCH$_3$ | OCH$_3$ | **6** | 8 | $9.53 \times 10^{-8}$ | 7 | +1.04 |
| H | Cl | **7** | 4 | $6.62 \times 10^{-8}$ | 5 | +1.05 |
| Cl | H | **8** | 4 | $4.29 \times 10^{-8}$ | 3 | +1.05 |
| ┌—O—┐ | | **9** | 9 | $1.44 \times 10^{-8}$ | 1 | +1.65 |

[a] The rate of 7,7-dimethyl-*exo*-tosyloxynorbornane was obtained by lowering the rate of the corresponding brosylate by a factor of 3. Most of the rates cited are extrapolated from higher temperatures. [b] For the ethylene glycol ketal **5** and the dimethyl ketal **6** it was assumed that the inductive effects of the two ether linkages were additive and that the ethylene glycol ketal had the same over-all inductive effect as the dimethyl ketal. In order to be consistent the $\sigma^*$ values listed are for $\Sigma\sigma^*_{RC}$.

Table II. Acetolysis Rates at 25° for



| Compound R' | Compound R'' | Compound no. | Ref | Rate, sec$^{-1}$ [a] | $k_{rel}$ at 25° | $\sigma^*$ [b] |
|---|---|---|---|---|---|---|
| CH$_3$ | CH$_3$ | **10** | 5 | $6.27 \times 10^{-8}$ | 230 | −0.20 |
| H | H | **2** | 6 | $8.28 \times 10^{-8}$ | 310 | 0.00 |
| OCH$_3$ | H | **11** | 7 | $3.08 \times 10^{-8}$ | 110 | +0.52 |
| CH$_2$—<br>O | CH$_2$<br>O | **12** | 3 | $1.20 \times 10^{-8}$ | 45 | +1.04 |
| OCH$_3$ | OCH$_3$ | **13** | | $2.51 \times 10^{-9}$ | 9 | +1.04 |
| H | Cl | **14** | 4 | $2.69 \times 10^{-10}$ | 1 | +1.05 |
| Cl | H | **15** | 4 | $5.38 \times 10^{-10}$ | 2 | +1.05 |
| ┌—O—┐ | | **16** | 9 | $8.66 \times 10^{-8}$ | 320 | +1.65 |

[a] The rate of 7,7-dimethyl-*endo*-2-tosyloxynorbornane was obtained by decreasing the rate of the corresponding brosylate by a factor of 3. Most of the rates cited are extrapolated from higher temperatures. [b] For the ethylene glycol ketal **12** and the dimethyl ketal **13** it was assumed that the inductive effects of the two ether linkages were additive and that the ethylene glycol ketal had the same over-all inductive effect as the dimethyl ketal. In order to be consistent the $\sigma^*$ values listed are for $\Sigma\sigma^*_{RC}$.

random distribution. The success of the correlation of the 7-substituted *exo*-2-tosyloxynorbornanes with $\sigma^*$ for the 7-substituents and the failure of the similar correlation for the *endo* isomers was indicative of several points of interest. For the previously discussed[3,8] anomalous behavior of the 7-oxygenated *exo–endo* pairs our correlation shows that the *exo* isomers are behaving as would be expected on the basis of inductive effects while the *endo* isomers are the ones which were involved with some type of unusual interaction with the oxygenated function at C-7.[10]

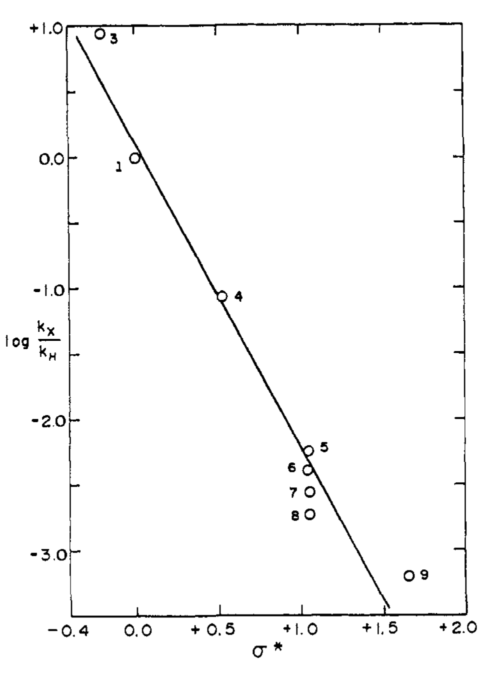


Figure 1. Plot of log $k_X/k_H$ *vs.* $\sigma^*$ for the acetolysis of 7-substituted *exo*-2-tosyloxynorbornanes.

Unfortunately the correlation shown in Figure 1 does not allow any definite conclusions to be reached in relation to the classical–nonclassical carbonium ion controversy by itself. The decrease in rate with increase in electron-withdrawing power of the 7-substituents would be predicted by both theories. In terms of classical carbonium ion theory, a linear decrease in rate should be noted. Nonclassical carbonium ion theory might predict that a break should occur in the plot when the electron-withdrawing group becomes strong enough to prevent delocalization of the developing positive charge to C-1. However, we have recently shown that participation is a function of the electron demand of the incipient carbonium ion.[11] Thus unless some of the electron-withdrawing groups completely eliminate delocalization of charge to C-1, a linear plot could result. If the chloro and carbonyl groups were powerful enough to eliminate any nonclassical ion formation, then the correlation shown in Figure 1 would be most consistent with the classical carbonium ion concept of the norbornyl cation.

When the rates of **2**, **10**, **14**, and **15** (which do not have oxygenated functions in the 7 position) were plotted *vs.* $\sigma^*$, a $\rho$ of −1.94 was obtained with a correlation coefficient of −0.983. This is close to the $\rho$ of −2.33 observed for the eight *exo* derivatives.[12] Although this plot indicates that electron-withdrawing substituents have a slightly larger effect on the rates of acetolysis of *exo*-2-tosyloxynorbornanes than on the rates of acetolysis of *endo*-2-tosyloxynorbornanes, the magnitude of

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(10) In the case of **13** it has been shown that this *endo*-tosylate solvolyzes with MeO-4 neighboring group participation: P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, 2429 (1968). The type of interaction involved with the other 7-oxygenated functions is unknown.

(11) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **91**, 1246 (1969).

(12) The $\rho\sigma^*$ plot for the *endo* derivative is not particularly good. Although $\rho$ represents the least-squares line for these four points it should be noted that an increase of the rate of acetolysis of **10** by a factor of 4 or a decrease in the rate of acetolysis of **15** by a factor of 4 would make the $\rho$ for the four *endo* tosylates the same as the $\rho$ for the eight *exo* tosylates. Inclusion of the rate for the *anti*-7-methoxybicyclo-[2.2.1]heptan-*endo*-2-ol *p*-toluenesulfonate gave a $\rho$ of −1.92 for the five-point graph. Since the methoxyl group of **11** is *anti* to the leaving tosylate function, the types of interaction which it could have with the incipient carbonium ion are limited.

this difference was very small. *In fact, the comparison of the two plots indicates that if there was no anchimeric assistance in the solvolysis of* **9**, *the maximum rate factor attributable to anchimeric assistance in the solvolysis of exo-2-tosyloxynorbornane* (**1**) *would be less than 5.*

**Acknowledgment.** This work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

[13] Alfred P. Sloan Research Fellow, 1967–1969.

[14] National Science Foundation Cooperative Predoctoral Fellow, 1962–1963, 1964–1966.

[15] National Science Foundation Trainee, 1965–1968.

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*Received December 23, 1968*

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## Carbonium Ions. III.
## Acetolysis of 2-Arylethyl Tosylates

*Sir:*

In the analysis of solvolytic reactions involving primary and secondary arenesulfonate esters with neighboring aryl groups it has been proposed for many years that neighboring aryl group bridging can occur in the ionization step as one of the reaction paths leading to products.[1,2] In systems of the type shown in eq 1 this analysis leads to the conclusion that there are two

$$\mathrm{ArCH_2CH_2OTs} \xrightarrow{\mathrm{HOAc}} \mathrm{ArCH_2CH_2OAc} + \mathrm{HOTs} \qquad (1)$$

competing paths for displacement of tosylate, which are designated as $k_\Delta$ and $k_s$. These paths are simultaneous reactions, each with its own characteristics, and there is no crossover between them. The $k_\Delta$ path involves aryl participation, as the tosylate group leaves, to give phenonium ion and this accounts for scrambling of the two carbons of the ethyl side chain.[3] The $k_s$ path involves direct SN2 displacement by nucleophile. Winstein and coworkers[2] have pointed out that only a fraction ($F$) of the phenonium ions goes on to product, while a fraction ($1 - F$) returns to covalent starting material. This dictates that the relationship between the rate constants for these two paths and the titrimetric rate constant will be $k_t = Fk_\Delta + k_s$. The rate constant for scrambling in the starting material will be $k_{14} = (1 - F)k_\Delta$.

It has been proposed by Brown and coworkers[4] that there are serious inconsistencies in the preceding theory.

In an extension of methods used by earlier workers[2d,5] a complete analysis of all rate constants ($k_t$, $k_\Delta$, $k_s$, and $k_{14}$) and $F$ factors for the acetolysis of 2-phenylethyl tosylate has been carried out[6] in the absence of acetate ion. Using the methods previously described[6] the acetolysis of 2-*p*-chlorophenylethyl, 2-*p*-methylphenylethyl, and 2-*p*-methoxyphenylethyl tosylates in the absence of acetate ion have been analyzed. In each case the product acetate was shown to be stable to rearrangement in the reaction mixture. The per cent rearrangement in the product acetate for each compound was determined at two temperatures for the initial stage of reaction (time = 0) and the final stage of reaction (time = ∞) and the results are shown in Table I.

**Table I.** Rearrangement in Product of Acetolysis of 2-Arylethyl-1-$^{14}$C Tosylates (0.5 *M*)

| Aryl group | Temp, °C | % rearr at time = 0 | % rearr. at time = ∞ |
|---|---|---|---|
| *p*-Chlorophenyl | 90 | 3.0 | 11.7 |
| | 115 | 4.4 | 15.5 |
| Phenyl[a] | 90 | 11.9 | 30.3 |
| | 115 | 14.6 | 33.4 |
| *p*-Methylphenyl | 90 | 35.4 | 47.4 |
| | 115 | 35.8 | 48.4 |
| *p*-Methoxyphenyl | 65 | 43.7 | 48.8 |
| | 90 | 43.4 | 49.6 |

[a] Data for the phenyl compound taken from ref 6.

Using standard literature procedures[2d,7] the titrimetric rate constants, $k_t$, and the rate constants for scrambling of the starting tosylate, $k_{14}$, were determined under conditions identical with those used for the product rearrangement studies and these are shown in Table II. Also shown in Table II are the values for various other rate constants and parameters calculated by the procedure given earlier.[6] For those rate constants and parameters calculated by the time = 0 and time = ∞ methods, Table II shows the average of the two approaches with the difference between each method and the average being shown as the ± error. Some of the values in Table II can be compared to the results of earlier workers. Jenny and Winstein[2d] studied the *p*-methoxyphenylethyl tosylate at one temperature and the values they obtained were $k_t^{75} = 6.9 \times 10^{-6}$ sec$^{-1}$, $k_{14}^{75} = 1.91 \times 10^{-5}$ sec$^{-1}$, $k_\Delta^{75} = 2.6 \times 10^{-5}$ sec$^{-1}$, $F = 0.266$. The values we obtain for $k_\Delta$ and $F$ are slightly different from those of Jenny and Winstein. We would caution against a rigorous interpretation based on the magnitude of $F$ since its determination is rather sensitive to a number of factors.

Since $k_s$ is influenced only by the inductive effects of the aryl group and its substituent while $k_\Delta$ is a function of the electron-donating ability of the aryl group the trends observed for $k_s$ and $k_\Delta$ in Table II are reasonable. The ranges of $\Delta S^{\ddagger}$ for the $k_\Delta$ and $k_s$ paths are in agreement with predictions.[2] The relative relationship of $k_\Delta$ and $k_t$ is summarized in Table III to dramatize why $k_t$ values alone should not be used as a test for participation. It should be noted in Table II that determination

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[1] (a) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **71**, 3875 (1949); (c) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1075 (1963); (d) D. J. Cram, *ibid.*, **86**, 3767 (1964); (e) D. J. Cram and J. A. Thompson, *ibid.*, **89**, 6766 (1967).

[2] (a) S. Winstein, *Bull. Soc. Chim. France*, 55C (1951); (b) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953); (c) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956); (d) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); (e) S. Winstein and R. Baker, *J. Am. Chem. Soc.*, **86**, 2071 (1964); (f) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, **87**, 3504 (1965); (g) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968).

[3] The definition % scrambling = 2 × % rearrangement will be used.

[4] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); (c) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968).

[5] J. W. Clayton and C. C. Lee, *Can. J. Chem.*, **39**, 1510 (1961).

[6] J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *J. Amer. Chem. Soc.*, **91**, 1154 (1969).

[7] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).