# Increased Electron Demand in the Solvolysis of Secondary 2-Norbornyl Tosylates[1]

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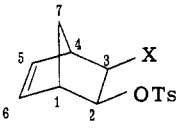
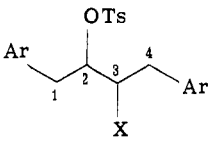
**Abstract:** Placement of an electron-withdrawing group at the 3 position of an *exo*-2-norbornyl tosylate increases electron demand at the 2 position during solvolysis. Whereas analogous substitution in the 2-norborn-5-enyl series greatly enhances the amount of 5,6 double bond participation, no such enhancement of participation from the 6,1 single bond is observed in the 2-norbornyl series, as measured by the exo/endo rate ratios. This result is consistent with the absence of $\sigma$ participation. The steric effect of the electron-withdrawing 3-endo substituent is found to be relatively small for the groups studied, by comparison with the effect of cyclohexyl.

Participation by a double bond[2] or by an aryl group[3] in the solvolysis of a secondary tosylate can be enhanced by the presence of an adjacent electron-withdrawing group. Thus the ratio of the acetolysis rate for *exo*-2-norborn-5-enyl tosylate (**1**, X = H) compared with that of its saturated analogue is only 0.29, whereas that of the 3-tosyloxy derivative (**1**, X = OTs)



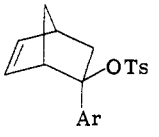

**1**



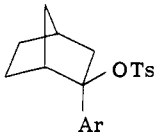

**2**

is 500.[2] Identical results are obtained when X is OAc or even when the adjacent group is endo. Similarly, the percent of aryl participation increases from 35 to 94% in **2** (Ar = $C_6H_5$) when X is changed from H to OTs. When Ar = *p*-$CH_3C_6H_4$, the increase is from 66 to 99%.[3] The electron-withdrawing X group (OTs or OAc) destabilizes the development of positive charge in the transition state. Electron demand at the 2 position is thereby increased (compared with the case when X is H), and the system has a greater need for participation. The double bond in **1** and the aryl group in **2** respond by providing stronger assistance to departure of the leaving group.

The most controversial of the modes of participation is that by $\sigma$ bonds.[4] With success in observing enhanced participation in the above $\pi$ systems, we wanted to extend the method to the focal point of the $\sigma$ bond participation controversy, the 2-norbornyl system. Recent experimental approaches to this problem have included application of the Gassman-Fentiman[5] method of manipulating electron demand. By this method, a 2 aryl group, as in **3** and **4**, eliminates the need for anchimeric




**3**

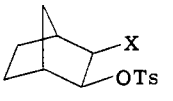



**4**

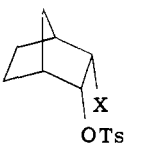
assistance by stabilizing the developing positive charge. Thus the strong double-bond participation in 7-norbornenyl systems can be removed by appropriate aryl substitution at the 7 position.[5] If the aryl group at the 2 position in **3** or **4** is sufficiently electron withdrawing, the tertiary system can be made to resemble the secondary system, in terms of electron demand at the 2 position. Various properties such as the exo/endo ratio and the percent exo product can then be examined over the entire series and compared to that in the secondary system. Whereas double-bond participation could be clearly perceived as the aryl group in **3** became more electron withdrawing,[6] analogous changes were not observed in **4**.[7] Although these results simultaneously provide strong evidence for double-bond participation and strong evidence against $\sigma$ participation, they are subject to the immediate criticism that tertiary systems may have fundamental differences from secondary systems. The ultimate test for $\sigma$ participation must be performed on a secondary norbornyl system.

The method we previously applied to double-bond and aryl systems permits increased electron demand at the site of charge development within the framework of a secondary system.[2,3] Substitution at the 5 or 6 positions in the norbornenyl system or at the 6 or 1 positions of the norbornyl system makes a fundamental electronic alteration in the participating entity. Although valid experiments can be carried out on such systems, e.g., 5-methylnorbornenyl, their results do not answer the question of participation in the parent system. The point of substitution for our method is the 3 position. Substitution further away, e.g., at the 4 position, would deliver too small a polar effect at the 2 position to be effective. Substitution at the 3 position retains the secondary nature of the site of positive charge development and does not alter the nature of the participating double bond or $\sigma$ bond to any significant extent. Furthermore, our method does not significantly alter the hybridization of the 3 carbon orbitals (as occurs in a 3-*exo*-methylene or a 3-spiro[2] system). Changing the 3 carbon from $sp^3$ to $sp^2$ alters the steric environment around the 2 carbon atom and probably changes the mechanism to $\pi$ or $\sigma\pi$ conjugation.

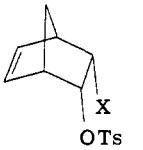
The specific system needed to test the effects of increased electron demand in the norbornyl series is **5**, in which the X




**5**




**6**




**7**

group is electron withdrawing. For comparison with an analogous system in which participation is supposedly impossible, we also need an endo tosylate, as in **6**. The cis relationship between X and the leaving group assures that direct *n*-type participation, which occurs optimally back side (antiperiplanar), is not possible. In the present paper we report the synthesis and acetolysis of the relevant systems to test the effect of increased electron demand on $\sigma$ participation in a secondary system.

## Results

The compounds needed for this study were the exo and endo tosylates **5** and **6**, with X = H, OTs, and OAc. For comparison with the unsaturated series, kinetic data were also needed for

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the exo and endo tosylates **1** and **7**, with X = H and OTs. The data for the unsaturated ditosylates, **1** and **7** (X = OTs), and for the saturated exo acetoxy tosylate, **5** (X = OAc), were available from our previous study.[2] Although the rate data for the saturated exo ditosylate were also available from our previous study,[2] we repeated the measurements in order that both components of this critical exo/endo rate ratio be measured by the same hands. The data for the saturated monotosylates, **5** and **6** (X = H), have already been reported.[8] Surprisingly, the rates of acetolysis of the unsaturated monotosylates, **1** and **7** (X = H), have never been measured, although a generation of chemists have reported figures based on calculations from the brosylates.[9] We felt that it was advisable to prepare the compounds and make the actual measurements. Consequently, the compounds whose synthesis was required for this study were the saturated exo and endo ditosylates (**5, 6,** X = OTs), the saturated endo acetoxy tosylate (**6,** X = OAc), and the unsaturated exo and endo monotosylates (**1, 7,** X = H).

The saturated exo ditosylate (**5,** X = OTs) was prepared as before.[2] For the preparation of the endo ditosylate, cyclopentadiene and vinylene carbonate were condensed to give the endo Diels–Alder adduct, which was hydrogenated and reduced to give the endo diol, which in turn gave **6** (X = OTs) on reaction with tosyl chloride. All tosylations followed the standard Tipson procedure.[10]

The unsaturated exo monotosylate (**1,** X = H) was readily available from *exo*-2-norborn-5-enyl acetate by reduction with lithium aluminum hydride and treatment with tosyl chloride. To obtain the unsaturated endo monotosylate (**7,** X = H), a mixture of *exo*- and *endo*-2-norborn-5-enyl acetates was reduced to the analogous mixture of alcohols, which was oxidized to 2-norborn-5-enone with $CrO_3 \cdot pyr_2$; reduction of the ketone with $NaAlH_2(OCH_2CH_2OCH_3)_2$ gave 2-norborn-5-enol, which was 90% endo. This 9/1 mixture was converted to the tosylate, and the more reactive residual exo isomer was removed by brief acetolysis to give pure **7** (X = H).

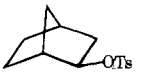
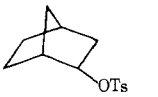
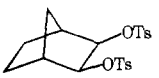
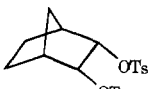
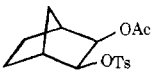
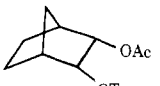
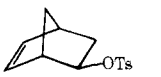
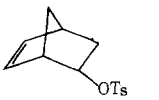
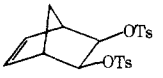
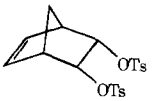
The saturated endo acetoxy tosylate (**6,** X = OAc) was prepared by treatment of the cis-endo diol with 1 equiv of tosyl chloride to give crude hydroxy tosylate, which was treated with acetic anhydride and sulfuric acid to give the desired material.

The saturated trans (exo,endo) ditosylate was obtained from the analogous unsaturated trans diol[2] by hydrogenation and tosylation.

The methods for obtaining acetolysis rates have been described by us previously.[3] Each compound was acetolyzed at three temperatures in order to obtain activation parameters. Normally, simple first-order behavior was observed. In some cases, a steady decrease in the rate was observed with time, so the rates were extrapolated to zero time. The saturated trans compound exhibited an initial rate decrease, which was quickly followed by an increase. As a result, no accurate extrapolation to zero time could be made, so no rate data on this compound are reported. The rates of all the relevant compounds are given in Table I, the rate ratios in Table II, and the activation parameters in Table III.

The products of the acetolysis of the various saturated ditosylates and acetoxy tosylates are relatively similar (Table IV). The products of the unsaturated substrates have been reported previously.[2] The ditosylates are more prone to elimination pathways, giving the unsaturated monoacetates, than are the acetoxy tosylates. For the trans substrate, the major product at 120 °C was an acetoxy tosylate. Product analysis at 200 °C, at which temperature the intermediate acetoxy tosylate should be consumed, exhibited more diacetates.

**Table I.** Rates of Buffered Acetolysis

| Compd | Temp, °C | $k$, $s^{-1}$ | Corr coeff |
|---|---|---|---|
|  | 25.0 | $(2.3 \times 10^{-5})^{a,b}$ | |
| | 100.0 | $(4.7 \times 10^{-2})^{a,b}$ | |
| | 150.0 | $(1.7)^{a,b}$ | |
|  | 25.0 | $(7.3 \times 10^{-8})^{a,b}$ | |
| | 100.0 | $(5.9 \times 10^{-4})^{a,b}$ | |
| | 150.0 | $(4.0 \times 10^{-2})^{a,b}$ | |
|  | 25.0 | $(5.8 \times 10^{-12})^{b}$ | |
| | 100.0 | $(3.6 \times 10^{-7})^{b}$ | |
| | 141.0 | $3.22 \times 10^{-5}$ | 0.999 |
| | 150.0 | $7.26 \times 10^{-5}$ | 0.999 |
| | 150.0 | $(6.4 \times 10^{-5})^{b}$ | |
| | 160.0 | $1.82 \times 10^{-4}$ | 0.999 |
|  | 25.0 | $(1.15 \times 10^{-13})^{b}$ | |
| | 100.0 | $(1.97 \times 10^{-8})^{b}$ | |
| | 150.0 | $(5.7 \times 10^{-6})^{b}$ | |
| | 180.4 | $1.10 \times 10^{-4}$ [c] | |
| | 190.3 | $2.87 \times 10^{-4}$ [c] | |
| | 200.3 | $5.74 \times 10^{-4}$ [c] | |
|  | 25.0 | $(2.5 \times 10^{-10})^{b,d}$ | |
| | 100.0 | $(4.0 \times 10^{-6})^{b,d}$ | |
| | 150.0 | $(3.8 \times 10^{-4})^{b,d}$ | |
|  | 25.0 | $(2.2 \times 10^{-11})^{b}$ | |
| | 100.0 | $(4.7 \times 10^{-7})^{b}$ | |
| | 150.0 | $(5.1 \times 10^{-5})^{b}$ | |
| | 161.6 | $1.45 \times 10^{-4}$ | 1.000 |
| | 171.8 | $2.98 \times 10^{-4}$ | 1.000 |
| | 181.4 | $6.38 \times 10^{-4}$ | 0.999 |
|  | 35.0 | $5.15 \times 10^{-5}$ [c] | |
| | 45.0 | $1.43 \times 10^{-4}$ [c] | |
| | 56.0 | $3.84 \times 10^{-4}$ [c] | |
| | 35.0 | $3.97 \times 10^{-5}$ [c] | |
| | 45.0 | $1.10 \times 10^{-4}$ [c] | |
| | 55.0 | $3.68 \times 10^{-4}$ [c] | |
| | 25.0 | $(1.40 \times 10^{-5})^{b,e}$ | |
| | 100.0 | $(1.63 \times 10^{-2})^{b}$ | |
| | 150.0 | $(4.5 \times 10^{-1})^{b}$ | |
|  | 109.7 | $1.07 \times 10^{-4}$ | 1.000 |
| | 120.5 | $2.92 \times 10^{-4}$ | 0.999 |
| | 130.2 | $6.42 \times 10^{-4}$ | 0.998 |
| | 105.2 | $6.22 \times 10^{-5}$ | 1.000 |
| | 115.0 | $1.55 \times 10^{-4}$ | 0.999 |
| | 125.0 | $4.16 \times 10^{-4}$ | 0.999 |
| | 25.0 | $(3.2 \times 10^{-9})^{b,f}$ | |
| | 100.0 | $(4.1 \times 10^{-5})^{b}$ | |
| | 150.0 | $(3.4 \times 10^{-3})^{b}$ | |
|  | 25.0 | $(7.0 \times 10^{-9})^{b,d}$ | |
| | 100.0 | $(1.04 \times 10^{-4})^{b,d}$ | |
| | 150.0 | $(9.5 \times 10^{-3})^{b,d}$ | |
|  | 25.0 | $(5.0 \times 10^{-14})^{b}$ | |
| | 100.0 | $(3.7 \times 10^{-9})^{b}$ | |
| | 150.0 | $(7.1 \times 10^{-7})^{b}$ | |
| | 195.0 | $3.72 \times 10^{-5}$ | 0.999 |
| | 205.0 | $7.66 \times 10^{-5}$ | 0.997 |
| | 215.0 | $1.59 \times 10^{-4}$ | 0.994 |

[a] From ref 8. [b] Calculated from the Arrhenius activation parameters (Table III). [c] Initial rate constant; the rate was observed to decrease with time. [d] From ref 2. [e] Estimated in ref 9 to be $1.5 \times 10^{-5}$ $s^{-1}$. [f] Estimated in ref 9 to be $1.9 \times 10^{-9}$ $s^{-1}$.

## Discussion

Participation in the double-bond series can be expressed either in terms of the ratio $k_{unsatd}/k_{satd}$ (comparison of the rate of the unsaturated exo molecule with that of the identical system lacking the double bond, **1/5**) or the ratio $k_{exo}/k_{endo}$ (comparison of the rate of the unsaturated exo molecule with that of the corresponding endo molecule, **1/7**). In both cases, the denominator, either the exo-saturated or the endo-unsaturated system, represents a molecule that cannot have double-bond assistance. Because the saturated system has no analogy to $k_{unsatd}/k_{satd}$, we shall use the $k_{exo}/k_{endo}$ criterion

**Table II.** Acetolysis Rate Ratios[a]

| Compds | X | 25 °C | 100 °C | 150 °C |
|---|---|---|---|---|
| **5/6** | H | 300 | 80 | 40 |
| **5/6** | OTs | 50 | 20 | 11 |
| **5/6**[b] | OAc | 11 | 9 | 7 |
| **1/7** | H | 4 000 | 400 | 130 |
| **1/7** | OTs | 140 000 | 28 000 | 13 000 |

[a] Calculated from the rate constants in Table I, which in turn came from the Arrhenius activation parameters in Table III; differences from literature sources[2,8] are strictly due to round off; in most cases only one significant digit is allowed. [b] The exo and endo rates for **5/6**-OAc were measured by different individuals; so this ratio may have higher error than the others.

(**5/6**) throughout this discussion. Unless otherwise stated, all rate ratios refer to 25 °C.

The exo/endo rate ratio is determined by at least two factors, the baseline difference between the two epimeric positions and the anchimeric assistance. Earlier workers failed to assess the contribution of the baseline ratio, which depends on the steric and solvation differences between the two positions in the absence of anchimeric assistance. Thus the exo/endo rate ratio of 4000 for **1/7** (X = H) in the unsaturated series (the previously and frequently quoted value of 8000 was an estimate; see Table I, footnotes *e* and *f*) is meaningless without a measure of the baseline ratio. In his study of tertiary systems with variable electron demand,[6] Brown established the baseline ratio to be ~300. Thus the exo/endo ratio of 4000 is indeed indicative of anchimeric assistance. When the electron-withdrawing 3-tosyloxy group is placed on the ring, **1/7** (X = OTs), the ratio increases further to 140 000. The double bond alone (X = H) contributes an acceleration of only a factor of ~10 (300-4000), but, when the 3-tosyloxy group increases electron demand at the 2 position, the total accleration is a very respectable factor of ~500 (300-140 000). A plot of these figures was reproduced in the preliminary communication.[11]

If this approach can be carried over to the saturated systems, a similar estimate of the baseline exo/endo ratio must be made. The tertiary systems of Brown[7,11] again supply a figure, this time of ~200-300. Lower figures have been suggested, but without experimental justification.[4] The value in the secondary systems, **5/6** (X = H), of 300 therefore appears to indicate little or no anchimeric assistance. The values we find for the addition of a 3-tosyloxy group (50) or an acetoxy group (11) indicate further that a considerable increase in electron demand elicits no participation from the 6,1 bond. It appears that the phenomenon of $\sigma$ participation is still submerged with respect to other kinetic processes at the level of electron demand in the systems we have studied. The acetoxy ratio (11) may be unnecessarily low. It is the only ratio whose components were measured by different individuals.

The 3-acetoxy and 3-tosyloxy groups undoubtedly exert strong field/induction effects on the reactivity at the 2 position.

**Table IV.** Products of Buffered Acetolysis (Percent)[a]

| Compd | X | Temp, °C | Diacetates | Monoacetates |
|---|---|---|---|---|
| **5** | OTs | 160 | 20 | 80 |
| **6** | OTs | 200 | 28 | 72 |
| *b* | OTs | 120 | 21[c] | 79[c] |
| | | 200 | 60 | 40 |
| **5** | OAc | 161.6 | 74 | 26 |
| **6** | OAc | 181.4 | 76 | 24 |

[a] Uncalibrated VPC yields. [b] *trans*-2,3-Norbornyl ditosylate. [c] Relative amounts of monoacetates and diacetates; the principal product was an acetoxy tosylate.

Thus the extrapolated rate at 25 °C for X = H in the exo series of $2.3 \times 10^{-5}$ s$^{-1}$ decreases for X = OAc to $2.5 \times 10^{-9}$ and for X = OTs to $5.8 \times 10^{-12}$. Because these effects are paralleled in the endo series, there is only a modest effect on the exo/endo ratio (300/11/50).

The ratios quoted up to now have all referred to 25 °C. The temperatures of data collection range up to 215 °C (**7**, X = OTs), so that enormous extrapolations are required. Our extrapolated rates (Table I) are normally quoted to only two significant digits, and the extrapolated rate ratios (Table II) to only one. Because systematic errors in the extrapolations might mislead us, we have also calculated the ratios at 100 °C (in the middle of most data ranges) and at 150 °C (above most) (Table II). None of our conclusions is affected by consideration of the ratios at other temperatures. Rate ratios normally tend to decrease with temperature. The unsaturated series (H → OTs) exhibits a large increase in the exo/endo ratio (from 130 to 13 000) even at 150 °C, and the saturated series still exhibits a small decrease (from 40 to 7). We conclude that our inferences from the rate ratios at 25 °C are not an accident of systematic errors in extrapolation.

Certain questions must be examined before these conclusions can be considered to be firm. Can the 3 substituent supply some other effect in addition to that proposed? Can the saturated system (**5/6**) have some fundamental difference from the unsaturated system (**1/7**), which exhibits inductive enhancement of participation so definitely?

In order to decide whether the 3 substituent offers some other effect, the best approach is to examine the kinetic properties as a function of substituent. In addition to the rates reported in the present study (H, OTs, OAc), Kleinfelter et al. have reported the rates for phenyl and cyclohexyl in the saturated series (**5, 6,** X = $C_6H_5$, $C_6H_{11}$).[12] The relative rates for the di-exo (2-OTs, 3-X) compounds ($H/C_6H_5/C_6H_{11}$) are 1.00/0.00758/1.04; for the di-endo compounds 1.00/2.35/20.9. The di-exo/di-endo ratio is 0.95 for phenyl and 15 for cyclohexyl. The dominant effect in the di-exo series appears to be dipolar (induction, field), as we have assumed in this study. In fact, log $k_X/k_H$ for the di-exo systems gives an excellent linear plot as a function of $\sigma^*$.[12] The di-endo compounds of Kleinfelter (**6,** X = $C_6H_5$, $C_6H_{11}$), however, react rather

**Table III.** Activation Parameters[a]

| Compd | X | $E_a$, kcal mol$^{-1}$ | Log $A$ | $\Delta H^{\ddagger}$, kcal mol$^{-1}$ | $\Delta S^{\ddagger}$, gibbs | Corr coeff |
|---|---|---|---|---|---|---|
| **5**[b] | H | 22.4 | 11.8 | | | |
| **6**[b] | H | 26.5 | 12.3 | | | |
| **5** | OTs | 32.5 | 12.6 | 31.9 | −2 | 1.000 |
| **6** | OTs | 35.5 | 13.1 | 34.9 | 0 | 0.997 |
| **5**[c] | OAc | 28.5 | 11.3 | 27.8 | −9 | |
| **6** | OAc | 29.3 | 10.9 | 28.8 | −10 | 0.999 |
| **1**[d] | H | 20.8 | 10.4 | 20.3 | −12 | 0.999 |
| **7**[d] | H | 27.8 | 11.9 | 27.2 | −5 | 1.000 |
| **1**[c] | OTs | 28.3 | 12.6 | 27.6 | −3 | |
| **7** | OTs | 33.0 | 10.9 | 32.4 | −10 | 1.000 |

[a] Three temperatures in each case. [b] From ref 8. [c] From ref 2. [d] Average of parameters for the separate determinations given in Table 1.

more rapidly than the endo parent (**6**, X = H), phenyl by a factor of 2.35, cyclohexyl by 20.9. Introduction of a 3-endo substituent to a 2-endo-tosyloxy system therefore appears to create steric congestion (3-X against 5-H) that is relieved in the solvolytic transition state. This effect is not present in the 3-exo-substituted, 2-exo-tosyloxy system, which does not experience the buttressing of the 5,6-endo protons. If it is assumed that the relative rates of the di-exo series are determined entirely by field/induction factors, then the deviations of the relative rates of the di-endo series give a crude measure of the steric effect caused by the interaction of the 3-endo group with the 5,6-endo protons. These factors are ~300 (2.35/0.00758) for phenyl and 20 (20.9/1.04) for cyclohexyl. In a completely equivalent calculation, these same figures may be obtained by dividing the 3-H exo/endo ratio (300) by that for 3-X (300/0.95 ~ 300 for phenyl; 300/15 = 20 for OAc).

Can this steric effect explain the apparent lack of an increase in the exo/endo ratio for the 3-tosyloxy and 3-acetoxy systems in the present study? We think not. The phenyl ring is only slightly larger than the cyclohexyl group, by both the $E_s$ and $A$ value criteria, but the steric effect on endo reactivity decreases by 300/20 = 15. The acetoxy and tosyloxy groups ($A$ values in the range 0.5–0.7) are considerably smaller than the phenyl and cyclohexyl groups ($A$ values in the range 2.4–2.8). It is reasonable therefore that the steric effect of the 3-endo acetoxy and tosyloxy groups should be appreciably smaller than that of cyclohexyl. The decrease in the exo/endo rate ratio, from 300 for X = H to 11 for X = OAc and 50 for X = OTs, may be the result of a residual small steric effect. Even in the extreme case that the steric effects of OAc and OTs are as large as that of cyclohexyl (20), multiplication of the exo/endo ratio by the factor of 20 brings the value for OAc up to only 220 (11 × 20) and that of OTs up to 1000 (50 × 20). In actuality, the steric correction should be much smaller than that for cyclohexyl. Thus even after a maximal correction for the steric factor, there is little or no evidence for inductive enhancement of $\sigma$ participation.

The previous two paragraphs have addressed the first question, concerning some special effect of the 3 substituent. The second question asks whether there might be a fundamental difference between the unsaturated and the saturated series. The argument is quite similar to that given for the first question. Saturation of the double bond introduces the two endo 5 and 6 protons. The steric interaction of these protons with the 3-endo substituent would provide an acceleration not present in the unsaturated series. The question again is whether this effect is large enough to affect the conclusions. On the basis of the arguments given above, the steric effect of tosyloxy and acetoxy (when compared with those of the much larger phenyl and cyclohexyl) should not be significant. One might also question whether the polar effects are identical in the unsaturated and saturated series. The dihedral angle between the leaving group and the 3 substituent must be the same in both the ground state and the transition state for the field effect to be identical. Any differences should be small. Nonetheless, it is not necessary in the current study that the polar effects be identical in the saturated and unsaturated series, but only qualitatively similar, since at no stage is a direct comparison, e.g., via a ratio, made between the two series. Furthermore, the 3 substituent is the same distance (two bonds) removed from the participating entity (5,6 double bond or 6,1 single bond), so that any direct effect should be similar and quite small.

## Conclusions

Introduction of an exo electron-withdrawing group at the 3 position of 2-norbornyl tosylate gives rise to no enhancement of the exo/endo rate ratio, in contrast to the observations in the 2-norborn-5-enyl system. Three conclusions are consistent with these observations. (1) Participation by the 6,1 single bond is so weak that increased electron demand fails to render it observable. (2) Participation by the 6,1 bond in the departure of the 2-exo tosylate is enhanced to the same extent as participation by the 7,1 bond in the departure of the 2-endo tosylate. Equal contributions to both departures would leave the exo/endo ratio approximately unchanged. Although 7,1 participation in the solvolysis of endo tosylates has been suggested,[13a] its presence entirely vitiates the original Winstein concept of participation in exo tosylates only. Furthermore, recent experiments have indicated that the *endo*-2-norbornyl solvolysis is best described as a $k_C$ process, rather than $k_\Delta$ or $k_s$.[13b] (3) There is a flaw in the method, such as either a special effect other than induction/field exerted by the 3 substituent or a fundamental difference between the norbornyl and norbornenyl systems. The principal candidate is a steric acceleration for the 3-substituted, 2-endo tosylate brought about by the buttressing effect of the 5,6-endo protons. These effects, though not large, have been observed when the 3 substituent is phenyl or cyclohexyl. They would be much less important for acetoxy and tosyloxy, which are considerably smaller groups. Even allowance for a steric effect as large as that of cyclohexyl gives an increase in the exo/endo ratio for OAc or OTs of no more than 3.

We fail to observe inductive enhancement of participation in the 2-norbornyl system. As with any negative observation, the conclusions are subject to equivocation (previous paragraph). There seems no doubt that adjacent electron-withdrawing groups can significantly enhance double-bond[2] and phenyl[3] participation, but no such results transpire with $\sigma$ participation. The results are best explained in terms of the absence of $\sigma$ participation in the parent 2-norbornyl system.

Our conclusions refer only to participation in the solvolytic transition state. These experiments do not speak to the issue of delocalization in the intermediate 2-norbornyl cation, which has been studied in fluorosulfonic acid[14] and other media.[15]

## Experimental Section

Spectral, kinetic, and other instrumental equipment has been described earlier.[3]

***cis,exo*-2,3-Norbornyl ditosylate** (**5**, X = OTs) was available from our earlier study.[2]

***cis,endo*-2,3-Norborn-5-enyl carbonate.** The Diels–Alder reaction was carried out as described by Kwart and by Newman.[16] A solution of 8.15 g (0.095 mol) of vinylene carbonate (Aldrich) and 6.5 g (0.049 mol) of freshly distilled dicyclopentadiene (Eastman) in 32 mL of benzene was sealed in a Pyrex tube, which was heated at 200 °C for 8 h. The tube was opened and the solvent removed by vacuum distillation to give a brown solid, which was dissolved in ether, decolorized with activated charcoal, and finally recrystallized from ether/hexane to give 12.32 g (86%) of the desired compound: NMR ($CDCl_3$) $\delta$ 1.25 (d, 1 H), 1.75 (d of t, 1 H), 3.25 (m, 2 H), 4.96 (t, 2 H), 6.17 (t, 2 H).

***cis,endo*-2,3-Norbornanediol.** To a solution of 4.5 g (0.0298 mol) of *cis,endo*-2,3-norborn-5-enyl carbonate in 75 mL of ethanol was added 0.45 g of 10% Pd/C in a Parr shaker. The shaker was initially charged with 50 psi of $H_2$ and then recharged whenever the pressure fell below 25 psi. When the NMR spectrum showed no remaining alkene resonances, the solution was filtered and the solvent removed. The carbonate was reduced by treatment with 1.25 g (0.0328 mol) of $LiAlH_4$ in ether. Treatment of the alkoxide with NaOH solution and removal of the solvent gave 3.12 g (82%) of the diol after recrystallization from acetone/hexane: mp 209–211 °C; NMR ($CCl_4$) $\delta$ 1.14 (m, 4 H), 1.70 (m, 2 H), 2.25 (br s, 2 H), 3.76 (br s, 2 H), 4.03 (br s, 2 H). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.65; H, 9.40.

***cis,endo*-2,3-Norbornyl Ditosylate (6, X = OTs).** According to the Tipson procedure,[10] 1.28 g (10.0 mmol) of *cis,endo*-2,3-norbornanediol was treated with 4.2 g (22 mmol) of tosyl chloride. Recrystallization from acetone/hexane gave 3.98 g (92%) of the desired ditosylate: mp 120–122 °C; NMR ($CCl_4$) $\delta$ 1.30 (m, 4 H), 1.73 (m, 2 H), 2.38 (m, 2 H), 2.42 (s, 6 H), 4.50 (t, 2 H), 7.42 (AB q, 8 H). Anal.

Calcd for $C_{21}H_{24}O_6S_2$: C, 57.78; H, 5.54. Found: C, 57.56; H, 5.51.

***cis,endo*-2-Acetoxy-3-norbornyl Tosylate (6, X = OAc).** *cis,endo*-2,3-Norbornanediol (1.0 g, 7.8 mmol) was treated with 1.63 g (8.6 mmol, 10% excess) of tosyl chloride by the method of Tipson.[10] After the standard workup procedure, the crude hydroxy tosylate was treated with an excess of $Ac_2O/H_2SO_4$.[17] The excess $Ac_2O$ was hydrolyzed with $H_2O$, and the HOAc thus formed was neutralized with $Na_2CO_3$. The organic phase was extracted into ether, which was then dried over $MgSO_4$. The solvent was removed by vacuum distillation to give a white semisolid material, which formed a white precipitate of the undesired ditosylate (**6**, X = OTs) when treated with hexane. The ditosylate was removed by filtration and the remaining hexane solution was concentrated by vacuum distillation to give a viscous oil. Crystallization from ether/pentane afforded 0.6775 g (28%) of the desired acetoxy tosylate (**6**, X = OAc): mp 68–69.5 °C; NMR ($CDCl_3$) $\delta$ 1.35 (m, 4 H), 1.80 (m, 2 H), 1.93 (s, 3 H), 2.42 (m, 2 H), 2.43 (s, 3 H), 4.70 (m, 2 H), 7.50 (AB q, 4 H). Anal. Calcd for $C_{16}H_{20}O_5S$: C, 59.61; H, 6.25. Found: C, 59.00; H, 6.24.

***trans*-2,3-Norbornanediol** was prepared in the manner used earlier.[2] The diol was recrystallized from $CHCl_3$/cyclohexane to give 1.10 g (74%): mp 201.5–204 °C; NMR ($CDCl_3$) $\delta$ 1.60 (m, 6 H), 2.25 (m, 1 H), 2.45 (m, 1 H), 3.0 (s, 2 H), 3.63 (m, 1 H), 4.20 (m, 1 H).

***trans*-2,3-Norbornyl ditosylate** was prepared from the trans diol in the manner of Tipson.[10] Recrystallization from ether/pentane gave 1.87 g (50%) of the desired ditosylate: mp 96.5–98 °C; NMR ($CDCl_3$) $\delta$ 1.4 (m, 6 H), 2.30 (m, 2 H), 2.43 (s, 6 H), 4.14 (m, 1 H), 4.55 (m, 1 H), 7.48 (AB q, 8 H). Anal. Calcd for $C_{21}H_{24}O_6S_2$: C, 57.78; H, 5.54. Found: C, 57.88; H, 5.72.

**2-Norborn-5-enone.** A solution of 11.0 g (72 mmol) of 2-norborn-5-enyl acetate (Aldrich) in anhydrous ether was added dropwise to 1.37 g (40 mmol) of $LiAlH_4$ in 300 mL of ether. After the addition was complete, the ether was refluxed for 2 h and the alcohol was released from the alkoxide by adding NaOH solution. After the solvent had been removed, the resulting alcohol was oxidized to the ketone by the procedure of Collins and Hess.[18] The alcohol, dissolved in anhydrous $CH_2Cl_2$, was added in one portion to a 3-necked flask fitted with a mechanical stirrer and containing a solution of 111 g (0.43 mol, 6-fold excess) of $CrO_3 \cdot pyr_2$ complex in 1 L of anhydrous $CH_2Cl_2$. A dark brown, viscous sludge precipitated on the sides and bottom of the flask. The liquid was filtered through a Celite pad and then washed with 400 mL of 5% NaOH, twice with 100 mL of 5% HCl, twice with 100 mL of saturated $NaHCO_3$, and once with saturated NaCl. After drying ($MgSO_4$), removal of the solvent, and distillation, 5.42 g (70%) of ketone was obtained: bp 86–88 °C (60 Torr).

***endo*-2-Norborn-5-enol.** To a solution of 7.8 g (0.0271 mol) of Red-al (Aldrich) in ether was added 5.42 g (0.0493 mol) of 2-norborn-5-enone in 50 mL of ether. After the addition was complete, the solution was refluxed for 2 h. The solution was cooled and hydrolyzed by the addition of 100 mL of 1/4 $H_2SO_4$. The layers were separated, and the aqueous phase was extracted with ether. The solvent was removed by vacuum distillation to give a waxy solid, which was recrystallized from hexane to give 3.42 g (63%) of alcohol, 90% endo according to the NMR spectrum.

***endo*-2-Norborn-5-enyl tosylate (7, X = H).** A pyridine solution of 1.5 g (13.6 mmol) of the 90% *endo*-2-norborn-5-enol was treated with 2.85 g (15.0 mmol) of tosyl chloride in the manner of Tipson.[10] After isolation, the mixture of endo and exo tosylates was dissolved in 50 mL of HOAc, to which 5 mL of 0.96 M KOAc in HOAc was added. The solution was heated at 100 °C for 20 min, after which time essentially all of the exo isomer but little of the endo isomer would have reacted. The tube was cooled and its contents poured into a brine solution, which was neutralized with $Na_2CO_3$. The organics were extracted into ether and dried with $MgSO_4$. Removal of the solvent left a yellow oil, which solidified on treatment with pentane. Recrystallization from pentane gave 0.62 g (17% yield) of the desired endo product: mp 61–64 °C; NMR ($CDCl_3$) $\delta$ 1.5 (m, 4 H), 2.43 (s, 3 H), 2.80 (m, 1 H), 3.05 (m, 1 H), 5.12 (m, 1 H), 6.10 (ABXX′ octet, 2 H), 7.52 (AB q, 4 H). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.49; H, 6.12.

***exo*-2-Norborn-5-enyl Tosylate (1, X = H).** A solution of 2.0 g (13.1 mmol) of *exo*-2-norborn-5-enyl acetate prepared earlier[2] was dissolved in ether and added dropwise to 0.30 g (9 mmol) of $LiAlH_4$ in 150 ml of ether. The mixture was then refluxed for 4 h. The alcohol was liberated by treatment of the alkoxide with $H_2O$ and 15% NaOH. Filtration and removal of the solvent gave 1–2 g of paraffin-like material. This crude alcohol was dissolved in pyridine and treated with 2.72 g (14.3 mmol) of tosyl chloride.[10] Recrystallization of the resulting residue from pentane gave 2.13 g (62% from the acetate) of the desired tosylate: mp 49–51 °C; NMR ($CDCl_3$) $\delta$ 1.50 (m, 4 H), 2.31 (s, 3 H), 2.80 (m, 2 H), 4.36 (t, 1 H), 5.90 (ABXX′ octet, 2 H), 7.40 (AB q, 4 H). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.37; H, 6.23.

**Kinetic studies** of the norbornyl systems were carried out as previously described for the aryl participation systems,[3] except that in those instances for which the rate constants were observed to change with time instantaneous rate constants were calculated for each recorded interval. Extrapolation of these rate constants to zero time produced the initial rate constants reported in Table I.

**Product studies** of the norbornyl systems were also carried out as described previously.[3] The only exception was the isolation of the acetoxy tosylate produced from *trans*-2,3-norbornyl ditosylate at 120 °C. The product mixture was separated on a preparative scale silica gel plate eluted with 15% THF/hexane. The acetoxy tosylate was the predominant product formed in the reaction: NMR ($CDCl_3$) $\delta$ 1.5 (m, 6 H), 2.00 (s, 3 H), 2.29 (m, 2 H), 2.50 (s, 3 H), 4.58 (d of d, 1 H), 4.75 (m, 1 H), 7.65 (AB q, 4 H).

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