collected on a General Electric–Datex diffractometer that used nickel-filtered copper radiation and a scintillation counter. The structure was solved by the usual heavy-atom methods based on bromine and full-matrix least-squares refinement of coordinates, isotropic temperature factors (bromine anisotropic), and scale factor reduced to *R* index to 10.6%. Hydrogen atoms were then located by a difference Fourier, and addition of these values to the structure-factor calculation and then application of anisotropic temperature factors and a second extinction factor[11] to the refinement reduced the *R* index to its final value of 5.6% (Figure 1).

This demonstration that the *trans*-decalin structure **4** is a major product of the acid-catalyzed cyclization of the dienal **3** is a rigorous test of the utility of the process, for the relatively low nucleophilicity of the terminal double bond might have resulted in the generation of mainly monocyclic material.[2b,c] Further work designed to incorporate the knowledge gained in this study in the triterpenoid synthetic problem itself is in progress.

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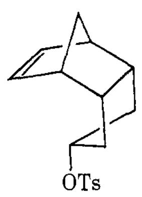
Acetolysis of a Norbornyl-Type Tosylate. An Unusual *exo*/*endo* Rate Ratio

Sir:

For many years it has been found that *exo*-2-norbornyl-type tosylates containing no other functional groups solvolyze more rapidly than their *endo* isomer.[1] In norbornyl itself at 25° the *exo*/*endo* rate ratio for acetolysis is 280, for the tricyclo[3.2.1.0^{3,6}]octyl system it is 192, and for some substituted cases it is 10.[2] We wish to report an example of an *exo*/*endo* acetolysis rate ratio of less than one.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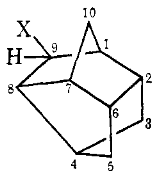
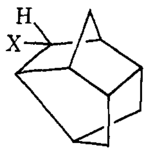
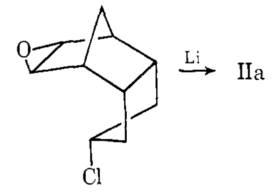


IIa, X = OH
b, X = OTs



IIIa, X = OH
b, X = OTs

Acetolysis of I (mp, alcohol 69.5–70.0°, tosylate 59–61°)[3,4] and saponification of the resulting acetate led to *exo*-tetracyclo[5.2.1.0.^{2,6}0^{4,8}]decan-9-ol (IIa; mp, alcohol 179–180°, tosylate 80–81°).[4] Oxidation with chromic acid[5] led to ketone (mp 184–185°)[4] and reduction of the ketone with lithium aluminum hydride led to IIIa (mp, alcohol 209–210°, tosylate 59–61°).[4] As a proof of structure of IIa an alternate synthesis was carried out by treating the chloro epoxide IV (mp 76–77°)[4] with lithium dispersion to close the ring.[2f,6] The alcohol product, obtained in 60% yield, was exactly identical with that from acetolysis of I. The nmr spectra were completely in agreement with structures IIa,b and IIIa,b. For II the dihedral angle that the methine hydrogen makes with adjacent protons on C$_1$ and C$_8$ is 70 and 90°, respectively, leading to a calculated[7] coupling constant of less than 1 Hz in both cases. The observed spectrum exhibits a broadened singlet for the methine hydrogen in both alcohol and tosylate (IIa has a width at half-height of 4 Hz, IIb has a width of 5 Hz). This is very similar to the spectrum reported for *exo*-tricyclo[3.2.1.0^{3,6}]octan-2-ol.[2f] The methine hydrogen of III makes a dihedral angle with the C$_1$ and C$_8$ protons of 60 and 27° leading to calculated coupling constants of less than 2 and 6.5 Hz, respectively. The experimental spectra show a broadened doublet with J of 6 Hz for both alcohol and tosylate. The similarities in the nmr spectrum of alcohols and tosylates suggest that ion-pair formation and internal return[8] had not occurred in the preparation of IIb and IIIb. As an additional precaution we treated IIb with sodium and naphthalene in tetrahydrofuran.[9] Alcohol in 85% yield was recovered which showed no signs of skeletal rearrangement.[10]



IV

Also, of interest are the rates of chromic acid oxidation of the two alcohols. In 40% aqueous acetic acid at 25° ($1.79 \times 10^{-3} M$ in chromic acid and $2.68 \times 10^{-3} M$ in alcohol) the rates of oxidation were 3.50×10^{-3} l. mol^{-1} sec^{-1} for IIa and 0.257 l. mol^{-1} sec^{-1} for IIIa. The *endo* alcohol is being oxidized faster by a factor of 73 than the *exo*, a ΔF difference of 2.54 kcal/mol. This rate ratio is similar to that observed for the *endo*-5,6-trimethylene-2-norbornanols where the rate ratio is 151.[11] This is very reasonable since models

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(1) This behavior does not necessarily hold true where there are other functional groups: P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968); *J. Amer. Chem. Soc.*, **88**, 2822 (1966).

(2) For discussion 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. Eng. News*, **45** (7), 87 (1967); *Chem. Brit.*, **2**, 199 (1966); (c) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966); (d) E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967); (e) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); (f) R. R. Sauers, R. A. Parent, and S. B. Damle, *ibid.*, **88**, 2257 (1966).

(3) Prepared by an extension and modification of work of T. H. Webb, Ph.D. Thesis, Duke University, Durham, N. C., 1962; *Diss. Abstr.*, **23**, 449 (1962).

(4) All new compounds gave a satisfactory elemental analysis. Experimental details will be reported shortly in the full paper.

(5) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Amer. Chem. Soc.*, **90**, 5564 (1968).

(6) R. R. Sauers, R. M. Hawthorne, and B. I. Dentz, *J. Org. Chem.*, **32**, 4071 (1967).

(7) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(8) E. C. Friedrich and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 2721 (1964); P. v. R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964).

(9) W. D. Closson, P. Wriede, and S. Bank, *ibid.*, **88**, 1581 (1966).

(10) Although a small amount of epimerization had occurred, estimated by infrared spectroscopy to be about 15%. There are major differences in the infrared and nmr spectra of the epimeric alcohols and tosylates. We believe that there was less than 5% of epimeric impurity (IIIb) in the sample of tosylate (IIb) used for this experiment.

Table I. Acetolysis Rates of *p*-Toluenesulfonates

Tosylate	Temp, °C	k_1, sec^{-1}	Rel rate 25°		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu, 25°
IIb	25.0[a]	7.10×10^{-9}	1.0	0.15	29.2	2.07
	75.0	9.72×10^{-6}				
	90.0	5.85×10^{-5}				
	100.0	1.74×10^{-4}				
IIIb	25.0[a]	2.33×10^{-8}	3.3	0.48	28.5	2.27
	75.0	2.73×10^{-5}				
	85.0	7.93×10^{-5}				
	100.0	4.59×10^{-4}				
Cyclohexyl[b]	25.0	4.88×10^{-8}		1.00		
exo-Norbornyl[c]	25.0	2.33×10^{-5}				
N*endo*-orbornyl[c]	25.0	8.28×10^{-8}				
endo-5,6-Trimethylene-*endo*-2-norbornyl[d]	25.0	8.60×10^{-9}				
exo-Tricyclo[3.2.1.0^{3,6}]-oct-2-yl[e]	25.0	9.12×10^{-8}				
endo-Tricyclo[3.2.1.0^{3,6}]-oct-2-yl[e]	25.0	4.75×10^{-10}				

[a] Calculated from data at other temperatures. [b] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). [c] Reference 2e. [d] H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci., U. S.*, **56**, 1653 (1966); H. C. Brown and W. G. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967); H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967). [e] Reference 2f.

show that the steric interactions seem to be approximately the same.

In Table I are the acetolysis rate results. The product of acetolysis of both IIb and IIIb after saponification is largely IIa. The absolute yield by vpc of IIa using dodecyl alcohol as internal standard was 83 and 85%, respectively, with less than 5% of IIIa present in both cases. Samples collected by preparative vpc were identical with authentic alcohol.

Included in Table I are the rates of tosylates of some other norbornyl type ring systems. Assessment of factors involved in the rates of IIb and IIIb is difficult by direct comparison with model compounds. For example, comparison of IIb with *exo*- and *endo*-norbornyl would suggest that IIb is solvolyzing much slower than would be expected for an *exo*-tosylate. Comparison of the rate of IIIb with *endo*-norbornyl and with *endo*-5,6-trimethylene-*endo*-2-norbornyl would indicate that IIIb is solvolyzing at a "normal rate." If *endo*-tricyclo[3.2.1.0.^{3,6}]oct-2-yl tosylate were used as the model, rate enhancement would appear to be present for both IIb and IIIb.

The Schleyer equation[12] was used in an attempt to evaluate the factors involved in the rates. The carbonyl frequency used was 1753 cm^{-1}. Torsional strain relief for IIb was estimated using angles of 27 and 60° for the C_8H–CO and C_1H–CO angles, respectively. For IIIb we used angles of 27 and 60° for the C_4C_8–CO and C_1C_2–CO interactions. The assumption was made that no nonbonded strain was relieved in the *exo* compound. The same assumption was made for the *endo* compound IIIb since in many rigid polycyclic ring systems this has been found to be true.[13] The Schleyer equation predicts that both *exo* and *endo* isomers will solvolyze by a factor of 6.0×10^{-4} slower than cyclohexyl. Experimentally the results show that both isomers are solvolyzing more rapidly than predicted. The *exo* rate is faster by a factor of 250 and the *endo* faster by a factor of 795 than predicted. This higher than predicted rate for an *exo* isomer has been widely found before, both where there are rearrangements and also where rearrangements do not take place.[2,12,14] The high rate of the *endo* isomer could be largely explained if we assume that ground-state strain is relieved in the transition state. However, it is not clear why ground-state strain would be relieved in this case and not in others.[13] The possibility exists that the *endo* compound is ionizing with anchimeric assistance. We find no direct evidence for this since the large majority of product is unrearranged. However, anchimeric assistance cannot be eliminated since it is possible that only one form of a resonance hybrid is reacting with solvent.

We are actively engaged in further examination of this and other ring systems in an attempt to clarify this unusual solvolytic behavior.

Acknowledgment. We wish to thank the Petroleum Research Fund administered by the American Chemical Society and the Rutgers Research Council for financial support. We also wish to thank Dr. B. Senkowski for determining the infrared carbonyl frequency.

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(12) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964).

(13) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966); H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967); H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967).

(14) Among the possibilities for rearrangement of IIb would be C_1–C_2 bond migration leading to a different ring system and degenerate rearrangements such as C_4–C_8 bond migration and migration of *endo*-3-hydride to C_9. This will be considered in the full paper.

(15) National Science Foundation Undergraduate Research participant.

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Metalloboranes. IV. The $B_9H_{10}S^-$, $B_9H_{11}(L)^{2-}$, and $B_8H_{12}{}^{2-}$ Ligands

Sir:

We report the syntheses of three new classes of *nido*-metalloboranes. These are metal complexes in which the metal–boron skeletons are icosahedral frag-