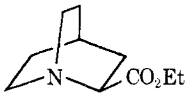
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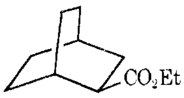
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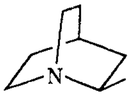
in 30:70 water–acetone. Extrapolation of these measurements to 25° gave values of $k_{B_{10}} = 2.03 \times 10^{-2}$ l./(mol sec), $k_{B_{11}} = 4.85 \times 10^{-4}$ l./(mol sec), and $k_{A_{11}} = 1.11 \times 10^{-5}$ l./(mol sec). Utilizing these values and the approximation specified[8] in the Taft relationship[9] allowed us to calculate $\Delta\sigma^* = \sigma^*_{12} - \sigma^*_{13} = 0.66$. If we assume that the difference in the inductive effects of the moieties **14** and **15** will be similar to that of **12** and **13**, we can use the $\rho$ of $-3.49$ determined for secondary tosylates,[10] or the $\rho$ of $-2.33$ calculated for *exo*-norbornyl tosylates,[11] to calculate the expected difference in the rates of solvolysis of **3** and **4** based on inductive effects alone.[12] Using the $\rho$ value for acyclic secondary tosylates,[10] we obtain a predicted rate difference of $2.8 \times 10^6$, while the $\rho$ for *exo*-norbornyl tosylates[11] led to a predicted difference of $2.0 \times 10^4$. Since these values are based on inductive effects alone, an increase in these differences by as much as $10^3$ could be added if neighboring group participation were involved in the solvolysis of **4**, **6**, and **8**. As a result of the various approximations and uncertainties involved, the best quantitative picture we can present indicates that the bridgehead nitrogen atoms of **3**, **5**, and **7** are providing a rate acceleration of at least $10^3$ and possibly of as much as $10^8$ to the leaving of a suitable group from the 2 position. We presume that this accelerating effect is due to overlap of the nonbonding electrons on nitrogen with the developing p orbital at the 2 position. It should be noted that the methanolysis of **3** and **7** gave *exo*-2-methoxy-3,3,4-trimethyl-1-azabicyclo[2.2.1]heptane as the only product (99% yield).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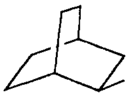
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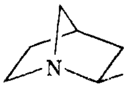
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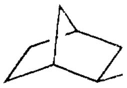
15

**Acknowledgment.** We are indebted to the National Cancer Institute of the Public Health Service for support of this investigation and to Drs. J. Hine and G. R. Meyer for helpful discussions.

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(8) Since the base-catalyzed hydrolysis rates reflect primarily inductive influences while acid-catalyzed hydrolysis rates reflect primarily steric factors, the acid-catalyzed hydrolysis rates for **11** were used as approximate acid-catalyzed hydrolysis rates for **10** (which could not be measured directly for obvious reasons) in the calculation of a Taft $\sigma^*$ value for **10**.

(9) For a detailed discussion see R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13; see also R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).

(10) A. Streitwiester, Jr., *ibid.*, **78**, 4935 (1956).

(11) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. Hornback, *ibid.*, **91**, 4282 (1969).

(12) In order to calculate this rate difference, the difference in the measured $\sigma^*$ values of 0.66 was multiplied by 2.8 in order to compensate for moving the reactive center one carbon closer to the nitrogen atom. The usefulness of this approach has been questioned in cases where alkyl groups are involved [C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961), has suggested that "$\sigma^*$ values for alkyl groups are not consistent with the generality of the Taft equation"].

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## The 4-Psinortricyclyl Cation System

*Sir:*

It was indicated previously that the same carbonium ion species are formed from the epimers of the 3-psinortricyclyl system under hydrolytic conditions.[1] In contrast, we now find that the solvolytic chemistries of the 4-psinortricyclyl epimers are strikingly dissimilar.

*exo*-4-Psinortricyclanol[1,2] (**1**-OH) was converted to the corresponding ketone with $CrO_3$–pyridine. Reduction with $LiAlH_4$ or Vitride gave a 3:97 mixture of **1**-OH and **2**-OH, respectively, separable by glpc.[3] Hydrogenation of **1**-OH and **2**-OH (10% Pd/C, 95% EtOH) produced *exo*- and *endo*-2-norborneol, respectively. Sulfonate esters of **2**-OH may be prepared routinely (tosylate mp ~28°; brosylate mp 47.0–48.5°), but attempts to prepare **1**-OTs with tosyl chloride–pyridine resulted in the isolation of nortricyclyl tosylate (**3**-OTs). However, oxidation of the epimeric mixture of sulfinate esters derived from **1**-OH with $RuO_4$ in $CCl_4$[4] in a 5° cold room produced a solution which contained 74% **1**-OTs and 26% **3**-OTs, as judged from the relative areas of their $\alpha$ H signals at $\tau$ 5.54 and 5.70, respectively. Since **1**-OTs proved to be much more reactive than **3**-OTs, this mixture was used for kinetic determinations.

Preliminary titrimetry indicated that only a small fraction of 1 equiv of tosylic acid is liberated from **1**-OTs in buffered acetic acid medium. Consequently, the rate of ionization (solvolysis plus ion pair return, *vide infra*) was measured by following the disappearance of the $\alpha$ H absorption in a temperature regulated nmr probe (0.02 *M* NaOAc buffer). The acetolysis rate for **2**-OTs was measured by routine titrimetry of *ca.* 0.01 *M* solutions containing a slight excess of NaOAc. Nmr examination of recovered sulfonate ester after *ca.* 1 acetolysis half-life failed to reveal any contamination by rearranged tosylate. Table I contains a summary of the rate data. The 2-norbornyl systems are included for comparison. Product data are given in Table II.

**Table I.** Acetolysis Rates for the 4-Psinortricyclyl and 2-Norbornyl Tosylates at 25°

| Compound | $k$, sec$^{-1}$ |
|---|---|
| *exo*-2-Norbornyl | $2.33 \times 10^{-5}$ [a] |
| *endo*-2-Norbornyl | $8.28 \times 10^{-8}$ [a] |
| **1** | $(6.3 \pm 0.6) \times 10^{-4}$ [b] |
| **2** | $(1.06 \times 10^{-6})$[c] |

[a] P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965). [b] Measured directly by nmr monitoring; probe temperature was 24.5 ± 0.5°. [c] Extrapolated from data acquired at higher temperatures; $\Delta H^{\ddagger} = 24.8 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -2.5 \pm 0.6$ eu.

The rate acceleration of **1**-OTs relative to *exo*-2-norbornyl[5] is presumably due to relief of strain in **1**-OTs

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(1) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **93**, 1275 (1971).

(2) Satisfactory spectral and analytical data were obtained for all new compounds except that **1**-OTs was prepared without isolation of intermediates and was not purified.

(3) The equilibrium between **1**-OH and **2**-OH (aluminum isopropoxide–isopropyl alcohol–acetone (trace), 99.6°) is *ca.* 81:19, respectively, established from either side.

(4) J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **92**, 1660 (1970).

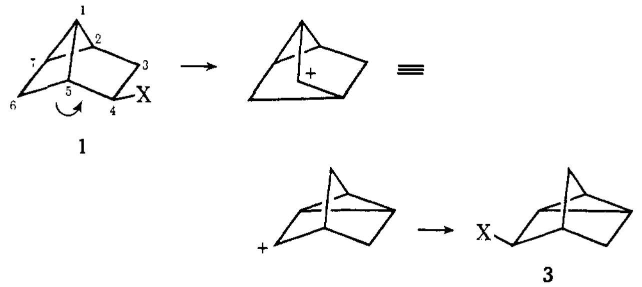
(5) Since the measurement for **1**-OTs includes ion pair return, it might better be compared with $k_\alpha$ for *exo*-2-norbornyl. Assuming $k_\alpha/k_t$ for the tosylate to be the same as for the brosylate,[6] the value in Table I for *exo*-2-norbornyl is increased by a factor of 4.6.

Table II. Acetolysis Products from 4-Psinortricyclyl Tosylates[a]

| Compd | 3-OTs | 3-OAc + 5-norbornenyl-OAc | 2-OAc | Unknown |
|---|---|---|---|---|
| **1**-OTs[b,c] | 78 | 21.5 | | 0.5 |
| **2**-OTs[d] | | 3 | 97 | Trace |

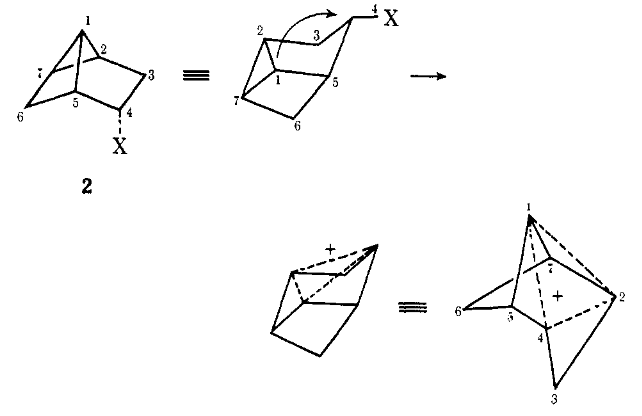
[a] Relative per cent yields; solutions were 0.01–0.05 *M* in substrate and buffered with sufficient sodium acetate to neutralize liberated tosylic acid. Products were identified by spectral comparisons with authentic samples. [b] 24.5°. [c] Corrected for initial contamination by **3**-OTs. [d] 75°.

as it ionizes with participation of the 5,6 bond. Table II shows that the vastly predominant products are indeed derived mainly from the nortricyclyl cation system which is formally related to **1** by a nondegenerate Wagner–Meerwein rearrangement. The major events are ion-pair return to unreactive **3**-OTs[7] and solvolytic capture of the nortricyclyl cation.[8] Thus, **1** represents a new route to the nortricyclyl ion-pair system.[9]



It might have been anticipated that **2**-OTs would be slightly less reactive than *endo*-2-norbornyl due to inductive destabilization of charge by the β-cyclopropyl ring.[10] In fact, Table I shows it to be substantially more reactive. Most striking is the finding that while there is a small amount of leakage to the nortricyclyl cation, the predominant solvolytic product is unrearranged *endo*-acetate, **2**-OAc. *exo*-Acetate **1**-OAc, which is completely stable to the reaction conditions, was not detected (<0.1%). The dichotomy between the products derived from **1**-OTs and **2**-OTs is highlighted when compared with the renowned 2-norbornyl system where there is predominant leakage from the endo epimer to that species which derives from the exo epimer.

It is proposed that **2**-OTs ionizes with anchimeric assistance of the 1,2 bond to give the trishomocyclopropenyl cation **4**. Endo directed capture of nucleophile at $C_2$ or $C_4$ would then account for net retention of configuration.[11] To test for the intermediacy of **4**, **2**-OTs-*4-d* and **2**-OTs-*3,3,4-d*$_3$ were acetolyzed in separate experiments. In each case nmr analysis (250 MHz) indicated equal deuterium concentrations at $C_2$ and $C_4$ of recovered **2**-OAc. The mass and nmr spectra of **2**-OAc recovered from solvolysis of **2**-OTs in DOAc indicated that there is little or no proton exchange with solvent during the course of the reaction.



Thus, the rate, product, and scrambling data for **2**-OTs are all consistent with the formulation of **4** as the major ionic intermediate. However, the full story regarding this cation is yet to be told, since we find that the sample of **2**-OAc recovered from *either* of the two deuterium labeled precursors contains not 0.5 D at $C_2$ and $C_4$, as would be expected on the basis of statically bridged **4**, but rather 0.24 ± .02 D at each of these positions.[12a] It thus appears that cation **4** experiences a degenerate isomerization under the solvolytic conditions, probably one which scrambles four of the five methine protons.[12b]

**Acknowledgments.** The author is grateful to Professors W. L. Mock and R. F. Sprecher for helpful discussions, to B. Aufderheide, Dr. P. Balaram, and Dr. J. Dadok for assistance in recording nmr spectra, and to J. Boal for mass spectral determinations. Spectra (250-MHz) were recorded at the NMR Facility for Biomedical Studies, NIH Grant No. RR 00292.

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(6) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965).

(7) No olefinic hydrogens could be detected in this material, indicating the absence of *exo*-5-norbornenyl tosylate.

(8) The small amount of unknown acetolysis product appears (glpc) not to be **1**-OAc.

(9) The extent to which the relative reactivities of **1**-X and **3**-X reflect the difference in their ground-state energies is not yet clear. Clarification of this factor should lead to a more detailed description of the electron delocalization during ionization of **1**-X, and we hope to elaborate on this point in the future.

(10) (a) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1856 (1964); (b) Y. E. Rhodes and T. Takino, *ibid.*, **92**, 5270 (1970); (c) M. J. S. Dewar and J. M. Harris, *ibid.*, **92**, 6557 (1970).

(11) (a) H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968); (b) J. S. Haywood-Farmer and R. F. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); (c) P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2551 (1970); (d) G. D. Sargent and M. A. Herkenham, *ibid.*, **94**, 2892 (1972); (e) M. S. Baird and C. B. Reese, *Chem. Commun.*, 523 (1972).

(12) (a) The analysis is based on the acetate methyl group as internal standard. (b) More recent results indicate that it is the methine proton at $C_1$ which remains unique, and that the two methylene positions are scrambled equally. This raises the intriguing possibility that the intermediate is a $C_{2v}$ bridged species, the prototype of which has recently been discussed theoretically.[13]

(13) W-D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

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## Unusual Metalloporphyrins. XIV. The Structure of [*meso*-Tetraphenylporphinato]bis[tricarbonylrhenium(I)]

*Sir:*

X-Ray structural studies have established that the metal atoms in some metalloporphyrins are 0.3–0.5 Å out of the plane of the four pyrrole nitrogen atoms of a porphyrin molecule.[1] Even greater displacements of metal atoms from the plane of four isoindole nitrogen

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(1) J. L. Hoard, *Science*, **174**, 1295 (1971).