

from the compression in C-C-C angles at carbons 3, 5, and 7 produced on partial flattening at C-4, and from the distortion of angles at C-4 resulting from the inability of this carbon to reach full planarity.

A similar situation, though less extreme, is obtained in the bi- and tricyclooctyl^{13a} systems. Triflate **13** is more reactive than **10**, but less reactive^{13b} by a factor of 10^2 than **16**. Once again, both trends are well accounted for by calculations¹² based only on strain effects (Table I).

It is clear from our observations that the proximity of the face of a three-membered ring provides little or no stabilization for a developing positive charge. We infer from this that the approach of an electrophile to the edge of a cyclopropane ring must be a great deal more favorable than approach to the face.

Consideration of the Walsh model¹⁴ of cyclopropane offers an explanation for this edge-face reactivity difference. When interacting with the face, the empty orbital of an electrophile must mix with the three sp^2 orbitals pointed toward the center of the ring. Interaction with an edge occurs between the empty orbital and cyclopropane electrons in more pure p-like orbitals. Even though the electron density in the center of the ring is probably relatively high,¹⁴ the lower energy of sp^2 orbitals (ionization potential $\cong 14.7$ eV¹⁵) will make them much more reluctant than p orbitals (ionization potential $\cong 11.4$ eV^{15b}) to transfer electron density to the incoming electrophile.¹⁶

Acknowledgments. We are grateful to the National Institutes of Health (Grant No. GM16231-01) for partial support of this work, to Professor S. Julia for a sample of alcohol **12**, to Drs. W. C. Ripka and J. C. Kauer for samples of 1,4-dichloro- and 1,4-dibromobicyclo[2.2.2]octanes, and to Professor P. von R. Schleyer for informing us of related work being carried out in his laboratory.

(13) (a) S. Julia and G. Guerey, *Bull. Soc. Chim. Fr.*, 3002 (1965). (b) The rate for **16** was estimated by determining an approximate triflate-bromide rate ratio from the solvolysis rates of 1-norbornyl bromide^{13c} and 1-apocamphyl triflate (**10**), and then applying this factor to the known^{13c} solvolysis rate of 1-bicyclo[2.2.2]octyl bromide. Corrections for differing γ values were made when necessary. (c) M. Finkelstein, Ph.D. Dissertation, Yale University, New Haven, Conn., 1955.

(14) Cf. A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(15) (a) Approximated as one-third of the sum of the ionization potentials^{15b} of a carbon 2s orbital and two carbon 2p orbitals; (b) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(16) We are carrying out EHT and CNDO-II calculations on the 1-nortricyclyl cation which will be described in a full paper. Preliminary results, however, of the EHT calculations indicate that very little charge is transferred to the cyclopropane ring carbons of the cation, in accord with our experimental results.

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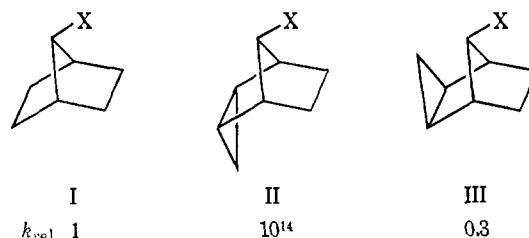
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Received January 29, 1970

Solvolytic Reactivity of 4-Nortricyclyl Triflate. A Carbonium Ion Analog of a Face-Protonated Cyclopropane

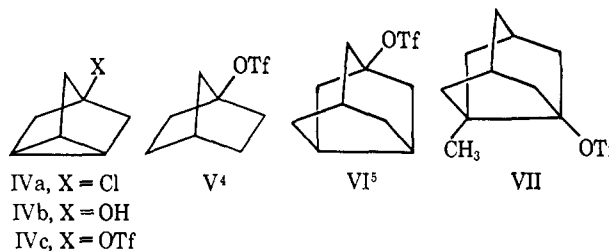
Sir:

In favorable cases, participation by a neighboring cyclopropane ring can rival that by a double bond.¹ The orientation is very important. Thus, II, in which edge participation is possible, shows a remarkable rate enhancement over I, which enhancement is completely absent in III.^{1a,e}



These observations are qualitatively consistent with theoretical calculations on protonated cyclopropane² and protonated nortricyclene.³ Considerably greater proton binding energy is found for the edge-protonated form than for the corresponding face-protonated isomer. Significant stabilization is nevertheless indicated for face protonation.

In an attempt to obtain further information concerning the extent of participation by the face of remote cyclopropane in solvolysis reactions, we have now studied the solvolytic reactivity of 4-tricyclo[2.2.1.0^{2,6}]heptyl trifluoromethanesulfonate (4-nortricyclyl triflate, IVc) and compared its reactivity with that of three other bridgehead triflates, V-VII.



The 4-nortricyclyl system (IV) uniquely permits the generation of an electron-deficient center in a position fixed directly and centrally above the cyclopropane ring.⁶ Participation by the cyclopropane ring should result in an enhanced reactivity relative to that predicted on the basis of steric effects alone.

We have employed computer-conformational analysis to quantitatively evaluate the significance of such

(1) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) M. J. S. Dewar and J. M. Harris, *ibid.*, **90**, 4468 (1968), and references cited therein; Y. E. Rhodes and T. Takino, *ibid.*, **90**, 4469 (1968); (c) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968); (d) R. Muneyuki, T. Yano, and H. Tanida, *J. Amer. Chem. Soc.*, **91**, 2408 (1969); (e) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(2) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969), and references cited therein.

(3) G. Klopman, *ibid.*, **91**, 89 (1969).

(4) 1-Norbornanol: D. B. Denney and R. R. DiLeone, *ibid.*, **84**, 4737 (1962).

(5) 1-Noradamantanol: J. S. Wishnok, P. v. R. Schleyer, A. Nickon, G. Pandit, and R. Williams, to be published.

(6) The distance between the 4 position and the plane of the cyclopropane ring is found to be 2.1 Å; cf. J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, **25**, 369 (1969).

Table I. Solvolysis Data

Compd	Solvent	Temp, °C	k , sec ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
IVc	50% aq C ₂ H ₅ OH 0.03 M (C ₂ H ₅) ₃ N	212.4	2.47×10^{-5} ^a	28.8	-21.2
		230.1	8.12×10^{-6} ^a		
		255.0	3.01×10^{-4} ^a		
		100.0	2.45×10^{-9} ^b		
		100.0	1.1×10^{-11} ^c		
V	50% aq C ₂ H ₅ OH	75.2	3.05×10^{-6} ^d	26.8	-2.5
		99.8	4.19×10^{-4} ^d		
		100.0	4.27×10^{-4} ^b		
		124.8	2.28×10^{-6} ^a		
		155.3	3.11×10^{-4} ^a		
VI	HOAc	100.0	1.98×10^{-6} ^b	28.2	-9.4
		24.95	1.68×10^{-4} ^d		
		50.8	3.90×10^{-3} ^d		
VII ^e	HOAc	100.0	4.68×10^{-1} ^b	28.7	+6.4
		100.0	2.90×10^{-3} ^b		
		100.0	2.90×10^{-3} ^b		

^a Determined titrimetrically. ^b Calculated. ^c Estimated assuming the same $k_{50\% \text{ EtOH}}/k_{\text{HOAc}}$ ratio as that found for V. ^d Determined conductometrically. ^e Reference 11.

participation. This involves the calculation of the enthalpy difference between ground state and transition state as measured by the calculated strain energy difference between hydrocarbon and carbonium ion.^{7a} This enthalpy difference has been found to be directly proportional to the log of the solvolysis rate for a wide variety of bridgehead substrates.⁷ Only slight modifications have been made in the program used

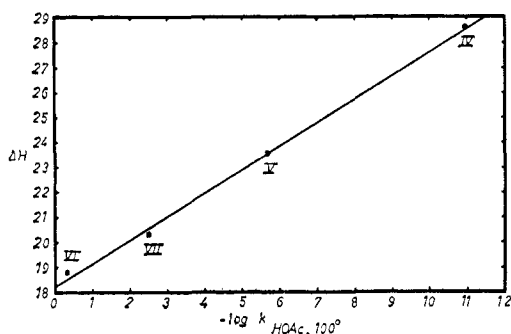


Figure 1. Calculated hydrocarbon-carbonium ion strain differences (ΔH) plotted against $-\log$ of the experimental rate constants at 100° in acetic acid.

earlier.^{7a} Further improvement in accuracy is achieved by the use of slightly "harder" C...H and C...C nonbonded interaction functions and by the use of "natural"^{7b} rather than tetrahedral bond angles as the standard of reference.^{7d} Also, we have found it best to compare rate data for bridgehead substrates having the same leaving group, a procedure adopted here.

The tricyclic alcohol IVb [mp 126–128°; nmr (CCl₄) δ 1.06 (1 H, s), 1.40 (6 H, s), and 3.06 (1 H, s); *Anal.* Calcd for C₇H₁₀O: C, 76.32; H, 9.15. Found: C, 76.35; H, 9.07] was prepared by lithiation and subsequent oxygenation⁹ of the corresponding chloride, IVa.^{6,10} The liquid triflate ester IVc [nmr (CCl₄)

(7) (a) G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967); (b) P. von R. Schleyer, P. R. Isele, and R. C. Bingham, *J. Org. Chem.*, **33**, 1239 (1968); (c) P. von R. Schleyer, paper presented at the International Symposium on Conformational Analysis, Brussels, Belgium, Sept 1969; (d) R. C. Bingham, unpublished results.

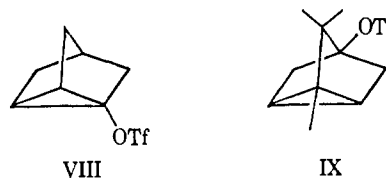
(8) Review: J. E. Williams, P. J. Stang, and P. von R. Schleyer, *Ann. Rev. Phys. Chem.*, **19**, 531 (1968).

(9) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, p 276.

(10) We are grateful to Dr. George L. Dunn of Smith, Kline and French Laboratories, Inc., for a sample of this material.

δ 1.89 (6 H, s) and 1.29 (3 H, s); ir (CCl₄) 1407, 1232, 1203, 1138, 1048, and 880 cm⁻¹] as well as the triflates (except VI) of the other alcohols were prepared in the usual manner.¹¹ The unstable triflate VI was most readily synthesized by treating equimolar amounts of the lithium alcoholate in ether and trifluoromethanesulfonic anhydride at room temperature under N₂; yield was nearly quantitative.

4-Nortricyclyl trifluoromethanesulfonate (IVc) proved to be the least reactive triflate we have yet measured.¹¹ IVc is much less reactive than the reference molecules V–VII (Table I) and even slower than 1-nortricyclyl triflate (VIII), the former record holder.¹¹ In buffered acetic acid the only reaction observed with IVc was solvent attack on the cyclopropane ring. Good first-order kinetics through at least three half-lives were observed, however, in 50% aqueous ethanol above 200°.¹²



The reactivities of all four triflates, IVc–VII, are correlated excellently (correlation coefficient 0.998, average deviation 10^{±0.2}) by the modified conformational analysis program (Figure 1).⁷ This computer method does not take into account electronic effects. Therefore, we conclude that there is no evidence for significant participation by the face of the cyclopropane ring in the solvolysis of IVc. Within the error limits of the computational method, normal bridgehead behavior is observed for IVc.¹³

(11) T. M. Su, W. F. Sliwinski, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969).

(12) While products were not rigorously determined due to the lack of material available, the glpc of the product mixture from IVc showed two major peaks, one of which was identical in retention time with IVa (the other presumably being the corresponding ether). For the similar trimethyl system IX, solvolysis in 60% EtOH afforded only the un-rearranged alcohol and ether: S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. Morris, *J. Amer. Chem. Soc.*, **92**, 3469 (1970). We wish to thank Professor Bergman for an exchange of information prior to publication.

(13) Review: R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicycl. Chem.*, **1**, 283 (1966).

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society. We would like to thank Dr. R. L. Hansen of the Minnesota Mining and Manufacturing Co. for generous gifts of trifluoromethanesulfonic acid and anhydride.

(14) National Institutes of Health Predoctoral Fellow, 1967-1970.

(15) National Science Foundation Fellow, 1965-1967; American Machine and Foundry Fellow, 1967-1969.

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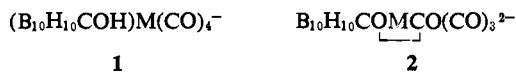
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Metalloboranes. V.¹ Carbonyl Insertion in the Formation of Icosahedral Metalloboranes

Sir:

We wish to report a new direct synthesis of quasi-icosahedral metalloboranes from the $B_{10}H_{13}^-$ ion and metal hexacarbonyls.² This synthesis uniquely involves incorporation of a carbon atom in the icosahedral framework by a carbonyl insertion into the $B_{10}H_{13}^-$ ion. The resulting metalloboranes comprise two classes of complexes formally derived from the $B_{10}H_{10}COH^{2-}$ ligand³



with M = chromium, molybdenum, and tungsten. The class 2 ions have an unusual ether linkage between a carbonyl ligand and the icosahedral framework. Unlike other carboranes and metalloboranes,⁴ all representatives of these two classes are partially degraded by base with removal of a carbon atom, not a boron atom, from the icosahedral framework to give a new set of *nido* metalloboranes, $B_{10}H_{12}M(CO)_4^{2-}$ (3).

Irradiation (350 nm) of tetrahydrofuran solutions of $NaB_{10}H_{13}$ and the metal hexacarbonyls (inert atmosphere) gave the $(B_{10}H_{10}COH)M(CO)_4^-$ class 1 anions⁵ in 50% yield and treatment of these with sodium hydride gave quantitative yields of the yellow $B_{10}H_{10}COMCO(CO)_3^{2-}$ class 2 ions.⁶

(1) Part IV: A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

(2) Metalloboranes which are 11-atom icosahedral fragments have been prepared from $B_{10}H_{13}^-$: (a) N. N. Greenwood and N. F. Travers, *J. Chem. Soc., A*, 880 (1967); *Chem. Commun.*, 216 (1967); (b) F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **7**, 2073 (1968).

(3) W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 3342 (1967). The $B_{10}H_{10}COH^{2-}$ ligand was not prepared in an uncomplexed form but was obtained in the $(B_{10}H_{10}COH)_2Ni^{2-}$ ion by reaction of nitrous acid and $(B_{10}H_{10}CNH_2)_2Ni$.

(4) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(5) Sample characterization of $[(CH_3)_4N](B_{10}H_{10}COH)Mo(CO)_4$. *Anal.* Calcd: C, 25.2; H, 5.62; B, 25.2; N, 3.26; O, 18.6; Mo, 22.3; formula wt, 430.2. Found: C, 25.6; H, 5.55; B, 25.2; N, 3.29; O, 18.0; Mo, 22.4; mol wt (osmometry- CH_3CN), 211; equiv wt (titration of acid form), 395. ¹¹B nmr (32 MHz) (CH_3CN) [$B(OCH_3)_3 = 0$] 16.4 ($J = 108$), 23.71 ($J = 124$), 27.67 ($J = 128$ Hz), 31.38 (sh), 33.35 ppm (sh). Ir (THF) 3355 (m) (OH), 2510 (s) (B-H), 2063 (s), 1978 (s), 1950 cm^{-1} (s) ($C\equiv O$); (Nujol) 3480 cm^{-1} (s) (OH).

(6) Sample characterization of $[(C_4H_9)_4N]_2[B_{10}H_{10}COMCO(CO)_3]$. *Anal.* Calcd: C, 53.0; H, 9.79; B, 12.9; O, 9.54; Mo, 11.4; formula wt, 838. Found: C, 52.6; H, 9.81; B, 14.4; O, 10.7; Mo, 11.9; mol wt (CH_3CN), 443. ¹¹B nmr (32 MHz) (CH_3CN) [$B(O-$

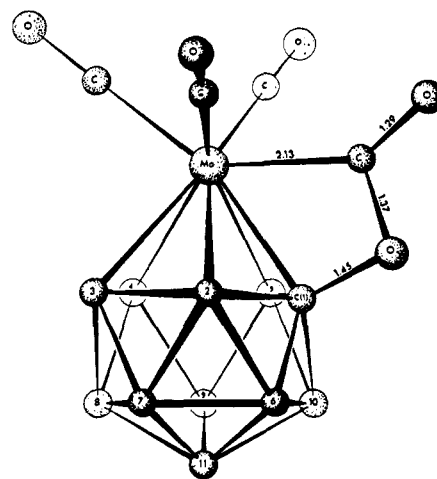
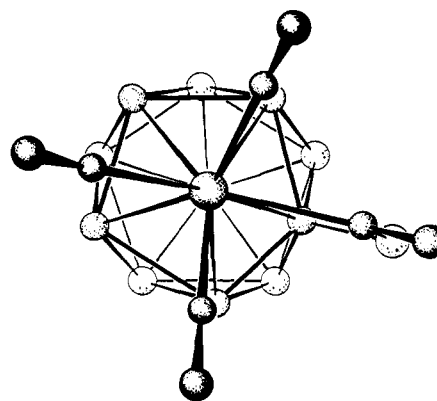
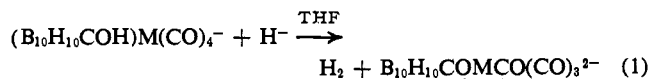


Figure 1. The bottom figure shows a side view of the $B_{10}H_{10}COMCO(CO)_3$ class 2 dianion with the terminal hydrogen atoms omitted. The top figure shows the corresponding top view of the dianion.



The structure of the class 2 boranes was established by a single-crystal X-ray analysis of the tetrabutylammonium salt of $B_{10}H_{10}COMoCO(CO)_3^{2-}$ class 2 ions from 4000 pieces of data collected on a four-circle automatic diffractometer using Mo $K\alpha$ radiation. Crystals are triclinic, space group $P\bar{1}$, with $a = 13.492$ (6), $b = 17.992$ (10), $c = 11.271$ (8) Å, $\alpha = 104.02$ (9), $\beta = 93.63$ (16), and $\gamma = 105.78$ (7)°. The observed and calculated densities for two formula units per cell are 1.12 and 1.10 g/cm^3 , respectively. No absorption correction was applied since the maximum μR was less than 0.1. The structure was solved by a combination of Patterson and Fourier techniques. The results are described for the least-squares refinement ($R = 0.09$) using the 2500 strongest reflections and a model with anisotropic thermal parameters for molybdenum and five carbonyl groups and isotropic thermal parameters for the remaining nonhydrogen atoms.

The X-ray structure (Figure 1) shows that the class 2 ions have a metal atom completing a $B_{10}C$ icosahedral CH_3 = 0] 24.70 ($J = 123$), 28.95 ($J = 148$ Hz), 31.28, 36.40 ppm. Ir (CH_3CN) 2490 (s) (B-H); 1992 (s), 1908 (s), 1883 (s) ($C\equiv O$); 1659 (> $C=O$); (Nujol) 2495 (B-H), 1980 (s), 1905 (s), 1875 (s) ($C\equiv O$); 1662 cm^{-1} (> $C=O$).