It seems reasonable to suppose that this difference would be felt in the corresponding transition states. Another example of what may be the same influence is reported in an accompanying paper.[2b]

[22] National Institutes of Health Predoctoral Fellow, 1964–1966.

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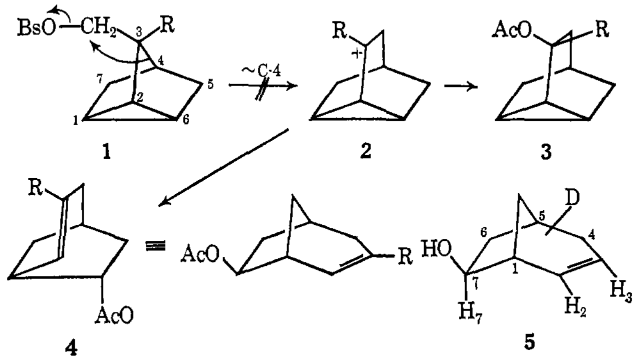
A Circuitous Mechanism for the Formation of a Cyclopropylcarbinyl Cation. On the Anomalous Relative Migratory Aptitude of a Cyclopropyl *vs.* a Cyclopentyl Ring in Nortricyclylcarbinyl Cation[1]

Sir:

Carbonium ion reactions of the nortricyclylcarbinyl system (**1**) produce large amounts of materials derived from the 3-tricyclo[3.2.1.0^{2,7}]octyl cation (**2**) which is captured either in the form of the corresponding very sensitive tricyclic product **3** or the closely related unsaturated isomer **4**.[2-4] The most straightforward mechanism imaginable for the **1** → **2** rearrangement involves migration of the cyclopentane ring carbon (C-4) to the methylene side chain, producing the very stable cyclopropylcarbinyl cation **2** directly. Nevertheless, the present experiments show that the **1** → **2** rearrangement shuns this path.

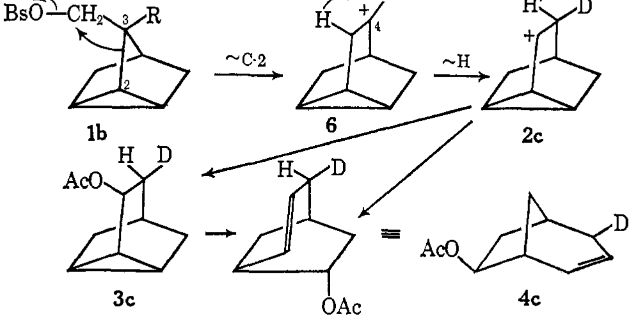


a, R = H; b, R = D

3-Nortricyclylcarbinol-3-*d* containing 0.83 D/molecule[5] is formed by lithium aluminum hydride reduction of a mixture of methyl and *t*-butyl esters of 3-nortricyclene carboxylic-3-*d* acid which results from the reaction of methyl 3-nortricyclenecarboxylate with potassium *t*-butoxide in boiling *t*-butyl alcohol-O-d. The location of the deuterium at C-3 follows from the method of synthesis and is confirmed by the nuclear magnetic resonance (nmr) spectrum (solvent CCl_4, tetramethylsilane internal standard, 60 MHz), which shows the signal of the carbinol methylene protons as a singlet at δ 3.34 rather than the doublet characteristic of the undeuterated compound.

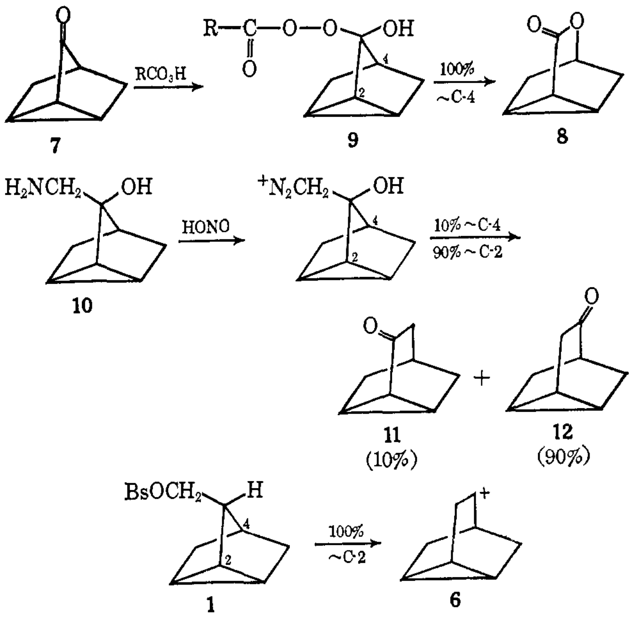
Solvolysis of the deuterated *p*-bromobenzenesulfonate **1b** in acetic acid (sodium acetate buffer) gives a mixture from which, after lithium aluminum hydride reduction and preparative vapor chromatography, bicyclo[3.2.1]oct-2-en-7-ol (**5**) is isolated. This material contains 0.82 D/molecule,[5] and its nmr spectrum shows the O–H and upfield C–H protons as a series of overlapping absorptions of intensity 8. Careful integration of the spectrum of this material (H-2 plus H-3 at δ 5.2–6.0 *vs.* H-7 at δ 4.13) shows the presence of 1.97 ± 0.04 vinyl protons. Therefore, not more than 3–4% of the product **5** is formed from the vinylically deuterated acetate **4b** that would result from the direct cyclopentane migration mechanism.

The results are consistent with a circuitous mechanism in which net cyclopropane ring carbon (C-2) migration gives the tricyclooctyl cation **6** (or a delocalized variant), either directly or through closely related intermediates.[4] The vicinal hydride shift already known[2b,4] to occur in this system then transforms **6** into the C-4-deuterated cyclopropylcarbinyl cation **2c**.



The exclusive cyclopropyl migration observed in **1b** provides a point needed to complete the pattern of structure *vs.* relative migratory aptitude in this series.

Baeyer–Villiger oxidation of nortricyclanone (**7**) gives lactone **8**, resulting from cyclopentyl migration[6] in the intermediate **9**. Nitrous acid deamination of the amino



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[1] We are grateful for grants in partial support of this work from the National Science Foundation (GP6212X), the National Institute of Arthritis and Metabolic Diseases (AM-07505), and the Air Force Office of Scientific Research (M2(967)62/1006-66).

[2] (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (b) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

[3] K. B. Wiberg and G. Wenzinger, *ibid.*, **30**, 2278 (1965).

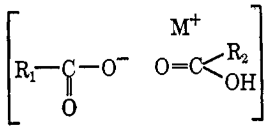
[4] (a) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, **90**, 3236 (1968); (b) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *ibid.*, **90**, 3238 (1968).

[5] Falling-drop analysis by Mr. J. Németh, Urbana, Ill.

[6] (a) R. R. Sauers, *Tetrahedron Letters*, 1015 (1962). (b) The structure is assigned from the nmr spectrum in concentrated sulfuric acid.[6a] Because of the possibility of rearrangement or selective destruction of the lactone that would result from cyclopropyl migration, the extent of the preference for cyclopentyl migration is not firmly established.

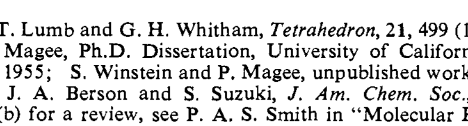
alcohol **10** gives 10% ketone **11**, resulting from cyclopentyl migration, and 90% ketone **12**, from cyclopropyl migration.[7]

The Baeyer–Villiger case is a mechanistic extreme in which the high electronegativity of the migration terminus (oxygen) and the exceptional strength of the C=O π bond thrust an inordinately large share of positive charge upon the migrating group M, *i.e.*, the resonance structure **13** is a large contributor to the transition state.[8,9] This factor dominates the rearrangement of **9**[6] and that of the corresponding Baeyer–Villiger intermediates in other model systems,[10] all of which show cyclopropyl to be a poor migrating group relative to other *sec*-alkyl groups. Presumably because the high s character of the migrating ring carbon in cyclopropyl makes it rather electronegative, the relative contribution of resonance structure **13** is diminished and hence the transition state is destabilized. When the migration terminus is carbon, as in cases **1** and **10**, the positive charge resides to a smaller extent on the migrating group, and cyclopropyl migration becomes *relatively* more important than in **9**. What is at first surprising is the *net preference* for migration of the less efficient migrating group (cyclopropyl) to give the less stable ring-expanded cation **6**, which only an appended hydride shift finally converts to the more stable cation **2**. The mechanism is curiously indirect, since **2** in principle could be generated in one step from **1** by migration of the better migrating group (cyclopentyl). This behavior seems to be largely a result of steric inhibition of cyclopropylcarbinyl resonance.[11] Although the fully developed cyclopropylcarbinyl cation **2** has the favorable "bisected" geometry,[12] the transition state **14**[13] for direct cyclopentyl migration leading to **2** does not. With the ordinary conjugative interaction thus damped, the cyclopropane ring is less efficient than a simple alkyl group as a stabilizer of adjacent positive charge.[11] When there is an additional contiguous source of electron supply to the migration origin (for example, the OH group in **10**), the effect is mitigated, and some cyclopentyl migration occurs.



$$\left[R_1-\underset{\underset{O}{\|}}{C}-O^- \quad \overset{M^+}{O=C\begin{smallmatrix}R_2\\OH\end{smallmatrix}} \right]$$

13



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(7) J. T. Lumb and G. H. Whitham, *Tetrahedron*, 21, 499 (1965).

(8) P. Magee, Ph.D. Dissertation, University of California at Los Angeles, 1955; S. Winstein and P. Magee, unpublished work.

(9) (a) J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, 81, 4088 (1959); (b) for a review, see P. A. S. Smith in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 577–591.

(10) R. R. Sauers and R. W. Uebersax, *J. Org. Chem.*, 30, 3939 (1965).

(11) For another example, see H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).

(12) See references cited in ref 4 and 11.

(13) Positions in 2 are designated to give its carbon atoms the same numbers as their counterparts in **14**.

(14) National Institutes of Health Predoctoral Fellow, 1964–1966.

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The Characterization and Molecular Configuration of Diazulenetetrairon Decacarbonyl

Sir:

We have recently shown that the complex $(CH_3)_3C_{10}H_5Ru_4(CO)_9$ has a 4,6,8-trimethylazulene ligand bonded to *three* atoms of a tetrahedral ruthenium cluster.[1] This unexpected result has prompted our examination of a polynuclear azulene–iron carbonyl complex which previously had been tentatively formulated[2] as "$(C_{10}H_8)_2Fe_5(CO)_{13}$." We now report that this species should be reformulated as $(C_{10}H_8)_2Fe_4(CO)_{10}$, that it does *not* contain a cluster of four metal atoms, but that it *does* show some features novel to azulene–metal carbonyl chemistry.

The complex was prepared by the method of Burton, *et al.*[2] Beautiful multifaceted deep-brown crystals of stoichiometry $(C_{10}H_8)_2Fe_4(CO)_{10}\cdot C_2H_4Cl_2$[3] were obtained by slow cooling of a solution in 1,2-dichloroethane–hexane. The compound crystallizes in the centrosymmetric monoclinic spacegroup C2/c (C_{2h}^6; no. 15) with $a = 17.296$ Å, $b = 15.541$ Å, $c = 12.915$ Å, $\beta = 114.53°$, $Z = 4$. Observed and calculated densities are 1.82 ± 0.02 and 1.805 g cm^{-3}. A set of X-ray diffraction data complete to $\sin\theta = 0.40$ (Mo Kα radiation) were collected with a 0.01° incrementing Buerger automated diffractometer, using a "stationary-background, ω-scan, stationary-background" counting sequence. The structure was solved by Patterson, Fourier, and least-squares refinement techniques, the discrepancy index at the present stage of refinement being $R_F = 6.61\%$ for 2040 independent nonzero reflections. Refinement is continuing.

The $(C_{10}H_8)_2Fe_4(CO)_{10}$ molecule has exact (*i.e.*, crystallographically required) C_2 symmetry (see Figure 1) and is derived from two *trans*-$C_{10}H_8Fe_2(CO)_5$ units which are linked both by a 4-*endo*-4′-*endo* carbon–carbon bond and by an $Fe_2(CO)_4$ bridge analogous to that found in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$,[4] the Fe–Fe distance being 2.519 ± 0.002 Å. (However, the site symmetry of the $Fe_2(CO)_4$ moiety is C_2 in the present complex as opposed to C_i in the parent molecule.[4] Thus the $Fe_2(CO)_4$ fragment in $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ is more-or-less planar, whereas there is an angle of 154.8° between the planes of the two carbonyl bridges in the $(C_{10}H_8)_2Fe_4(CO)_{10}$ molecule.) As in previously examined azulene complexes $\{C_{10}H_8Fe_2(CO)_5$,[5] $C_{10}H_8Mo_2(CO)_6$,[6,7] (*i*-

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(1) M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, **90**, 800 (1968).

(2) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(3) (a) Mass spectroscopy showed the parent-iron peak at *m/e* 760. The accidental mass relationship $^{56}Fe = 2(^{12}C^{16}O)$ precluded an unequivocal structural assignment, but led to the partial formula $(C_{10}H_8)_2Fe_n(CO)_{18-2n}$. (b) The dichloroethane molecule is present only as solvent of crystallization.

(4) O. S. Mills, *Acta Cryst.*, **11**, 520 (1958).

(5) M. R. Churchill, *Chem. Commun.*, 450 (1966); *Inorg. Chem.*, **6**, 190 (1967).