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ON THE CONFORMATION OF THE CYCLOPROPYL CATION

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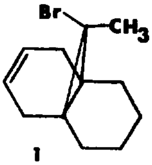
Our previous studies with several tricyclic halocyclopropanes indicate that in these systems "full-fledged" cyclopropyl cations are not reaction intermediates; rather, a partially opened species is implicated which begins to resemble a perpendicular allyl cation.[2] Examination of molecular models demonstrates that conversion of an intermediate of this type to an allyl cation of normal conformation is highly unfavorable. The energy difference between a cyclopropyl and a perpendicular allyl cation (unsubstituted) is relatively small. This has been computed by Schleyer, Pople, and Radom to be on the order of 4 kcal/mole, the allyl ion being more stable. Substitution of a methyl group on the central carbon of the three carbon system shifts the stability to the cyclopropyl ion to the extent of some 14 kcal/mole.[3] Thus it was reasoned that the epimeric tricyclic derivatives 1 and 2 should ionize to true cyclopropyl ions and that a perusal of products as well as rate data would provide insight into the stereochemistry of the cyclopropyl cation which theoretical calculations indicate should be a planar species.[4]



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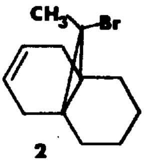

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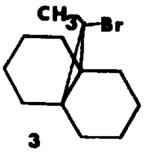

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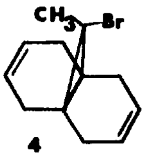

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Compounds 1 and 2 were synthesized from the corresponding dibromide.[5] Their stereochemistry was assigned by examination of their nmr spectra as well as the nmr spectra of compounds 3 and 4 (see Table I).

TABLE I

Pertinent NMR Data

Compound	CH_3-	CH_3O-
1	1.88ppm from TMS	
2	1.72	
3	1.88	
4	1.76	
5	1.40	3.39
6	1.20	3.41

The silver ion assisted methanolysis of both 1 and 2 was carried out. The products of the reaction as well as yields are reported in Table II; rates and activation parameters are contained in Table III.

TABLE II

Solvolysis Products

Compound	R/I[a]	5[b]	6[b]	7	Absolute yields
1	6.7	87%	13%	5-10%	75-80%
2	32	3%	97%	0-1%	80-85%

[a] Retention to inversion ratio. [b] Relative yields.

TABLE III

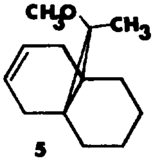
Rate Data (95% MeOH)

Compound	Temp, °C[a]	k, l.mole^{-1} min^{-1}	ΔH‡, kcal mole^{-1}	ΔS‡, eu	$k_{rel}^{25°}$
1	40.1	2.54×10^{-3} (±.01)	19.5	-8.2	1
	50.0	7.66×10^{-3} (±.05)			
	60.1	1.77×10^{-2} (±.05)			
	25.0	5.13×10^{-4}[b]			
2	40.1	2.74×10^{-2} (±.02)	15.5	-16.3	14.4
	27.8	9.51×10^{-3} (±.19)			
	25.0	7.39×10^{-3}[b]			

[a] At least two runs were made at each temperature.

[b] This is an extrapolated value.

The stereochemistry of the epimeric ethers 5 and 6 was tentatively assigned on the basis of the position of absorption of their methyl hydrogens in the nmr. Less ambiguous assignment of their structures comes from an examination of their nmr spectra when dissolved with a europium shift reagent. The ether whose olefinic protons were shifted to a greater degree on addition of a given quantity of Eu(fod)$_3$ was assigned structure 5 (see Figure 1). It is noteworthy that both 1 and 2 solvolyze largely with *retention* of configuration.



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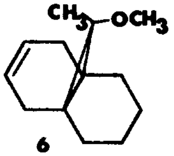

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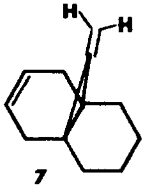

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Grob has recently demonstrated that the silver ion assisted solvolysis of *cis* and *trans*-1-chloro-1,2-dimethylcyclohexanes proceeds with predominant inversion of configuration.^{6} Presumably an encumbered, planar cation is an intermediate in these reactions--with solvent approaching the electron deficient center from the less hindered side. Our results, then, seemingly rule out the formation of a planar, encumbered ion (similar to that postulated by Grob) in the ionization of 1 and 2. Assuming that both 1 and 2 have essentially identical ground state energies (CH$_3$- is similar in size to Br-) then the rate data exclude extensive participation of unsaturation in the transition state during the solvolysis of 2. This is also borne out by the lack of rearranged products. In addition no products arising from a partially opened cyclopropyl cation were detected. One possible explanation for our data is a non-planar or "bent" cyclopropyl cation.

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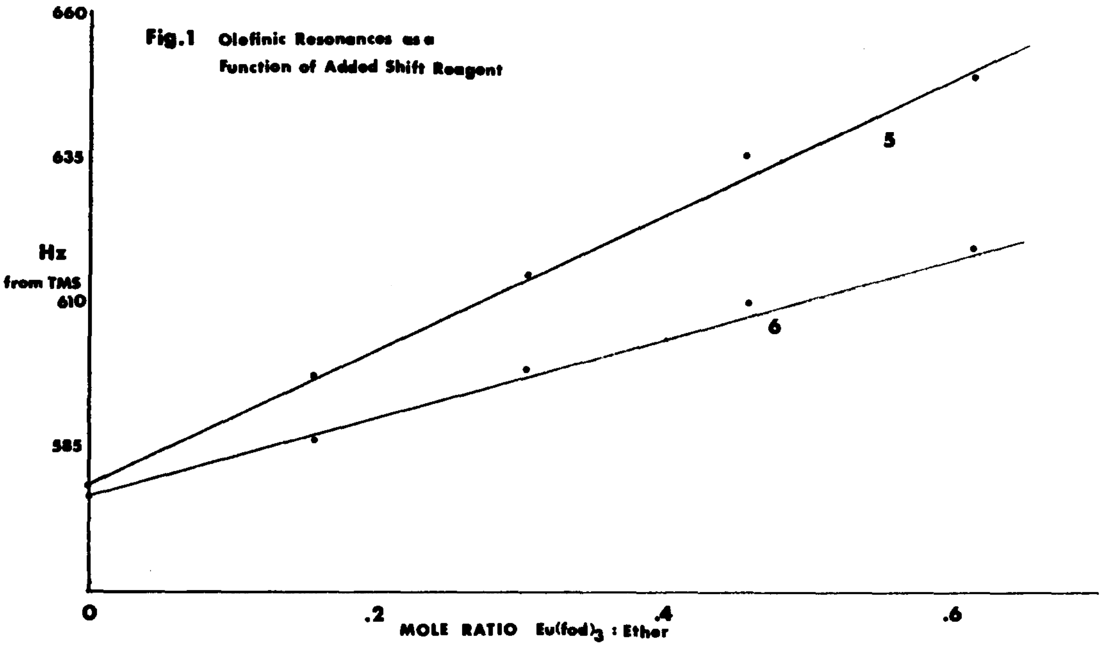

Fig.1 Olefinic Resonances as a Function of Added Shift Reagent

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1. a) University of Vermont undergraduate work-study participant.
   b) A.C.S. Project Catalyst High School Fellow.
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5. a) K. Kitatani, T. Hiyama, and H. Nozaki, J. Amer. Chem. Soc., 97, 949 (1975). We are indebted to Professor Nozaki for providing us with additional experimental details.
   b) All new compounds analyzed correctly. In addition to spectral data some compounds were either synthesized or converted to materials of known structure.
6. C. A. Grob and K. B. Becker, Helv. Chim. Acta, 56, 2723 (1973).