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ON THE CONFIGURATIONAL EQUILIBRATION OF α-CHLOROCYCLOPROPYL AND α-FLUOROCYCLOBUTYL RADICALS.

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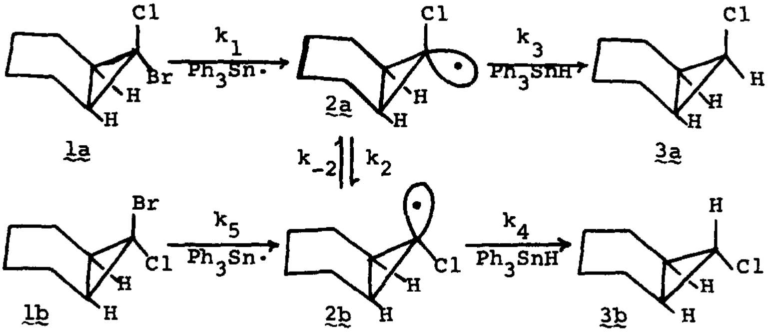
We have been prompted to investigate the effects of α-substituents on the inversion barriers of radicals[1] by the large difference in configurational stability between the unsubstituted cyclopropyl radical[2] and an α-fluorocyclopropyl radical.[3] We report here our results on the inversion rates of an α-chlorocyclopropyl and an α-fluorocyclobutyl radical.

It is known that reduction of an alkyl halide with tin hydride proceeds through a radical intermediate.[4] We therefore decided to investigate the reduction of the two isomers of 7-bromo-7-chloronorcarane (1) with Ph_3SnH as the product distribution would give some indication of the relative rate of inversion of the intermediate radical with respect to its rate of reduction.



Scheme I

The two isomers of 1 were separated by glpc (16 ft x 8 mm O.D. Pyrex column of 23% Carbowax 20M on 60/80 mesh Gas Chrom Q at 140°) to better than 99% isomeric purity. Each isomer was reduced with Ph_3SnH at 30° and the isomeric composition of the products[5] determined by glpc. Recovered 1 showed no isomerization and both isomers of 3 were stable to the reaction conditions. No 7-bromonorcarane was detected in the reaction mixture. The results of the reductions are shown in Table I.

TABLE I

Product Distribution from the Reduction of 1 with Ph_3SnH at 30°

Starting Material[6]	$[Ph_3SnH]$ (M)	% 3a	% 3b
		(max. error ± 1.3%)	
1a	3.95	84.2	15.8
1a	0.06	79.1	20.9
1b	3.95	68.8	31.2
1b	0.05	78.3	21.7

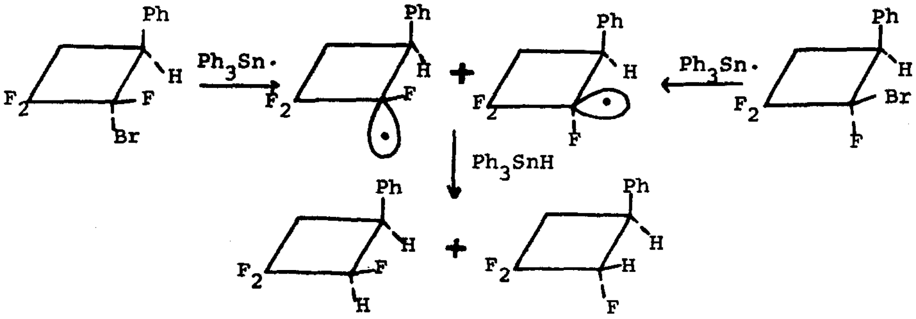
The less stable isomer of 3 predominates in the product mixture. Thus it is apparent that steric hindrance to the approach of Ph_3SnH to the intermediate radical must be an important factor in determining the product distribution.

It is clear that complete equilibration of the intermediate radicals has not been achieved before reduction. From an examination of Scheme I, the following expression can be derived for the reduction of 1b:

$$\frac{[3b]}{[3a]} = \frac{k_2k_4}{k_3k_{-2}} + \frac{k_4[Ph_3SnH]}{k_{-2}}$$

If it is assumed that k_3, the rate constant for reduction[7] of 2a, is 5×10^6 M^{-1} sec^{-1}, it can be shown that k_2, the rate constant for inversion of this α-chlorocyclopropyl radical, is 2×10^7 sec^{-1}.

The *cis* and *trans* isomers of 1,1,2-trifluoro-2-bromo-3-phenylcyclobutane[8] were separated by glpc to better than 97% isomeric purity. Each isomer was reduced in neat Ph_3SnH at 30° and the isomer ratios of the products determined by glpc.



Scheme II

The same 71:29 isomer ratio was obtained from each of the bromide isomers. If the α-fluorocyclobutyl radical is nonplanar, its rate of inversion is fast with respect to the rate of reduction with Ph_3SnH, in marked contrast to the α-fluorocyclopropyl radical.[3]

The energy barriers for radical inversions, calculated using the CNDO/2 approximation,[9] can be correlated with the trends observed in some radical inversions and should be useful for planning further experiments. Work is now in progress along these lines.

TABLE II

Results of CNDO/2 Calculations

Radical	Inversion Barrier (kcal/mole)
	10.5
	10.5
	5.4
	4.0
	1.9
	.8
•CHFCl	.7

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REFERENCES

(1) L. J. Altman and B. W. Nelson, *J. Amer. Chem. Soc.*, **91**, 5163 (1969); L. J. Altman and J. C. Vederas, *Chem. Commun.*, 895 (1969); L. J. Altman and T. R. Erdman, *Tetrahedron Lett.*, 4891 (1970).

(2) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(3) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970).

(4) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Amer. Chem. Soc.*, **84**, 3584 (1962); L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964).

(5) S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965).

(6) The configurations of **1a** and **1b** were assigned on the basis of the known configurations[5] of **3a** and **3b** and on a kinetic analysis of the system shown in Scheme I. The alternative assignment is inconsistent with the data obtained.

(7) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 1055 (1968).

(8) P. Tarrant, R. W. Johnson, Jr., and W. S. Brey, Jr., *J. Org. Chem.*, **27**, 602 (1962).

(9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970, p. 75. This program was obtained from the Quantum Chemistry Program Exchange, Bloomington, Indiana.