View Article Online / Journal Homepage / Table of Contents for this issue

Configurational Equilibration of α -Trifluoromethylcyclopropyl Radicals

By L. J. Altman* and J. C. Vederas

(Department of Chemistry, Stanford University, Stanford, California 94305)

Summary Reduction of cis- or trans-1-bromo-1-trifluoromethyl-2-phenylcyclopropane with a large excess of neat triphenyltin hydride at temperatures as low as 40° gives complete configurational equilibration before reduction can occur.

THERE has been much interest recently^{1,2} in the generation and trapping of cyclopropyl radicals before configurational equilibration can occur. Evidence has been presented³ that the reduction of alkyl halides by triphenyltin hydride proceeds through a free-radical intermediate. We report the results of reduction of *cis*- and *trans*-1-bromo-1-trifluoromethyl-2-phenylcyclopropane with a large excess of neat triphenyltin hydride (Table).

Complete configurational equilibration has occurred before reduction. This is especially interesting with respect to the findings of Ando *et al.*^{1,4} that the tri-n-butyltin hydride reduction of *gem*-halogenofluorocyclopropanes proceeds with complete stereospecificity at 130° and leads to only 8% isomerization at 165°. The rate of isomerization of α -fluorocyclopropyl radicals must therefore be at least two orders of magnitude slower than the isomerization of

	TABLE		
		Product distribution ^{b,c,d}	
Starting halidea.b.c	Temperature	<i>cis</i> -1-Trifluoromethyl- 2-phenylcyclopropane	trans-1-Trifluoromethyl 2-phenylcyclopropane
cis-l-Bromo-1-trifluoromethyl-2-phenylcyclo- propane ^e	. 80°	32.7	67.3
	60	31.0	69.0
	40	31.0	69.0
trans-1-Bromo-1-trifluoromethyl-2-phenylcyclo-			
propane ^f	. 80	29.8	70.2
	60	30.0	70.0
	40	30.8	69 ·2

^a Reductions were run in neat triphenyltin hydride with AIBN as initiator.

^b Satisfactory analyses have been obtained for all new compounds.

^c Configurations are tentatively assigned on the basis of n.m.r. spectra.

^d Distributions determined by v.p.c. analysis of crude reaction mixture and are determined with an error of $\pm 0.7\%$.

e Contaminated with 1.2% of *trans*-isomer. ^t Contaminated with 0.07% of the *cis*-isomer.

a-trifluoromethylcyclopropyl radicals.⁵ Thus, an explanation of the configurational stability of α -fluoro-radicals based on electronegativity⁶ is not likely. One attractive interpretation is that the planar transition state is destabilized relative to the tetrahedral radical by increased overlap with the fluorine nonbonding electrons.

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society and Eli Lilly and Company for partial support of this research.

(Received, June 18th, 1969; Com. 879.)

¹T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, J. Amer. Chem. Soc., 1967, 89, 5719.

² J. Jacobus and D. Pensak, Chem. Comm., 1969, 400. ³ H. G. Kuivila, Accounts. Chem. Res., 1968, 1, 299; H. G. Kuivila, L. W. Menapace, and C. R. Warner, J. Amer. Chem. Soc., 1962, 84, 3584; L. W. Menapace and H. G. Kuivila, ibid., 1964, 86, 3047. T. Ando, personal communication.

⁵ Tri-n-butyltin hydride reduction of t-butyl radical proceeds at one-sixteenth the rate of triphenyltin hydride reduction of t-butyl radical, D. J. Carlsson and K. J. Ingold, J. Amer. Chem. Soc., 1968, 90, 1055; ibid., p. 7047.
⁶ H. A. Bent, Chem. Rev., 1961, 61, 275.

Published on 01 January 1969. Downloaded by University of Warsaw on 25/10/2014 10:36:18.