Configurational Equilibration of α-Trifluoromethylcyclopropyl Radicals

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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 presented[3] 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 halide[a,b,c]	Temperature	*cis*-1-Trifluoromethyl-2-phenylcyclopropane	*trans*-1-Trifluoromethyl-2-phenylcyclopropane
cis-1-Bromo-1-trifluoromethyl-2-phenylcyclopropane[e]	80°	32·7	67·3
	60	31·0	69·0
	40	31·0	69·0
trans-1-Bromo-1-trifluoromethyl-2-phenylcyclopropane[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 ±0·7%.

[e] Contaminated with 1·2% of *trans*-isomer.

[f] Contaminated with 0·07% of the *cis*-isomer.

α-trifluoromethylcyclopropyl radicals.[5] Thus, an explanation of the configurational stability of α-fluoro-radicals based on electronegativity[6] 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.

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