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Propellanes. XV. Stereoselectivities of Cyclopropyl Radicals Generated Via Tin Hydride Reduction.[1]

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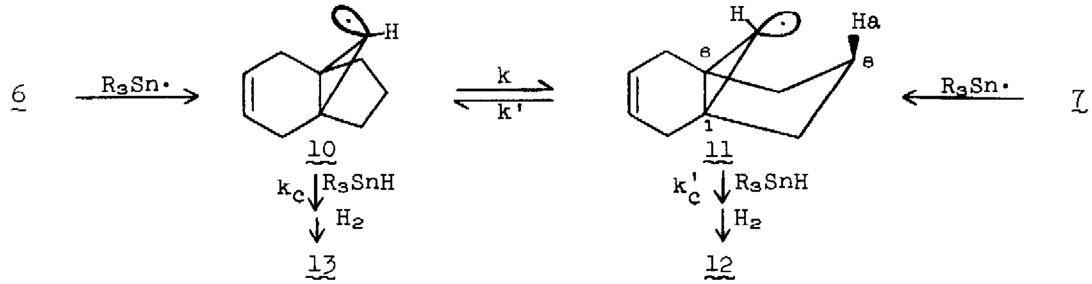
A number of reports have appeared concerning the configurational stability of cyclopropyl radicals. So far, only α-fluoro-[3] and α-chlorocyclopropyl[4] radicals have been trapped prior to equilibration; all others[4b,5] have behaved indistinguishably from planar (although probably rapidly inverting) radicals. We wish to report evidence for the pre-equilibrative trapping of some α-hydridocyclopropyl radicals.

Our observations began with the previously reported[6] reduction of 2 to give 6 and 7 (Table I). Data for the reduction of two related dibromides (1 and 3) are also included in Table I. Initial stereochemical conclusions are impossible to draw, since a priori either bromine atom of each dibromide could be removed. An analogous dilemma does not ensue when monobromides 4-8 are reduced;[7] Table II reports the results.

The three *syn* bromides (4, 6, 8) each undergo smooth reduction in hot benzene solution to yield primarily inverted product. Contrariwise, *anti* bromides 5 and 7 do not react under these conditions (72 hr). However, when the temperature was raised enough to overcome the activation barrier of the chain initiation step, 5 was reduced rapidly. Bromide 7 was reduced at lower temperature through the use of benzoyl peroxide as an initiator. Importantly, both 5 and 7 reduced solely with *retention* of configuration (within pmr limits). This makes it seem unlikely that the inversion observed for the *syn* bromides (4, 6, 8) was due to blocking of one side by a departing $(\underline{n}Bu)_3SnBr$ (as observed by Altman[8] in a Ph_3SnH reduction), but rather is consistent with the stereochemical results obtained in other bicyclo[3.1.0] systems.[5a,b]

Since the epimeric bromides 6 and 7 (also 4 and 5) do not give identical product distributions, the most likely intermediates are pyramidal cyclopropyl radicals[9] (eqn. 1). The predominance of 12 may be controlled primarily by $k_c' >$



(1)

k_c, or by the greater stability of 11 over 10. In order to investigate this point further, a mixture of monobromides 6 and 7 ([total bromide]=0.56M, $[nBu_3SnH]=0.62M$, $[(PhCO_2)_2]=0.008M$, 60°) was reduced in benzene solution. The relative rate of reduction was $k_7/k_6 = 1.5 \pm 0.3$; that is, 7 actually reacts with a tin radical slightly faster than 6! Since $R_3Sn\cdot$ abstraction of a bromine atom is a relatively slow process,[10] the transition state presumably resembles the resultant alkyl radical. Contrariwise, R_3SnH donation of a hydrogen atom is rapid, whereby the transition state for that process should resemble the alkyl radical as well. Therefore, the currently most reasonable explanation for the similar reactivity of 6 and 7, but the different reactivities of 10 and 11, is that 7 is more stable than 6, and 11 more stable than 10 (see Figure 1).

Why is 11 more stable than 10? Possibly steric interaction between a half-filled orbital and H_{8a} is more favorable than the corresponding H-H interaction in 10. More intriguing is the possibility that there may be partial opening of the cyclopropane ring (C_1-C_6 bond), an electronic explanation which may better account for the distinct favoring of 11. Studies are underway to dissect these factors.

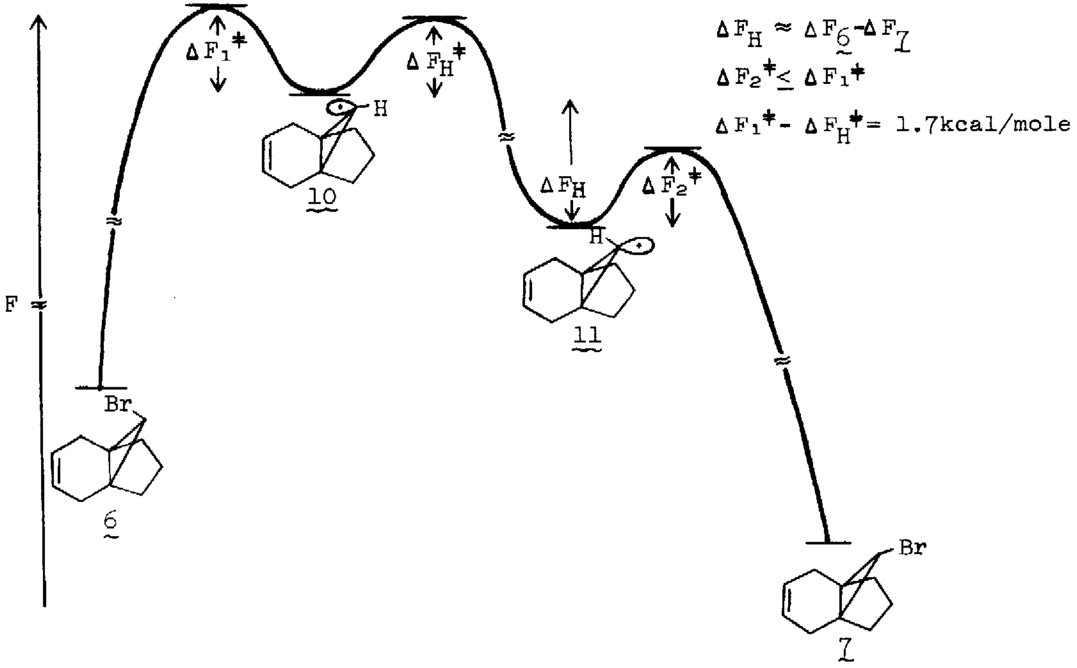
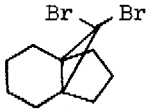
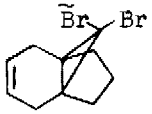
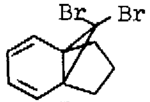


Figure 1. Free energy relationships among some cyclopropyl radicals and transition states.

Table I. Reduction of Some Dibromides

Cpd	Product Stereochemistry Br syn to 6 ring	:	 Br anti to 6 ring	Yield
 1	80 (4)	:	20 (5)	79%[a]
 2	77 (6)	:	23 (7)	84%[a]
2	82	:	18	~80%[b]
2[c]	82	:	18	--
 3	87 (8)	:	13 (9)	65%[a]
3	84	:	16	57%[d]

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[a] Reaction performed by adding 1 eq. $(nBu)_3SnH$ to neat dibromide at room temperature. The initially exothermic reaction was allowed to stir for 2-3hr.

[b] Reaction in benzene soln. ([2]=0.7M) with $(nBu)_3SnH$ at 85° for 18 hr.; no double reduction observed.

[c] Reaction in benzene ([2]=0.2M) at 80° for 12 hr., with $(nBu)_3SnD$ as reducing agent; 2% double reduction observed.

[d] Reaction in benzene ([3]=0.7M) with nBu_3SnH at 80° for 20 hr.; no double reduction observed. The low yield is in part due to a thermal dibromocarbene loss suffered by 3.

References and Footnotes

1. We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for partial support of this work.

2. Fellow of the Alfred P. Sloan Foundation, 1976-8.

3. (a) T. Ishihara, K. Hayashi, T. Ando and H. Yamanaka, *J. Org. Chem.*, **40**, 3264 (1975); (b) T. Ishihara, E. Ohtani and T. Ando, *Chem. Comm.*, 367 (1975); (c) T. Ando, H. Yamanaka, F. Namigata and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (d) T. Ando, F. Namigata, H. Yamanaka and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967).

4. (a) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971); (b) cf., however, L. A. Singer and J. Chen, *ibid.*, 939 (1971) and ref. 3a; (c) see L. J. Altman and R. C. Baldwin, *ibid.*, 981 (1972) for studies of a related oxiranyl radical.

5. (a) P. K. Freeman, L. L. Hutchinson and J. N. Blazevich, J. Org. Chem., 29, 3606 (1974); (b) J. Hatem and B. Waegell, Tetrahedron Lett., 2023, 2019 (1973); (c) T. Ando, K. Wakabayashi, H. Yamanaka and W. Funasaka, Bull. Chem. Soc. Jap., 45, 1576 (1972); (d) K. Sisido, S. Kozima and K. Takizawa, Tetrahedron Lett., 33 (1967); (e) H. M. Walborsky, C. Chen and J. L. Webb, ibid., 3551 (1964); (f) H. M. Walborsky, F. J. Impastato and A. E. Young, J. Am. Chem. Soc., 86, 3283 (1964); (g) D. E. Applequist and A. H. Peterson, ibid., 82, 2372 (1960).

6. P. Warner and S. Lu, J. Org. Chem., 41, 1459 (1976).

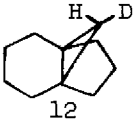
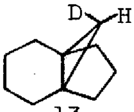
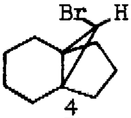
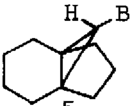
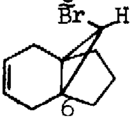
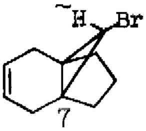
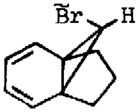
7. Compound 9, the epimer of 8, was not obtained pure in useful amounts.

8. (a) L. J. Altman and B. W. Nelson, J. Am. Chem. Soc., 91, 5163 (1969); (b) L. J. Altman and T. R. Erdman, Tetrahedron Lett., 4891 (1970).

9. As seen from the experiments with 5 and 7, concentration is not a factor in determining product stereochemistry, as is also not temperature (in the range studied). Additionally, cage effects for 5 and 7 would favor some loss of stereospecificity,[8] and can therefore not account for our results.

10. H. G. Kuivila, Accts. Chem. Res., 1, 299 (1968).

Table II. $(nBu)_3SnD$ Reduction of Some Cyclopropyl Bromides in Benzene Solution

Cpd [M]	[SnD]	T(°C)	t(hr)	 12		 13 [a]
 4 [.78]	.78M	85	96	94	:	6
 5 [1.3]	3.92M	125^b	4^b	100	:	0
 6 [.78]	.78M	85	96	91	:	9
 7 [.18]	.38M	60^c	20^c	100	:	0
 8 [.78]	.78M	85	96	95	:	5

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a Product data are given as a ratio of saturated hydrocarbons (12/13), since pmr analysis was carried out at this stage; when necessary, prior hydrogenation (Pt, Et_2O) was effected. D incorporations were ≥95% (mass spec);

b No reaction occurred after 72 hr at 90°. The abrupt temperature dependence is not surprising for an induced chain reaction; c Initiated by 0.017M benzoyl peroxide.