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Communications

Stereoselectivity in Free Radical Reduction of *cis*- and *trans*-3-Chlorobicyclo[3.1.0]hexane by Tri-*n*-butyltin hydride

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A number of investigations¹⁻⁶ have been carried out to determine whether nonclassical free radicals, analogous to nonclassical carbonations,⁷ appear as reaction intermediates. Free radical reduction of norborn-2-en-5-yl halides and of nortricycyl halides with tri-*n*-butyltin hydride provided the same mixture of norbornene and nortricyclene.¹ With triphenyltin hydride, however, nortricycyl bromide yields a higher ratio of nortricyclene to norbornene in the absence of solvent than in pentane solution indicating the presence of discrete norbornenyl and nortricycyl free radicals. As to a 7-norbornenyl radical, there has been considerable controversy concerning its nonclassical nature. According to a SCF-MO-CNDO calculation, the 7-norbornenyl radical was purported to be at least as nonclassical as the corresponding cation.² Chemical evidence supporting the nonclassical structure was the observation that reduction of both *syn*- and *anti*-7-bromonorbornene with tri-*n*-butyltin deuteride in hexane led solely to *anti*-7-deuterio-norbornene.³ However, re-investigation of this reaction drew inconsistent results with the previous observation and the existence of the nonclassical radical intermediate was ruled out.⁴ The most definitive evidence for the classical structure of the 7-norbornenyl radical, generated by photolysis of *t*-butyl *anti*-peroxy-2-norbornene-7-carboxylate, was obtained by examination of its esr spectrums. The radical chlorination of *endo*-tricyclo[3.2.1.0^{2,7}]octane with *t*-butyl hypochlorite was also studied. At high concentrations of *t*-butyl hypochlorite the first formed radical intermediate was trapped to yield *anti*-8-chloro-*endo*-tricyclo[3.2.1.0^{2,7}]octane before there was much rearrangement to the second radical intermediate, while at low concentrations of *t*-butyl hypochlorite chlorine abstraction by the rearranged radical was the major course.

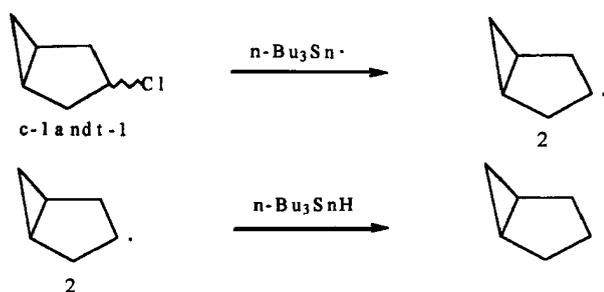
On this basis, it was proposed that there is an equilibrium between the *endo*-tricyclo[3.2.1.0^{2,7}]oct-8-yl radical and its rearranged one.⁵

All of these results can be accommodated by assuming discrete classical radical intermediates and it has not been found necessary to invoke any type of delocalized radical intermediates.

Anchimeric assistance found in the solvolysis of *exo*-5-norbornenyl,⁸ *anti*-7-norbornenyl,⁹ and *endo-anti*-tricyclo[3.2.1.0^{2,7}]oct-8-yl¹⁰ substrates might be the case in the formation of structurally related radical intermediates. Indeed, in the radical chlorination of *endo-anti*-tricyclo[3.2.1.0^{2,7}]octane with *t*-butyl hypochlorite, attack of *t*-butoxy radical occurred at C-8 to an extent of 93% or greater.⁶ Since the anchimerically assisted solvolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate was shown to afford the nonclassical trishomocyclopropenyl cation,¹⁰ it seems of interest to examine some degree of Anchimeric assistance by a neighboring cyclopropyl bond in transition state producing the 3-bicyclo[3.1.0]hexyl radicals(2).

Thus, the effect of the cyclopropane on the rate of chlorine abstraction by tri-*n*-butyltin radicals was examined by competition methods in reduction of *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane (**c-1** and **t-1**) and chlorocyclopentane with tri-*n*-butyltin hydride, which has been known to proceed by a free radical chain mechanism (Scheme 1).¹¹

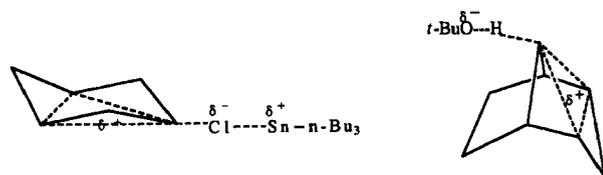
A mixture of equimolar amounts of the *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane (**c-1** and **t-1**)¹² and chlorocyclopentane (0.75-1.50 mmol, respectively) in 5 mL of methylcyclohexane was heated with half molar amount of tri-*n*-butyltin hydride to the total chlorides at 60 °C for 74 h. in the presence of azobisisobutyronitrile. The relative reactivities



Scheme 1.

Table 1. Relative Reactivities of the *cis*- and *trans*- Chloride (**c-1** and **t-1**) to Chlorocyclopentane for Chlorine Abstraction by tri- *n*-Butyltin Radicals at 60 °C

Run	Chlorocyclopentane	c-1	t-1	k(c-1)	k(t-1)
1	1.00	2.01	0.60	3.35	
2	1.00	1.96	0.57	3.43	
3	1.00	1.79	0.50	3.59	
		1.92 ± 0.09	0.56 ± 0.04	3.46 ± 0.10	



Scheme 2.

of the **c-1** and **t-1** to chlorocyclopentane for chlorine abstraction by tri- *n*-butyltin radicals were found to be 1.92 ± 0.09 and 0.56 ± 0.04 , respectively, on the basis of analysis of the unreacted chlorides by GC (Table 1).¹¹

The fact that the *cis*-chloride (**c-1**) is 3.5 times as reactive as the *trans*-chloride (**t-1**) might be attributed to some degree of the Anchimeric assistance to chlorine abstraction in the transition state, in spite of the steric shielding of the *cis* face of the ring skeleton by the cyclopropane methylene. The high preference for C-8 hydrogen abstraction observed in radical chlorination of *endo*-tricyclo[3.2.1.0^{2,4}]octane⁶ may be rationalized by postulating the rigid chair conformation as compared with the flexible chair and boat conformation for 3-bicyclo[3.1.0]hexyl derivatives (Scheme 2).

Thus, the similar tendency of *cis* preference by analogy with that observed in the solvolysis of *cis*-3-bicyclo[3.1.0]hexyl tosylate¹⁰ indicates that possibility of some trishomocyclopropenyl carbonation character must be due to contribution in the transition state for chlorine abstraction. Such polarization would be expected due to the nucleophilic

character of the tin radicals (Scheme 2).¹¹

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- Competitive reaction of **c-1** and **t-1** by tri- *n*-butyltin hydride was carried out as follows. In a general procedure, a mixture of equimolar amounts of the **c-1** and **t-1** and chlorocyclopentane (0.75–1.50 mmol, respectively) was placed in a glass ampoule, followed by 5 ml. of methylcyclohexane, half molar amount of tri- *n*-butyltin hydride to the total chlorides (1.13–2.25 mmol), 2 mol % of azobisisobutyronitrile (AIBN), and toluene as an internal standard. The ampoule was degassed with three freeze-thaw cycles under reduced pressure, sealed, and placed in a constant-temperature bath at 60 °C for 74 h. The unreacted chlorides were analyzed by GC using a 2 m column of 5% TCEP on HIMDS-treated Chromosorb W at 60 °C. The results are given in Table 1. In a separate experiment carried out in the absence of tri- *n*-butyltin hydride, **c-1** and **t-1** were confirmed not to undergo any interconversion under the reaction condition.
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