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ON THE CONFIGURATIONAL STABILITY OF AN OXIRANYL RADICAL. A COMPARISON OF THE RADICAL TRAPPING EFFICIENCIES OF TRIPHENYLTIN HYDRIDE AND *t*-BUTYL HYPOCHLORITE.

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In a previous communication[2] we had made the prediction that an oxiranyl radical[3] should show slightly enhanced configurational stability when compared to an α-chlorocyclopropyl radical. We report here our observations on the configurational stability of the 2,3-dimethyloxiranyl radical.

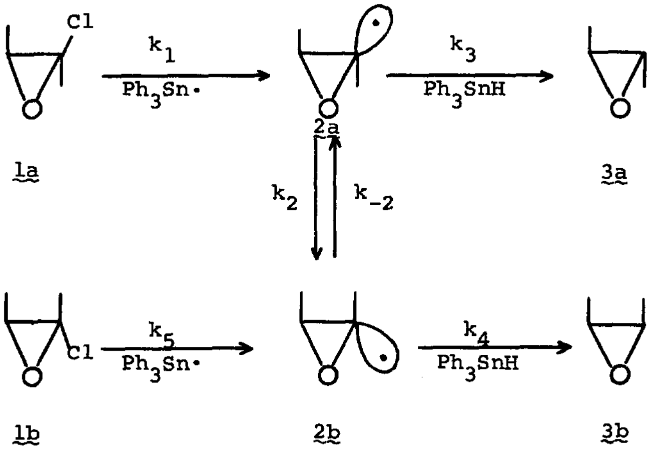
Similar to the approach used in our previous work, we decided to examine the reaction of the reaction of triphenyltin hydride[4] with *trans*- and *cis*-2-chloro-2,3-dimethyloxirane (**1a** and **1b** respectively). The chlorodimethyl oxiranes were initially prepared by base treatment[5] of 3,3-dichloro-2-butanol but as the yield of the *cis* isomer was especially low, we decided to employ free radical chlorination[6] of the respective oxiranes[7] as the preparative method. To our pleasant surprise, the chlorinations were very highly stereoselective. The results of the chlorinations are reported in Table 1.

TABLE 1

Results of the Photoinitiated Chlorination of *cis*- and *trans*-Dimethyloxirane with *t*-Butyl Hypochlorite at 0°

Starting Material	Conc. Starting Material	Conc. *t*-BuOCl	Solvent	Product Distribution % **1a**	% **1b**
cis (3b)	5.84 *M*	4.32 *M*	neat	1.5	98.5
cis (3b)	0.059 *M*	0.044 *M*	CCl_4	20.0	80.0
trans (3a)	5.86 *M*	4.18 *M*	neat	98.5	1.5
trans (3a)	0.053 *M*	0.046 *M*	CCl_4	81.0	19.0

The chlorodimethyl oxiranes were purified by preparative glpc[8] to greater than 99.9% purity. Each isomer was reduced[9] with neat triphenyltin hydride (3.95 *M*) at 30° and the isomeric composition of the products determined by glpc.



Scheme I

Reduction of the *trans*-chlorooxirane (1a) gave a mixture of 92% 3a and 8% 3b while the *cis*-chlorooxirane (1b) gave 45% 3a and 55% 3b. Complete equilibration of the intermediate oxiranyl radicals has obviously not been achieved before reduction occurred. The following expression can be derived for the reduction of 1b from an examination of Scheme I:

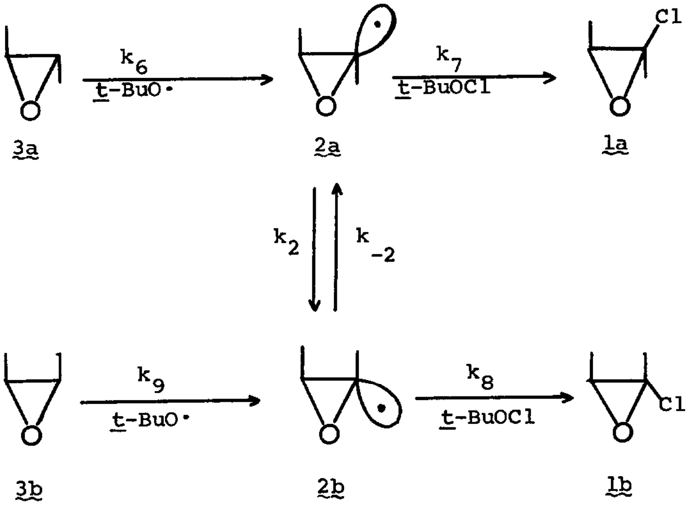
$$\frac{[3b]}{[3a]} = \frac{k_2k_4}{k_3k_{-2}} + \frac{k_4}{k_{-2}}\,[Ph_3SnH]$$

Similarly, the following expression can be derived for the reduction of 1a:

$$\frac{[3a]}{[3b]} = \frac{k_3k_{-2}}{k_2k_4} + \frac{k_3}{k_2}\,[Ph_3SnH]$$

If it is assumed that k_4, the rate constant for reduction[10] of 2b is 3.3×10^6 M^{-1} sec^{-1}, it can be shown that k_{-2}, the rate constant for inversion of this oxiranyl radical, is 1.1×10^7 sec^{-1}.

The chlorination of the dimethyloxiranes with *t*-butyl hypochlorite also proceeds *via* the intermediate radicals 2a,b.



Scheme II

It can be seen from the data in Table I that the rate of reaction of the intermediate radical with t-butyl hypochlorite at 0° is much faster than the rate of reduction. It is also apparent that the radical trapping efficiency of t-butyl hypochlorite is much greater than that of triphenyltin hydride. Following a similar kinetic analysis for the chlorination reaction to that of the reduction reaction, consistent inversion barriers are obtained if one assumes a rate constant of $3.2 \times 10^8\ \underline{M}^{-1}\ \text{sec}^{-1}$ for k_8. Thus t-butyl hypochlorite is ca. 100 times more effective than triphenyltin hydride in trapping radicals.

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(8) Preparative glpc was performed on a 6 ft x 8 mm O.D. Pyrex column of 25% Carbowax 20 M on 60/80 mesh Gas Chrom Q at 62°.

(9) Reductions were performed in sealed, degassed ampoules with AIBN as initiator and reactions were allowed to proceed for seven days before analysis. Control experiments show that the products are stable to the reaction conditions.

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