

DEHALOGENATION REACTIONS CATALYZED BY TRI-n-BUTYLTIN CHLORIDE.
COMPETITION FOR CARBON RADICALS BY BOROHYDRIDE AND TIN HYDRIDE.

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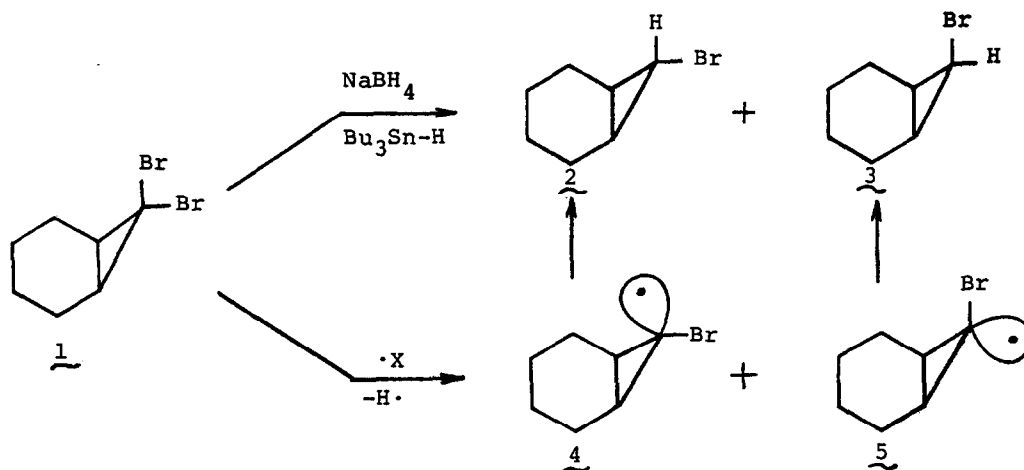
Trialkyltin hydrides are versatile dehalogenation reagents which are known to react with organic halides via a free radical chain mechanism.¹ A useful modification of this procedure has been described recently which employs stoichiometric quantities of sodium borohydride and catalytic amounts of trialkyltin chlorides.² Since we have shown that sodium borohydride can also perform free radical chain dehalogenations,³ it is of interest to know whether the catalytic amount of tin hydride or the borohydride is the immediate hydrogen atom source in these reactions.

Hydrogen atom transfers from tin hydrides to carbon radicals are known to be extremely fast ($k \approx 10^4$ - 10^6 M⁻¹ sec⁻¹)⁴ yet there have been no comparisons of hydrogen atom transfers from tin to those from boron. This rate ratio and the stoichiometrically significant hydrogen source has been determined by examination of kinetic isotope effects.

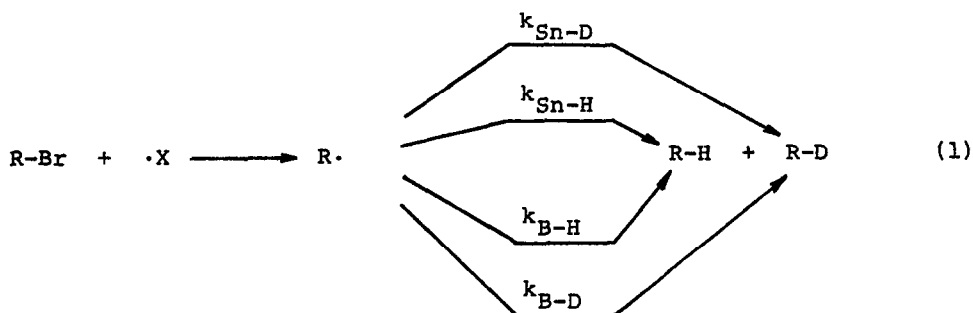
Reaction of 7,7-dibromonorcarane (1) with sodium borohydride⁵ or tri-n-butyltin hydride⁶ affords cis- and trans-7-bromonorcarane (2 and 3) in 79% and 82% yields, respectively (Scheme I). With equimolar amounts of sodium borohydride and sodium borodeuteride (Alfa, 99.8% D), a kinetic hydrogen isotope effect (k_{BH}/k_{BD}) of 4.5 is found for the formation of 2 and 3 in ethanol. This large value contrasts with the corresponding results for a tri-n-butyltin hydride-tri-n-butyltin deuteride mixture for which $k_{SnH}/k_{SnD} = 1.2$.⁷

When 1 is reduced by a catalytic system of NaBH₄-NaBD₄ (1:1) and 0.05 eq. of tri-n-butyltin chloride, 2 is formed with an apparent isotope effect of 1.8 whereas the value for 3 is 1.3 (Table I).

Scheme I



Considering that this observed isotope effect is a composite measurement resulting from competition for the intermediate carbon radicals 4 and 5 by the four isotopic species present as in eq. (1), the deuterium content of the products, $[R-H]/[R-D]$, can be related to the relative rate of hydrogen transfer to the intermediate carbon radical from tin and boron (k_{SnH}/k_{BH}) according to eq. (2).



$$\frac{k_{Sn-H}}{k_{B-H}} = \frac{1 - \left(\frac{[R-H]}{[R-D]} \frac{k_{B-D}}{k_{B-H}} \right)}{\left(\frac{k_{Sn-D}}{k_{Sn-H}} \frac{[R-H]}{[R-D]} \right) - 1} \left(\frac{[B-H]}{[Sn-H]} \right) \quad (2)$$

Thus, substitution into eq. (2) for the formation of 2 produces $k_{\text{Sn-H}}/k_{\text{B-H}} = 3.8 \times 10^2$ whereas a value of 2.7×10^3 is determined for the formation of 3. These rate ratios indicate that under the conditions of the reaction with only a catalytic concentration of tri-n-butyltin chloride, 45% of the hydrogen delivered to the trans-bromocyclopropyl radical 4 derived directly from the borohydride whereas the cis-radical 5 obtained no more than 5% by this route. Upon reduction of the sodium borohydride concentration to one equivalent, the observed isotope effect for the formation of 2 dropped to 1.3 in agreement with expectations based on these rate ratios and assumptions implicit in eq. (2).

It appears that sodium borohydride competes effectively with tri-n-butyltin hydride for the more hindered of the stereoisomeric intermediate cyclopropyl radicals 4 and 5. Accordingly, sodium borohydride-trialkyltin chloride dehalogenations can be expected to have different stereoselectivities than that which is found with stoichiometric amounts of the tin hydride reagent.⁸ Further, the absolute rate of hydrogen atom transfer from sodium borohydride to 4 and 5 can be estimated to be ca. 10^2 - $10^3 \text{ M}^{-1} \text{ sec}^{-1}$.

Table I. Hydrogen Isotope Effects for Dehalogenation of 1.

<u>1</u>	Relative Molar Concentrations					$k_{\text{H}}/k_{\text{D}}$	
	NaBH ₄	NaBD ₄	n-Bu ₃ Sn-H	n-Bu ₃ Sn-D	n-Bu ₃ SnCl	<u>2</u>	<u>3</u>
0.3	2.0	2.0	---	---	---	4.5	4.5
0.3	---	---	1.0	1.0	---	1.2	1.2
0.3	1.0	1.0	---	---	0.05	1.3	1.3
0.3	2.0	2.0	---	---	0.05	1.3	1.8

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Notes and References

1. (a) H. G. Kuivila, L. W. Menapace and C. R. Warner, J. Am. Chem. Soc., **84**, 3584 (1962); (b) H. G. Kuivila, Acc. Chem. Res., **1**, 299 (1968).
2. E. J. Corey and J. W. Suggs, J. Org. Chem., **40**, 2554 (1975).
3. J. T. Groves and K. W. Ma, J. Am. Chem. Soc., **96**, 6527 (1974).
4. D. J. Carlsson and K. U. Ingold, J. Am. Chem. Soc., **90**, 1055 (1968).
5. In a typical experiment, 0.5 g (1.95 mmol) 1 and 0.22 g (5.78 mmol) NaBH₄ was dissolved in 25 ml absolute ethanol while the reagents were exposed to air. The reaction mixture was stirred vigorously under nitrogen for 48 hr. A mild exotherm developed after 15-20 minutes and hydrogen was evolved. Products were isolated by ether-water work-up. Stereoisomeric ratios were determined by analytical glpc.
6. D. Seyferth, H. Yamasaki and D. L. Alleston, J. Org. Chem., **28**, 703 (1963).
7. Deuterium isotope effects were determined by comparing mass spectral peak intensities in the parent (m/e 174) and parent-bromine (m/e 95) regions at 45 eV on a DuPont DIMASPEC GC-mass spectrometer using an OV-17 column. The m/e intensity ratios 174/175, 176/177, 95/96 constituted three independent measures of the isotope effect from each spectrum after appropriate corrections for ¹³C natural abundance.
8. The reduction of 9,9-dibromobicyclo[6.1.0]nonane (6) with tri-n-butyltin hydride has been reported to yield exclusively the cis-9-bromo product 7 and none of the corresponding trans isomer 8.⁶ In contrast, sodium borohydride produces 7:8 = 1.8.³ We have found, in contrast, that tri-n-butyltin hydride alone, or the sodium borohydride-tri-n-butyltin chloride catalytic system described above produces 7:8 = 2.7 ± 0.2. These ratios are a sensitive function of temperature and the differences observed are probably due to epimerization of the intermediate radicals corresponding to 4 ↔ 5 in Scheme I. Cf. T. Ishihara, K. Hayashi, T. Hudo and H. Yamanaka, J. Org. Chem., **40**, 3265 (1975).