NORBORNENYL- AND NORTRICYCLYL FREE RADICALS

Thesis by

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ABSTRACT

The number, symmetry, and product-forming capabilities of the intermediates in the photoinitiated reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride at temperatures between -10° and 22° were investigated. Three mechanisms were evaluated:

1. The 5-norbornenyl- and 2-nortricyclyl radicals isomerize reversibly with the former producing nortricyclene by abstraction of hydrogen from tri-n-butyltin hydride.
2. The 5-norbornenyl- and 2-nortricyclyl radicals isomerize reversibly, but some norbornene can be formed from the 2-nortricyclyl radical or some nortricyclene can be formed from the 5-norbornenyl radical by abstraction of hydrogen.
3. There is intervention of a "bridged" radical which may be formed reversibly or irreversibly from the 5-norbornenyl- and 2-nortricyclyl radicals.

Within small error limits, the ratios of norbornene to nortricyclene as a function of the concentration of tri-n-butyltin hydride are consistent with the first mechanism.

In the reductions with tri-n-butyltin deuteride, primary deuterium isotope effects of 2.3 and 2.1 for the abstraction of deuterium by the 2-nortricyclyl- and 5-norbornenyl radicals, respectively, were found. The primary deuterium isotope effects were invariant with the concentration of tri-n-butyltin deuteride,

although the ratios of norbornene to nortricyclene changed appreciably over this range. This is consistent with the first mechanism, and can accommodate the formation of either product from more than one intermediate only if the primary kinetic deuterium isotope effects are nearly equal for all reactions leading to the single product.

The reduction of endo-5-bromonorbornene-5, 6, 6-d_3 with tri-n-butyltin hydride or tri-n-butyltin deuteride leads to both unrearranged and rearranged norbornenes. The ratios of unrearranged to rearranged norbornene require that the 5-norbornenyl-5, 6, 6-d_3 radical isomerize to an intermediate with the symmetry expected of a nortricyclyl free radical. The results are consistent with mechanism 1, but imply a surprising normal secondary kinetic deuterium isotope effect of about 1.25 for the abstraction of hydrogen by the 5-norbornenyl-5, 6, 6-d_3 radical.

Approximate calculations show that there does not appear to be any substantial difference in the stabilities of the 5-norbornenyl and 2-nortricyclyl radicals.

Although the results can not exclude a small contribution by a mechanism other than mechanism 1, no such contribution is required to adequately explain the results.

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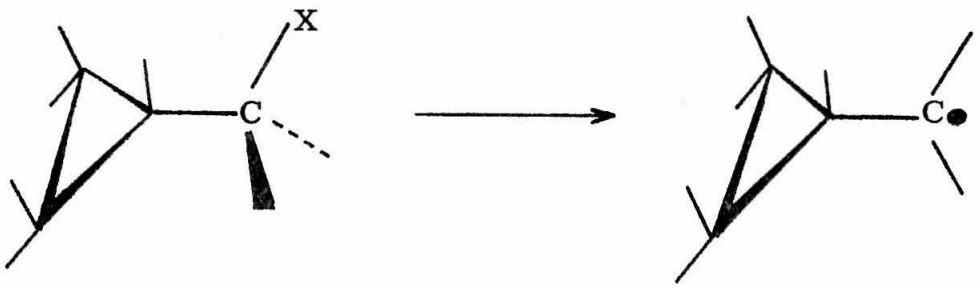
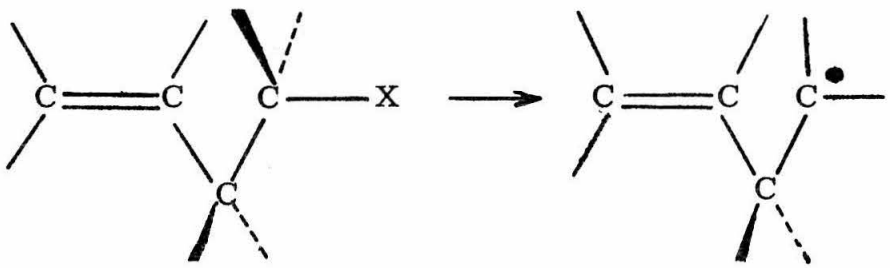
Section I. INTRODUCTION

Abstract of the Introduction

Free radicals generated from cyclopropylcarbinyl compounds,



or allylcarbinyl compounds,



may yield cyclopropylcarbinyl products, allylcarbinyl products, or a mixture of both. The radical intermediates may isomerize rapidly, often yielding identical product mixtures from isomeric cyclopropylcarbinyl- and allylcarbinyl starting materials, or from two isomeric allylcarbinyl starting materials. In other cases, the free radicals from either of a pair of isomeric starting materials can be "trapped" before they reach equilibrium, if there is a sufficiently reactive chain-transfer agent present.

Free radicals generated from unsubstituted, or methyl-substituted allylcarbinyl compounds, although frequently yielding no cyclopropylcarbinyl products, may isomerize apparently through an intermediate which is a cyclopropylcarbinyl free radical.

From esr spectroscopy, the cyclopropylcarbinyl free radical, and several substituted cyclopropylcarbinyl free radicals, as well as their respective isomeric allylcarbinyl free radicals, have been identified as intermediates, when free radicals are generated from the respective cyclopropylcarbinyl hydrocarbons. No evidence for the presence of any other free radical which might be an intermediate in the isomerizations of cyclopropylcarbinyl- or allylcarbinyl free radicals was found.

The hyperfine couplings in the esr spectra of the cyclopropylcarbinyl radical, and several alkyl-substituted cyclopropylcarbinyl radicals, and the enhanced rate of formation of free radicals at carbon atoms α to cyclopropyl groups suggest that cyclopropylcarbinyl free radicals are appreciably delocalized, and are better described as "nonclassical" radicals than as "classical" radicals. Similar characteristics do not appear to be present in isomeric allylcarbinyl free radicals.

This thesis will be concerned primarily with the norbornenyl- and nortricyclyl free radicals. The possibility of a "bridged" radical intermediate being involved in the isomerizations of the norbornenyl- and nortricyclyl free radicals, or of sufficient delocalization in the nortricyclyl radical to permit formation of norbornene

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from it, or similar delocalization in the norbornenyl radical which would permit formation of nortricyclene from it, will be explored.

The norbornenyl- and nortricyclyl free radicals will be generated by the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride. The bases for the choice of the norbornenyl- and nortricyclyl radicals for this study will be discussed as well as the use of organotin hydrides in free-radical reductions of alkyl halides.

A brief discussion of the principal objectives of the experimental work undertaken in this thesis is included at the end of the Introduction.

Part 1. Isomerizations of Cyclopropylcarbinyl- and Allylcarbinyl Free Radicals

Several recent reviews on both free-radical rearrangements in general (1), and cyclopropylcarbinyl- and allylcarbinyl free-radical rearrangements in particular (2), are available, so this introduction will be limited to a discussion of the most important characteristics of free radicals generated from either cyclopropylcarbinyl or allylcarbinyl compounds.

From the copolymerization of a series of hydrocarbons with styrene, Rosen found that the primary hydrogens of methylcyclopropane are more easily abstracted than the primary hydrogens of neopentane, the secondary hydrogens of n-butane, and even the tertiary hydrogens of 2, 3-dimethylbutane (3). Rosen explained the ease with which these primary hydrogens of methylcyclopropane are abstracted on the basis of anchimeric assistance from the cyclopropyl group, with formation of a homoallylic free radical intermediate.

In the free radical chlorination of methylcyclopropane, with either chlorine or t-butyl hypochlorite, the primary hydrogens of the methyl group of methylcyclopropane are found to undergo abstraction several times more rapidly than the primary hydrogens of neopentane (4). This enhanced reactivity was attributed to homoallylic conjugation in the cyclopropylcarbinyl free radical. Because the major product, in either chlorination, is cyclopropylcarbinyl chloride, there must be a free-radical intermediate which retains the ability to form

cyclopropylcarbinyl products. The formation of substantial amounts of allylcarbinyl chloride from the chlorination with t-butyl hypochlorite requires the presence of an intermediate from which this rearranged product may be formed. *

Other examples of the ability of a cyclopropyl group to enhance the rate of formation of free radical intermediates are also available. When the decomposition rates for a series of 2, 2′-azobis-2-cycloalkylpropionitriles are compared, the decomposition rate when the cycloalkyl group is cyclopropyl is much faster than when it is cyclobutyl, cyclopentyl, or cyclohexyl. The decomposition rate is also much faster than that found when any of a series of acyclic alkyl groups are present, instead of the cycloalkyl group in the azo compound (5). For the decomposition of t-butyl diphenylcyclopropylperacetate (I), Halgren observed a half-life of 93 ±7 minutes at 23° (7). His extrapolated half-lives for the decompositions of t-butyl triphenylperacetate (II) and t-butyl diphenylperacetate (III) at 23° were 90 minutes and 4100 minutes, respectively.

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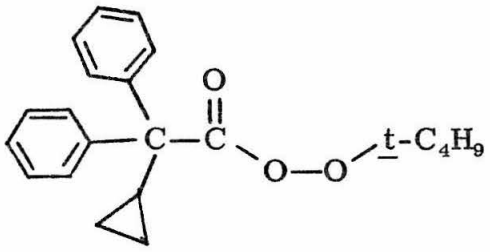
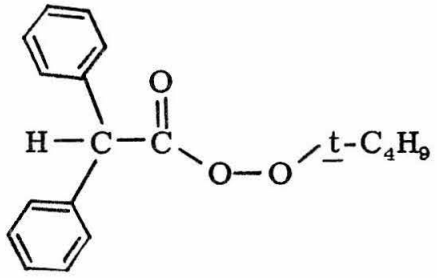
* The allylcarbinyl chloride could be a secondary product, formed from the solvolysis and rearrangement of the primary product, cyclopropylcarbinyl chloride (6).



I



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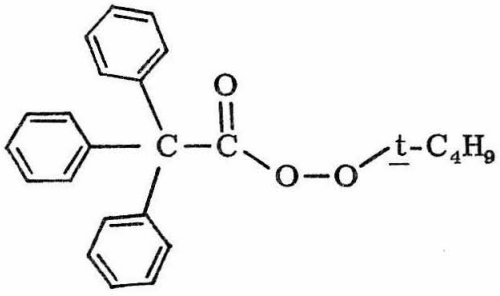

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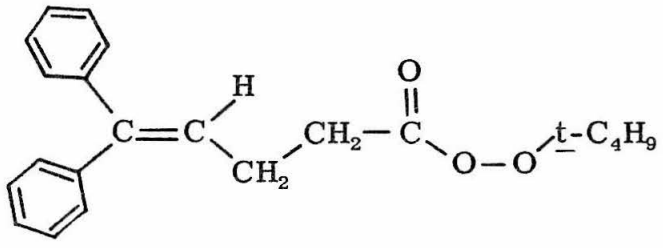

IV

The decomposition of t-butyl alkylperformates has been shown to be a concerted reaction, with a rate dependent upon the stability of the alkyl free radical, when the alkyl group is secondary or tertiary (8). Therefore, from Halgren's work, the cyclopropyl group is approximately as effective in stabilizing the free radical generated from (I), as the third phenyl group is in stabilizing the free radical generated from (II), because of the similarity in the decomposition half-lives of

(I) and (II).

The rate-enhancing effect of the cyclopropyl group in the formation of free radicals from cyclopropylcarbinyl compounds contrasts with the absence of any significant rate enhancement in the formation of free radicals from the isomeric allylcarbinyl compounds. The decomposition rate for t-butyl (γ,γ-diphenylallyl)peracetate (IV) is typical of rates of decomposition found for t-butyl alkylperacetates, where the alkyl group is a normal saturated primary alkyl group (7), or more than four orders of magnitude slower than the rate of decomposition of t-butyl diphenylcyclopropylperacetate (I). Similarly, the decomposition rates for endo- and exo-2-carbo-t-butylperoxy-norbornene and their saturated analogs, endo- and exo-2-carbo-t-butylperoxynorbornane are all within a factor of two (9).* All four of these decomposition rates are close to the rate for carbo-t-butyl-peroxycyclohexane (10), so there is evidently no appreciable enhancement in the rate of formation of free radicals from the norbornenyl compounds, relative rate enhancements found in the rate of formation of free radicals from similar cyclopropylcarbinyl compounds. Similar conclusions are arrived at from a comparison of the decomposition rates for endo- and exo-norbornane-2-carbonyl peroxide and endo- and exo-norbornene-2-carbonyl peroxide (12).

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*Bartlett and McBride (11) have shown that the difference in rates of decomposition of endo- and exo-2-carbo-t-butylperoxynornane is a factor of about three, with the exo isomer decomposing faster. They also showed that the endo isomer in Martin and DeJongh's work (9) was probably contaminated with exo isomer. The conclusions are not affected by this small difference, however (11).

Once free-radical intermediates have been generated from isomeric cyclopropylcarbinyl- or allylcarbinyl compounds, the intermediates usually isomerize rapidly. In some cases, this isomerization results in product ratios independent of starting material or chain-transfer agent concentration. Several studies involving formation of norbornene and nortricyclene from norbornenyl- and nortricyclyl radicals have found product ratios independent of starting material or chain-transfer agent concentration (13).

It is more common to find that the ratio of rearranged products to unrearranged products will depend on the concentration of the chain-transfer agent present, especially if the agent is very active. If the free-radical intermediates are generated from cyclopropylcarbinyl compounds, the ratio of cyclopropylcarbinyl- to allylcarbinyl products will increase with increasing concentration of chain-transfer agent. If the free-radical intermediates are generated from allylcarbinyl compounds, the ratio of allylcarbinyl products to cyclopropylcarbinyl products increases with increasing concentration of chain-transfer agent. Examples may be found in norbornenyl- and nortricyclyl compounds (14), (γ, γ-diphenylallyl)-carbinyl- and diphenylcyclopropylcarbinyl compounds (15), and cholesteryl- and cyclocholestanyl compounds (16). It is apparent, then, that the initially-generated free radical from either the cyclopropylcarbinyl- or allylcarbinyl starting material must retain the geometry and bonding of the starting material to account for these concentration effects. The problem is whether the only intermediates are the isomeric cyclopropylcarbinyl- and allylcarbinyl free radicals, which

equilibrate, but form products only of their respective structures. Other possibilities which might more easily explain the rapidity of the isomerization include the formation of an additional intermediate with a bonding and geometry intermediate between the cyclopropylcarbinyl- and allylcarbinyl radicals, or sufficient delocalization in either the cyclopropylcarbinyl- or allylcarbinyl radicals to allow formation of allylcarbinyl products from the former, or cyclopropylcarbinyl products from the latter.

Recent studies have provided better insight into the intermediates involved in the isomerization of the free radicals generated from cyclopropylcarbinyl- and allylcarbinyl compounds. From the decomposition of t-butyl (γ, γ-diphenylallyl)peracetate-α, α-d_2, with either cyclohexane or triethyltin hydride as the hydrogen donor, the 1, 1-diphenyl-1-butene produced has the deuterium equally distributed between the 3- and 4-positions (17).* In a comparable experiment, the free radical decarbonylation of 4-pentenal-2, 2-d_2 produces 1-butene-4, 4-d_2, which is a butene of unrearranged skeleton, and 1-butene-3, 3-d_2, which is a butene of rearranged skeleton. Although there was evidence of other labeled butenes in the products, these were the predominant products. The ratio of the unrearranged product to rearranged product increased from 0.96 to 1.49 as the concentration

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*Among other products formed in this reaction are the ortho-cyclization products, dihydronaphthalenes. In these products, the deuterium is approximately equally distributed between the two positions which correspond to the 3- and 4-positions of the 1, 1-diphenyl-1-butene.

of aldehyde was increased from 0.50 M to 6.0 M (18). To account for this scrambling, the intermediates must reach a configuration in which the α- and β-positions of the 3-butenyl-1, 1-d_2 free radical become chemically identical, unless a very reactive chain-transfer agent is present to "trap" the initially-generated free radical before it can isomerize.

From the free-radical decarbonylations of 3-methyl-4-pentenal (V) or 2-methyl-4-pentenal (VI), both 1-pentene and 3-methyl-1-butene are produced* (2a). From either aldehyde, the ratio of unrearranged product to rearranged product increases with increasing aldehyde concentration. As the aldehyde concentration decreases, the ratio of 1-pentene to 3-methyl-1-butene approaches the same value from either starting aldehyde.

The product ratios can easily be rationalized on the basis of initial formation of the α-methylallylcarbinyl free radical (VII) from (V), and the β-methylallylcarbinyl free radical (VIII) from (VI). These radicals then equilibrate through some intermediate. At low concentrations of aldehyde, the limiting product ratios will depend upon the relative concentrations of (VII) and (VIII), and their chain-transfer constants with the aldehyde. Because (VIII) is a secondary radical, and (VII) is a primary radical, (VIII) should be present in higher concentration than (VII) at equilibrium. However, (VII) should

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*Approximately 1% of the total products consists of cis- and trans-1, 2-dimethylcyclopropane, and no other products were detected in amounts as great as 1%.

Table 1. Decarbonylations of 2-Methyl- and 3-Methyl-4-pentenal (2a).

Olefin Ratios for the Decarbonylation of 3-Methyl-4-pentenal in Chlorobenzene at 129.6°

Aldehyde concn, *M*	1-Pentene/3-methyl-1-butene[a] Run 1	Run 2
Neat[b]	4.7 ± 0.1	5.1 ± 0.1
4.0	5.4 ± 0.1	5.4 ± 0.1
3.0	6.4 ± 0.2	6.4 ± 0.2
2.0	6.9 ± 0.3	6.9 ± 0.2
1.5	7.4 ± 0.1	7.6 ± 0.1
1.0	7.7 ± 0.1	7.7 ± 0.1
0.75	8.5 ± 0.1	8.0 ± 0.1
0.50	8.3 ± 0.1	7.8 ± 0.1
0.38	9.1 ± 0.2	8.5 ± 0.1
0.25	8.6 ± 0.1	8.6 ± 0.1
0.19	12.0 ± 0.1	9.1 ± 0.1
0.12	9.8 ± 0.4	8.7 ± 0.1
0.094	10.1 ± 0.1	8.5 ± 0.7

[a] Error quoted as maximum expected error based on two to four separate analyses. [b] At 6 *M* concentration.

Olefin Ratios for the Decarbonylation of 2-Methyl-4-pentenal in Chlorobenzene at 129.6°

Aldehyde concn, *M*	1-Pentene[a]/ 3-methyl-1-butene	Aldehyde concn, *M*	1-Pentene/ 3-methyl-1-butene
Neat[b]	12.5	0.50	10.7
4.0	11.8	0.38	9.8
3.0	10.9	0.25	10.0
2.0	10.3	0.19	10.1
1.5	10.0	0.12	10.0
1.0	10.0	0.094	10.0
0.75	10.0		

[a] Generally the average of two or more determinations. Maximum expected errors comparable to those in Table I. [b] At 6 *M* concentration.

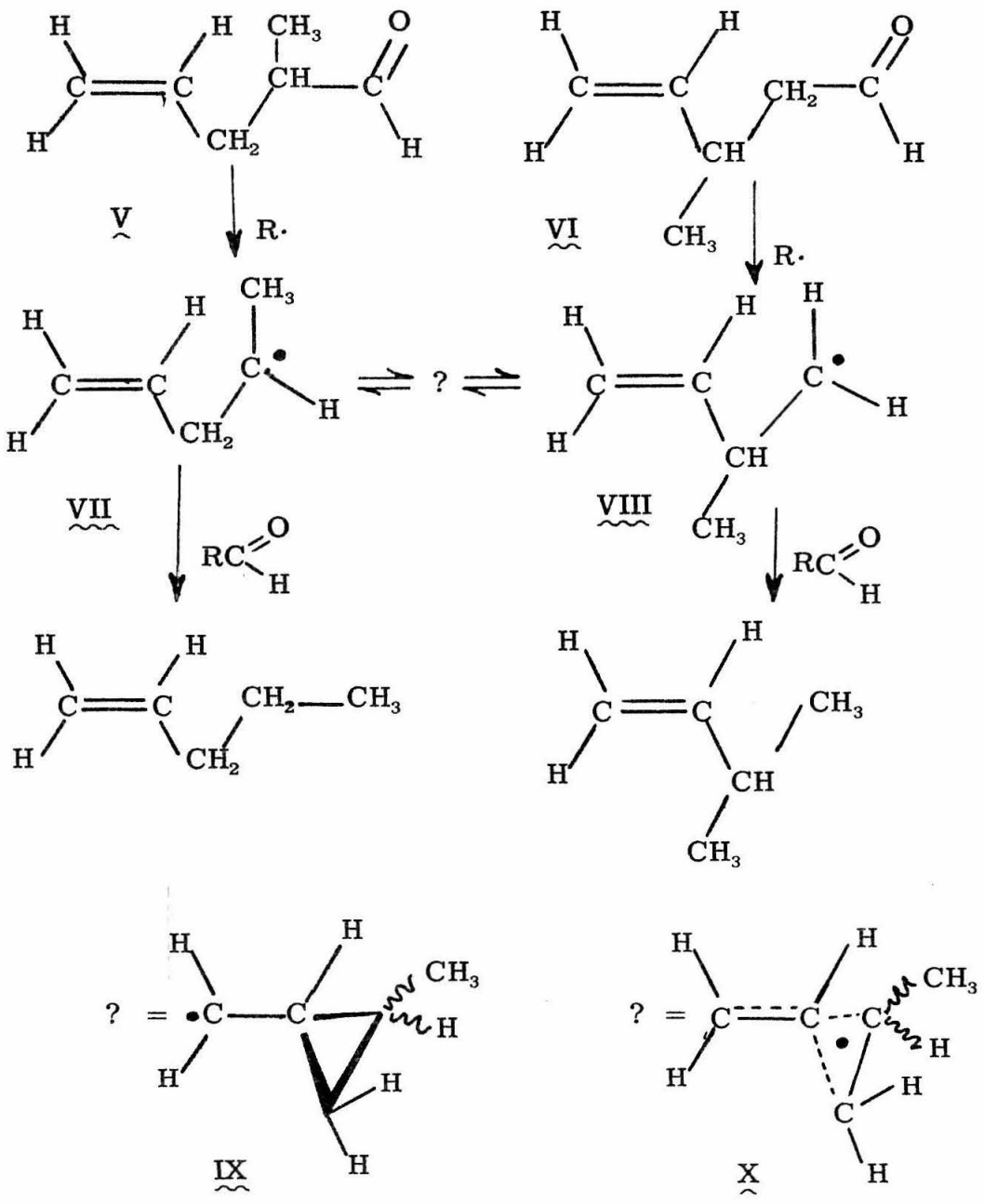

Figure 1. Intermediates in the Decarbonylations of 2- and 3-Methyl-4-pentenal (2a).

have a faster chain-transfer rate than (VIII), in the abstraction of hydrogen from the aldehyde. Because the limiting product ratios are about 9:1 in favor of 1-pentene, the relative concentrations of (VII) and (VIII) appear to be more important in determining the product ratios than the differences in relative chain-transfer constants. The problem which remains unanswered at this point, is whether the equilibration of intermediates involves a localized cyclopropylcarbinyl free-radical intermediate (IX) or some intermediate with partial characteristics of both allylcarbinyl free radicals and cyclopropylcarbinyl free radicals, but with a geometry and bonding between these two, which might be represented by the structure (X). It is conceivable that the traces of cis- and trans-1, 2-dimethylcyclopropane, and the isomerization of the allylcarbinyl radicals, (VII) and (VIII) could be accounted for by either possibility.*

The free-radical decarbonylations of 2-methyl-trans-4-hexenal (XI) and 3-methyl-trans-4-hexenal (XII) produce cis-2-hexene, trans-2-hexene, 4-methyl-trans-2-pentene, and 4-methyl-cis-2-pentene (20).

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*Although two previous studies showed that the decarbonylation of cyclopropylacetaldehyde yielded only 1-butene (19), the decarbonylation of dimethylcyclopropylacetaldehyde yields both 2-methyl-2-pentene and isopropylcyclopropane when the decarbonylation is done in concentrated benzyl mercaptan (19a). The ratio is about 4:1 in favor of the olefin. Therefore it is likely that a dimethylcyclopropylcarbinyl free radical can be formed in the decarbonylation of dimethylcyclopropylacetaldehyde, and in turn form cyclopropyl products. This makes its presence as an intermediate in the equilibration of (VII) and (VIII) quite likely.

Table 2. Decarbonylations of 2-Methyl- and 3-Methyl-trans-4-hexenal (20).

Product Ratios from the Decarbonylation of 2-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°[a]

Initial aldehyde concn, *M*	2-Hexene/ 4-methyl-2-pentene	*trans*-2-Hexene/ *cis*-2-hexene	4-Methyl-*trans*-2-pentene/ 4-methyl-*cis*-2-pentene
Neat	14.0 ± 0.1	4.2 ± 0.2	4.7 ± 0.2
4.0	13.4 ± 0.1	3.5 ± 0.1	*b*
3.0	12.7 ± 0.2	3.1 ± 0.2	4.7 ± 0.1
2.0	12.9 ± 0.1	3.1 ± 0.1	4.4 ± 0.2
1.5	12.8 ± 0.1	3.0 ± 0.1	*b*
1.0	12.2 ± 0.1	2.7 ± 0.1	*b*
0.75	12.2 ± 0.2	2.7 ± 0.0	4.8
0.50	11.8 ± 0.3	2.5 ± 0.2	*b*
0.38	12.0 ± 0.1	2.6 ± 0.1	4.4 ± 0.3
0.25	12.5 ± 0.2	2.6 ± 0.0	*c*
0.19	12.5 ± 0.1	2.5 ± 0.2	*c*
0.12	12.3 ± 0.4	2.5 ± 0.2	*c*
0.094	12.6 ± 0.2	2.5 ± 0.3	*c*

[a] Error quoted as maximum expected error and is based on two to four separate analyses. [b] Ratios not determined at all concentrations owing to the difficulty of analysis. [c] Too little olefins for reliable quantitative analysis.

Product Ratios from the Decarbonylation of 3-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°[a]

Initial aldehyde concn, *M*	2-Hexene/ 4-methyl-2-pentene	*trans*-2-Hexene/ *cis*-2-hexene	4-Methyl-*trans*-2-pentene/ 4-methyl-*cis*-2-pentene
Neat (6 *M*)	5.6 ± 0.1	2.1 ± 0.2	5.7 ± 0.3
4.0	6.5 ± 0.1	2.4 ± 0.1	6.0 ± 0.5
3.0	7.1 ± 0.1	2.6 ± 0.1	5.0 ± 0.2
2.0	7.7 ± 0.2	2.5 ± 0.1	4.9 ± 0.1
1.5	8.1 ± 0.1	2.6 ± 0.1	4.6 ± 0.5
1.0	8.7 ± 0.2	2.5 ± 0.2	4.4 ± 0.3
0.75	9.1 ± 0.1	2.4 ± 0.2	3.1 ± 0.3
0.50	9.6 ± 0.1	2.4 ± 0.2	3.2 ± 0.3
0.38	9.8 ± 0.4	2.4 ± 0.2	*b*
0.25	10.4 ± 0.2	2.2 ± 0.2	*b*
0.19	10.2 ± 0.2	2.2 ± 0.2	*b*
0.12	9.6 ± 0.2	2.6 ± 0.3	*b*
0.094	9.2 ± 0.3	2.3 ± 0.1	*b*

[a] Error quoted as maximum expected error and is based on two to four separate analyses. [b] Too little olefins for reliable quantitative analysis.

Similarly, the free-radical decarbonylation of cis-4-pentenal-5-d (XIII) produces both cis-1-butene-1-d and trans-1-butene-1-d (18). The cis:trans ratio is 1.03:1.00 at 1.0 M aldehyde concentration, and 1.42:1.00 at 7.3 M aldehyde concentration.

The presence of both cis and trans products in these experiments constitutes strong evidence that the (2-methylcyclopropyl)-1-ethyl radical (XIV), and the cyclopropylmethyl-α-d radical (XV), are intermediates in the isomerizations of the free radical intermediates from (XI) and (XII), or (XIII), respectively. For the cis-trans isomerizations, free rotation about the indicated bonds of (XIV) and (XV), which requires a cyclopropylcarbinyl free-radical structure, offers the best explanation.

At least in the unsubstituted, or methyl-substituted allylcarbinyl free-radical isomerizations, it seems reasonable to postulate that the intermediates are isomerized through a cyclopropylcarbinyl, or methyl-substituted cyclopropylcarbinyl free-radical intermediate. Whether there is also an additional intermediate, with bonding and geometry between these two extremes is still not known, but it seems reasonable to limit participation of such a species to a minor role in the mechanism. The generality of these conclusions is also not known. The absence of significant amounts of cyclopropylcarbinyl products in the unsubstituted or methyl-substituted systems, and some energetic approximations (19a) both indicate that the allylcarbinyl free radical, or methyl-substituted allylcarbinyl free radicals, are likely to be substantially lower in energy than their cyclopropylcarbinyl

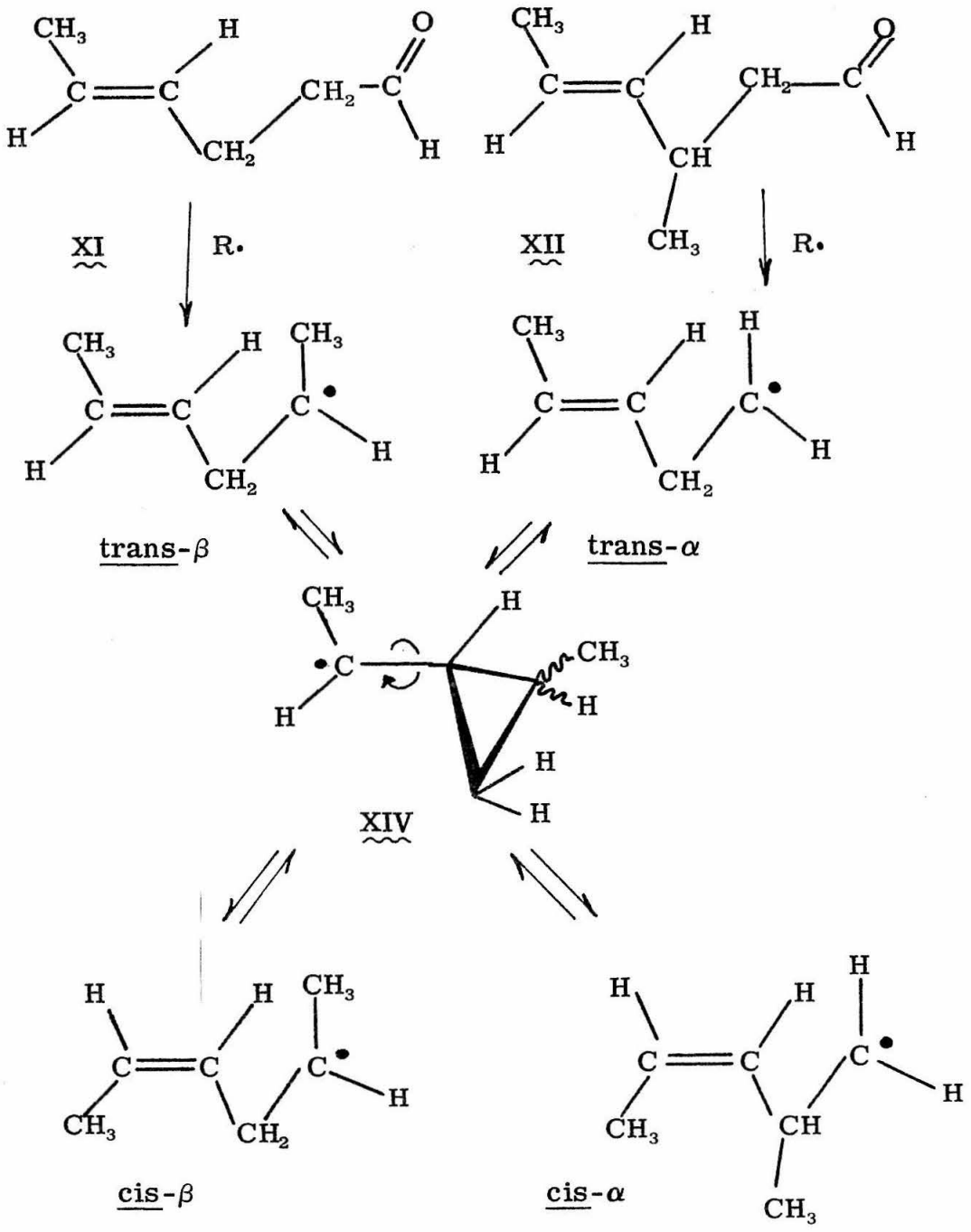

Figure 2. Intermediates in the Decarbonylations of 2- and 3-Methyl-trans-4-hexenal (20).

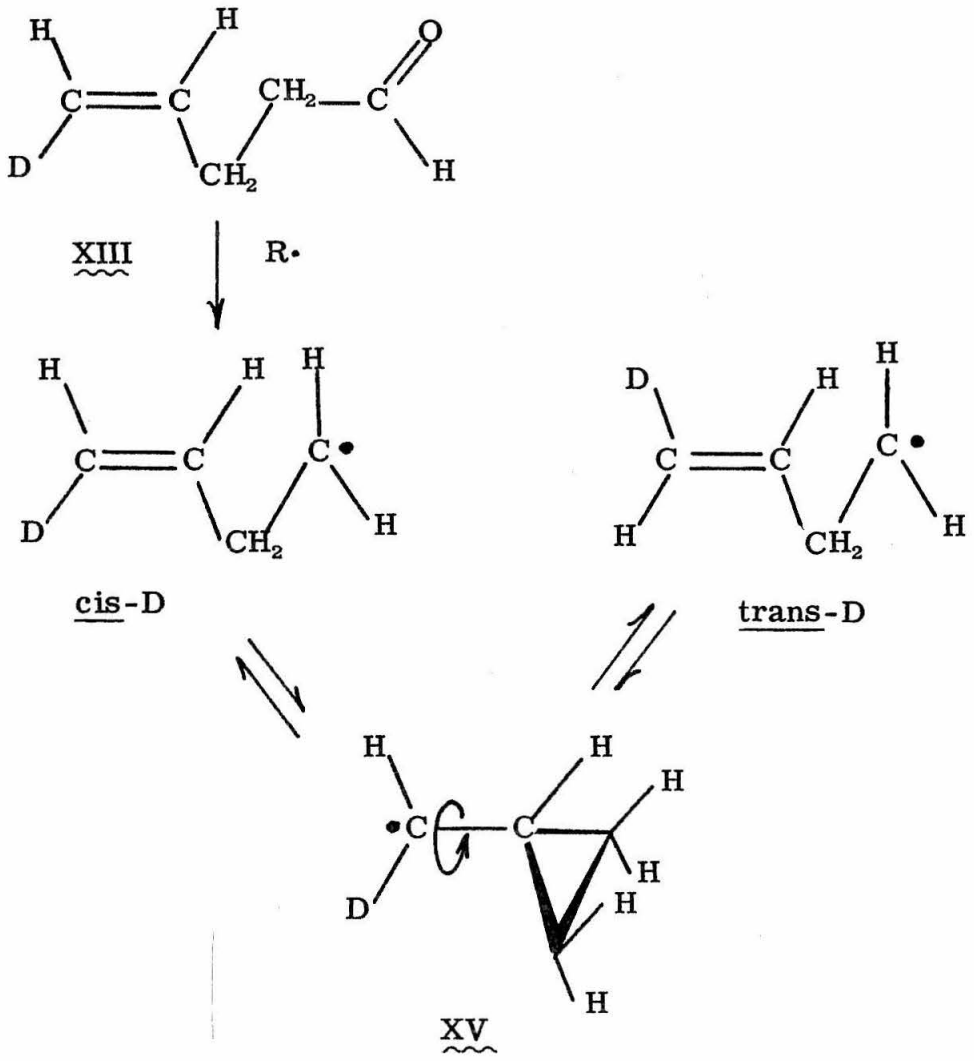

Figure 3. Intermediates in the Decarbonylation of cis-4-Pentenal-5-d (18).

free-radical isomers. Therefore, these systems are probably poor choices in which to search for an intermediate between the allylcarbinyl- and cyclopropylcarbinyl free radicals.

In a search for possible intermediates in free-radical isomerizations, it is natural to draw comparisons with carbonium-ion chemistry, where "non-classical" carbonium ions have been postulated as intermediates. A non-classical ion has been defined by Bartlett (21),

> "an ion is nonclassical if its ground state has delocalized bonding sigma electrons"

When carbonium ions are generated from cyclopropylcarbinyl- or allylcarbinyl compounds, it is common to find rates of formation which are several orders of magnitude more rapid than the rates of formation of carbonium ions from similar compounds which lack the cyclopropyl ring or olefinic bond (22). In reactions of cyclopropylcarbinyl- or allylcarbinyl compounds, the magnitude of the enhancement in the rate of formation of free radicals is substantial, but much smaller than the enhancement in the rate of formation of carbonium ions from similar compounds.

In the carbonium-ion reactions of cyclopropylcarbinyl- and allylcarbinyl compounds, in addition to cyclopropylcarbinyl- and allylcarbinyl products, cyclobutyl products are formed. Cyclobutyl products are not formed in the analogous free-radical reactions of

cyclopropylcarbinyl- and allylcarbinyl compounds.* Isotope-labeling studies have shown that carbonium ions from cyclopropylcarbinyl- and allylcarbinyl compounds have intermediates in which the three carbons other than the methinyl carbon become chemically equivalent (23), whereas in analogous free-radical intermediates, only two carbons become chemically equivalent (24).

Quite obviously, then, the geometry and stabilizing energies of free-radical intermediates from cyclopropylcarbinyl- and allylcarbinyl compounds are very different from those found in analogous carbonium-ion intermediates.

Molecular orbital calculations offer a reasonable explanation of the differences between the behaviour of free radical generated from cyclopropylcarbinyl- and allylcarbinyl compounds.** The most stable carbonium ion from cyclopropylcarbinyl- or allylcarbinyl compounds (and cyclobutyl compounds) is predicted to be the bicyclobutonium ion (XVI), whereas the most stable free radical from cyclopropylcarbinyl

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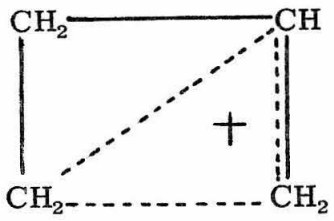
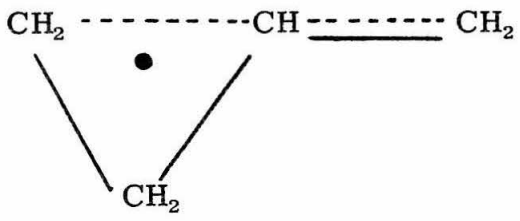
*Solely on the basis of gas chromatography retention time, Walling and Fredericks tentatively identified cyclobutyl chloride, in about 10% yield, as a product of the free-radical chlorination of methylcyclopropane with t-butyl hypochlorite (4). However, if the product is cyclobutyl chloride, it could well be a product of solvolysis and rearrangement of some of the cyclopropylcarbinyl chloride formed initially (6).

**The significance of the results of Extended Huckel Molecular Orbital Calculations, when used on non-benzenoid systems has been challenged (26).

or allylcarbinyl compounds is predicted to be the homoallylic free radical (XVII) (25). The homoallylic free radical is predicted to have



XVI



XVII

dotted lines in (XVI) and (XVII) indicate overlap of three p-orbitals, one on each carbon through which a dotted line passes (25).

a substantial stabilization energy associated with it, although this energy is not as great as the corresponding energy of stabilization predicted for the bicyclobutonium cation. Therefore, if the presence of "non-classical" carbonium ions is accepted, then it is reasonable to expect a similar, although more elusive, intermediate to exist in free radical reactions, on the basis of these molecular orbital calculations.

In the spectroscopic area, where electron spin resonance (esr) spectroscopy might seem to be a ready means of elucidating information about the geometry and bonding in free radicals, there has only recently been substantial success in observing the free radicals from cyclopropylcarbinyl- and allylcarbinyl compounds. Several years ago, Fessenden and Schuler obtained the esr spectrum of the

allylcarbinyl radical (27). The hyperfine splittings were typical of normal alkyl radicals, and could not be attributed to any "nonclassical" structure, where there would be substantial overlap of the p orbital containing the unpaired electron with some part of the olefinic pi orbital.

Very recently, after the present work was completed, the esr spectra for the cyclopropylcarbinyl- and allylcarbinyl free radicals, and for several substituted cyclopropylcarbinyl- and allylcarbinyl free radicals have been determined (28).

Although neither the allylcarbinyl free radical nor any of the substituted allylcarbinyl free radicals show any unusual hyperfine couplings, both the β- and the γ hyperfine couplings of the cyclopropylcarbinyl free radical and the substituted cyclopropylcarbinyl free radicals are most interesting. The unusually small β couplings have been interpreted to mean that the α-methylene group bisects the cyclopropyl ring, which leaves the β-hydrogen or β-methyl group in the node of the p orbital containing the spin. The unusually large γ couplings have been interpreted as evidence that there is partial donation of the spin into an antibonding orbital in the cyclopropane ring. This orbital must be antisymmetric with respect to the plane of symmetry of the free radical (i.e., a plane containing the α-methylene group, and bisecting the cyclopropane ring). These spectral results offer a reasonable explanation for the enhanced rates of formation of free radicals from cyclopropylcarbinyl compounds, and the lack of similar acceleration in the rates of formation of free

Table 3. Electron Spin Resonance Hyperfine Coupling Constants for Alkyl and Cycloalkyl Free Radicals [a]

Radical	a_α (gauss)	a_β (gauss)	a_γ (gauss)
$CH_3\cdot$	23.04	...	...
$CH_3CH_2\cdot$	22.38	26.87	...
$C_2H_5CH_2\cdot$	22.08	33.2	0.38
$(CH_3)_2CH\cdot$	22.11	24.68	...
$CH_2{=}CHCH_2CH_2\cdot$	22.23	29.7	0.61
$C_2H_5\dot{C}HCH_3$	21.8	24.5 (CH_3) 27.9 (CH_2)	b
$(CH_3)_2CHCH_2\cdot$	22.0	35.1	b
$(CH_3)_3C\cdot$	...	22.72	...
$C_2H_5\dot{C}HC_2H_5$	21.8	28.8	b
$(CH_3)_2\dot{C}CH_2CH_3$	...	22.8 (CH_3) 17.6 (CH_2)	b
$(CH_3)_3CCH_2\cdot$	22.7	...	b
$(C_2H_5)_3C\cdot$	...	17.3	b
$(C_2H_5)_3C\dot{C}HCH_3$	21.7	24.9	b
$RCH_2\dot{C}HCH_2R'$	21.0	24.8	b
Cyclo-$C_4H_7\cdot$	21.20	36.66	1.12
Cyclo-$C_5H_9\cdot$	21.48	35.16	0.53
Cyclo-$C_6H_{11}\cdot$	21.15	41 [c] 5	0.71
Cyclo-$C_7H_{13}\cdot$	21.8	24.7	b

[a] From Ref. 27, p. 2182.

[b] Not determined.

[c] Sum of β-coupling constants is 45.96 G.

Table 4. Electron Spin Resonance Coupling Constants of Some Cyclopropylcarbinyl and Allylcarbinyl Radicals [a]

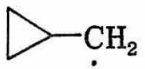
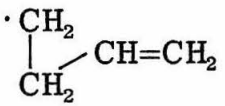
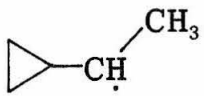
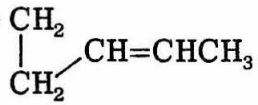
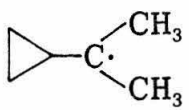
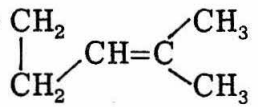
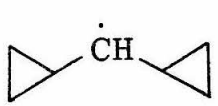
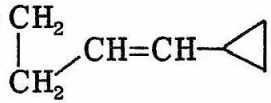
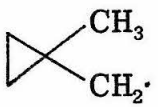
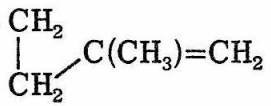
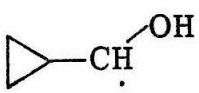
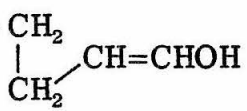
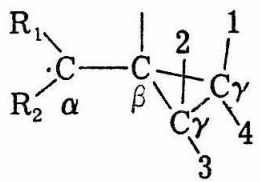
Cyclopropyl-carbinyl radial	Temp, °C	Coupling [b] constants, G	Allylcarbinyl radical	Temp, °C	Coupling constants, G [b] trans	cis
	-150	$\alpha = 20.74$ $\beta = 2.55$ $\gamma_1\gamma_2 = 2.98$ $\gamma_3\gamma_4 = 2.01$		-90	$\alpha = 22.17$ $\beta = 28.53$ $\gamma = 0.61$ $\delta = 0.35$	
	-153	$CH_3 = 22.3$ $\alpha H = 22.3$ $\beta = 2.9$ $\gamma_1\gamma_2 = 1.9$ $\gamma_3\gamma_4 = 1.1$		-114	$\alpha = 22.3$ $\beta = 29.3$ $\gamma = 0.7$	$\alpha = 22.3$ $\beta = 30.9$ $\gamma = 0.7$ $\delta = 0.7$
	-150	$CH_3 = 21.7_6$ $\gamma = 2.2_7$ $\gamma_1\gamma_2 = 1.6_9$ $\gamma_3\gamma_4 = 1.2_7$		-73	$\alpha = 21.9_8$ $\beta = 30.0_5$ $\gamma = 0.6_7$	

Table 4. (Cont'd)

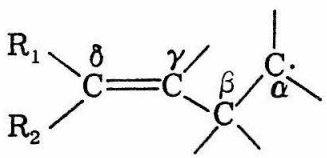
	-153	$\alpha = 19.5_0$ $\beta = 4.0_4$ $\gamma_1\gamma_2 = 2.2_7$ $\gamma_3\gamma_4 = 1.7_5$		-78	$\alpha = 22.0_6$ $\beta = 28.3_7$ $\gamma = 0.6_3$	$\alpha = 22.0_6$ $\beta = 29.8_6$ $\gamma = 0.6_1$ $\delta = 0.6_1$
	-131	$\alpha = 20.6_0$ $CH_3 = 0.7_8$ $\gamma_1\gamma_2 = 3.5_1$ $\gamma_3\gamma_4 = 1.9_5$		-70	$\alpha = 22.1_8$ $\beta = 26.8_6$	
				-48	$\alpha = 21.9_6$ $\beta = 28.2_6$ $\gamma = 0.6_9$	$\alpha = 21.9_6$ $\beta = 29.6_4$ $\gamma = 0.61$ $\delta = 0.6_1$

[a] Ref. 28a, 28b.

[b] Couplings are lettered or numbered according to the following:



Cyclopropyl-carbinyl radials



Allylcarbinyl radicals

radicals from allylcarbinyl compounds.

When cyclopropylcarbinyl radicals are warmed above -120°, or the various substituted cyclopropylcarbinyl radicals are warmed to between -100° and -50°, depending upon the number, location, and type, of substituent, the spectra show the features of the respective rearranged allylcarbinyl free radicals, superimposed on the original spectrum of the respective cyclopropylcarbinyl free radical. As the radicals are warmed further, the only remaining spectrum is that of the respective allylcarbinyl radical. Never is any spectrum of a "transitional" intermediate between these two radicals found in any of the systems studied. It is evident that any process which exchanges methylene groupings in the cyclopropylcarbinyl free radical is slow on the esr time scale, because the α-methylene group is not equivalent with the two methylene groups of the cyclopropyl group. Therefore, the cyclopropylcarbinyl free radical must have a lifetime of about 10^{-7} seconds or longer at 120° or below (28a).

Brief mention must be made of a recent communication that the reduction of either syn-7- or anti-7-bromonorbornene with tri-n-butyltin deuteride leads solely to anti-7-deuterionorbornene, which was interpreted as evidence of nonclassical stabilization of the anti-7-norbornenyl free radical (29). This result was based on some poorly resolved nmr spectra, and has since been corrected. The product is a mixture of anti-7-deuterionorbornene and syn-7-deuterionorbornene in the ratio of approximately 3:1, from either starting bromide (30). In a similar experiment, both syn-7- and anti-7-bromobenzonorbor-

nadiene were reduced with tri-n-butyltin deuteride, and the Diels-Alder adduct of the reduction product, 7-deuteriobenzonorbornadiene, with 1, 3-diphenylisobenzofuran was prepared. From the adduct, an accurate determination of the ratio of syn-7- to anti-7-deuteriobenzonorbornadiene, produced in the radical reduction of the bromides, can be made. In the nmr spectrum of the adduct, the syn-7- and anti-7-protons are clearly resolved, unlike the 7-protons in norbornenes and benzonorbornadienes. Integration of the nmr spectra showed the ratio of anti-7- to syn-7-deuteration to be 43:57 in the reduction of either syn-7- or anti-7-bromobenzonorbornadiene (31). While the authors of the former paper feel that their "nonclassical" radical interpretation is still qualitatively correct (30), the authors of the latter paper feel that such small differences in stereospecificity of deuteration are inconsistent with the "nonclassical" interpretation.*

It is apparent from the foregoing that there is a growing body of evidence to support the presence of cyclopropylcarbinyl- and allylcarbinyl free radicals in the isomerization of radical intermediates from unsubstituted- or alkyl-substituted cyclopropylcarbinyl-

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*In analogous carbonium ions, where the nonclassical interpretation has been made, there is complete stereospecificity of product formation, and very substantial activation energies for interconversion of the syn-7- and anti-7-carbonium ions (32).

or allylcarbinyl compounds. Certainly, too, it is apparent that unsubstituted- or alkyl-substituted cyclopropylcarbinyl free radicals have characteristics which are more easily explained if they are considered to be "nonclassical" free radicals, than if one attempts to call them "classical" free radicals. However, the generality of these observations when more complex cyclopropylcarbinyl- and allylcarbinyl free radicals are concerned is unknown. The possible existence of additional intermediates, comparable to some of the "nonclassical" carbonium ions postulated as intermediates in analogous cationic reactions has not received a thorough examination. It also seems possible that some cyclopropylcarbinyl free radicals may be sufficiently delocalized to form allylcarbinyl products, or even that some allylcarbinyl free radicals might be sufficiently delocalized to form some cyclopropylcarbinyl products, although the evidence to date renders the latter possibility less likely than the former.

Many of the studies to date involve unstabilized, or poorly-stabilized cyclopropylcarbinyl free radicals in equilibrium with the isomeric allylcarbinyl free radicals. In these cases, the allylcarbinyl free radicals should be of substantially lower energy than the isomeric cyclopropylcarbinyl free radicals, because of the strain of the cyclopropyl ring. Conversely, in the ($\underline{\gamma}$,$\underline{\gamma}$-diphenylallyl)-carbinyl- and diphenylcyclopropylcarbinyl free radicals, the latter is substantially more stable than the former (7). In either case, it seems that the search for any additional intermediates in the isomerizations of cyclopropylcarbinyl- and allylcarbinyl free radicals, or the formation

of allylcarbinyl products from the cyclopropylcarbinyl radical or the formation of cyclopropylcarbinyl products from the allylcarbinyl radical are unlikely to meet with success when the stability of either the cyclopropylcarbinyl- or isomeric allylcarbinyl free radical is substantially greater than that of the other.

Part 2. Selection of a Suitable Reaction to Study

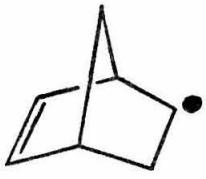
A. Norbornenyl- and Nortricyclyl Free Radicals

If one wishes to improve the chances for intervention of an additional free-radical intermediate, through which isomeric cyclopropylcarbinyl- and allylcarbinyl free radicals are interconverted, certain characteristics are desirable. First, the cyclopropylcarbinyl- and allylcarbinyl radicals should be as close to each other in energy as possible. Ideally, both the cyclopropylcarbinyl- and the allylcarbinyl radical should have some instability imparted by steric interactions, or strain energy, which might cause an intermediate between these two radicals to be energetically preferred to either.

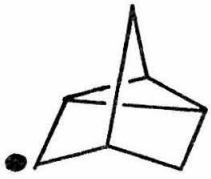
Neglecting temporarily the means of generating the free radicals, we can examine some of the available cyclopropylcarbinyl- and allylcarbinyl free radicals, with respect to the criteria outlined above. Certainly, the unsubstituted, or methyl-substituted cyclopropylcarbinyl- and allylcarbinyl free radicals are energetically unsuitable, because the allylcarbinyl radical is appreciably more stable than the isomeric cyclopropylcarbinyl radical (33). In order to lessen the energy difference, substituted cyclopropylcarbinyl- and allylcarbinyl free radicals, where the substituents will stabilize the cyclopropylcarbinyl radical, must be used. An obvious choice is

phenyl substitution, * but then ortho-cyclization products are obtained, which complicates interpretation of results based on product analysis (7).

A likely choice to overcome these difficulties is a pair of polycyclic free radicals. The most readily available of these are the 5-norbornenyl free radical (XIX) and the 2-nortricyclyl free radical (XX).



XIX



XX

Energetically, both parent hydrocarbons lie very close together. Schleyer has determined the equilibrium ratio of nortricyclene (NT) to norbornene (NB) to be 77/23 at the reflux temperature of 100-110° (34).

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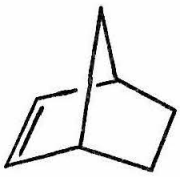
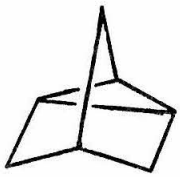
*In the case of the diphenylcyclopropylcarbinyl free radical and the (γ, γ-diphenylallyl)-carbinyl free radical, it has been calculated that the former is approximately 8 Kcal/mole more stable than the latter (7), so one phenyl group should leave the isomeric radicals quite close in energy.



NB



NT

Our results showed the equilibrium ratio to be about 85/15 in favor of nortricyclene at 103°, over a similar catalyst.* It is reasonable to expect that the energy of the norbornenyl- and nortricyclyl free radicals might also be similar, when both parent hydrocarbons have similar energies, because both free radicals are similarly-substituted secondary free radicals.

There is a possibility that the norbornenyl- and nortricyclyl free radicals are not close together in energy, in view of the finding that nortricyclenes are the only products of free-radical additions of several addends with low chain-transfer constants to norbornadiene (35). This could be interpreted as evidence that the nortricyclyl free radical is much more stable than the norbornenyl free radical.

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*Schleyer used Houdry S-90 silica-alumina catalyst to equilibrate norbornene and nortricyclene, while we used Houdry S-46 silica-alumina catalyst. In both studies, the equilibrium ratio was obtained from both norbornene and nortricyclene. The amount of monomeric hydrocarbons continually decreases through polymer formation as the equilibrations proceed.

However, other studies have shown that appreciable amounts of both norbornene and nortricyclene are obtained from the unsubstituted norbornenyl- and nortricyclyl radicals in equilibrium, in abstraction of hydrogen from either good (14a) or poor (13b) hydrogen donors. This implies that there is not any substantial difference in energy between the norbornenyl- and nortricyclyl free radicals.* Thus the results of the addition of low-chain-transfer addends to norbornadiene, where only nortricyclyl products are obtained (35), appear to be related either to the fact that the intermediate radicals are substituted, or to some secondary reaction which removes the norbornenyl products.

It appears, then, that free radicals generated from norbornenyl- and nortricyclyl compounds provide an energetically suitable system for study, if a suitable means of generating them, and forming products from them, can be found.

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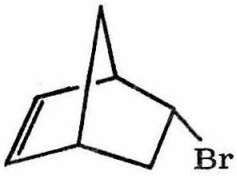
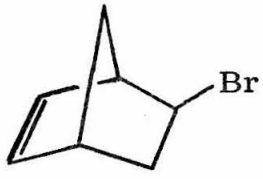
*Montgomery and co-workers (2a, 20) showed that in the presence of good hydrogen donors, the relative concentrations of the allylcarbinyl- and cyclopropylcarbinyl radicals appeared to be more important in determining the product ratio than differences in the activation energies for the abstraction reactions of the two radicals, at least in methyl-substituted cases.

B. Tri-n-butyltin Hydride as a Chain-Transfer Agent

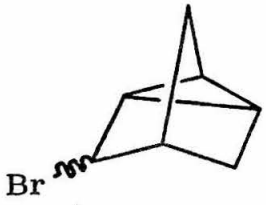
In undertaking studies of the products obtained from isomerizable intermediates, such as the norbornenyl- and nortricyclyl radicals, the first consideration is how to generate the radicals, and the second is what chain-transfer agent to use to form products from the radical intermediates. If one wishes to form products from the radical intermediates before they reach equilibrium, then a very reactive chain-transfer agent is required in the case of cyclopropylcarbinyl- and allylcarbinyl free radicals. The choices for this work were the photoinitiated reductions of endo-5-bromonorbornene (n-NBBr), exo-5-bromonorbornene (x-NBBr), and 2-bromonortricyclene (NTBr), with tri-n-butyltin hydride.



n-NBBr



x-NBBr



NTBr

Organotin hydrides are among the most reactive chain-transfer agents known, and they react with alkyl halides in a free-radical reaction, which may be easily initiated thermally, photochemically, or with peroxides or azo compounds, to yield monomeric hydrocarbons

as the reduction products, in essentially quantitative yield. It seems appropriate to discuss free-radical reductions of alkyl halides with organotin hydrides in some depth, because of the relatively recent use of this reaction in free-radical chemistry.*

That the reduction of alkyl halides with organotin hydrides is a free-radical reaction has been well established. Kuivila and co-workers systematically eliminated first an anionic mechanism then a cationic mechanism for these reactions from the following evidence (37):

1. Elimination of an anionic mechanism.

(i) Thermal reduction of optically active α-phenylethyl chloride with triphenyltin deuteride at room temperature yields racemic products.

(ii) Thermal reduction of either α- or γ-methylallyl chloride with triphenyltin hydride at room temperature yields the same mixture of 1-butene and 2-butene.

(iii) Reduction of propargyl bromide with tri-n-butyltin hydride yields a mixture of propyne and allene.

(iv) The reduction of 2-bromonortricyclene yields a mixture of nortricyclene and norbornene.

2. Elimination of a cationic mechanism.

(i) Cyclopropylcarbinyl chloride would not react with neat triphenyltin hydride after 5 hours at 130°, while both α- and

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*The first report of the reduction of an alkyl halide with an organotin hydride was in 1957 (36).

γ-methylallyl chloride are easily reduced at room temperature with triphenyltin hydride. This is opposite to the order of reactivity found in the generation of carbonium ions from these compounds.

(ii) The relative rates of halogen-atom extraction from alkyl halides, determined by competition studies in organotin hydride reductions, parallels those found for the methyl radical. These relative rates are quite different from those found for analogous nucleophilic substitution reactions.

(iii) The reductions of alkyl halides with organotin hydrides is catalysed by azobisisobutyronitrile, and retarded by hydroquinone.

(iv) Benzyl bromide reacts with organotin hydrides more rapidly than t-butyl bromide, which is the opposite order of reactivity to that found for the solvolyses of the corresponding chlorides.

Superficially, then, it seems that the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with organotin hydrides should be a satisfactory means of generating norbornenyl- and nortricyclyl free-radical intermediates. However, there are some possible pitfalls in the use of these free-radical reductions.

(i) Hydrostannation of olefinic bonds.

It was first reported that organotin hydrides would add ionicly to terminal olefins possessing a substituent with a

negative inductive effect (38). However, the hydrostannation of olefins has since proved to be much more general. Organotin hydrides have been found to add to simple nonactivated terminal olefins (39), and even internal olefinic bonds (40). As well, the hydrostannation of olefins has been found to be ionic, free radical, or a combination of both, depending upon the reactants and conditions (41). Hydrostannation of olefins is catalysed by ultraviolet irradiation (39b), free-radical initiators (40), or oxygen (42).

(ii) Reversible addition of organotin radicals to olefins.

In free-radical reactions of organotin hydrides, the intermediate organotin radicals have been found to undergo a reversible addition to olefins present (43). Both 1-hexene-cis-1-d and 1-hexene-trans-1-d are found to have undergone extensive cis-trans isomerization when irradiated in the presence of organotin hydrides, under conditions where free-radical hydrostannation of the olefinic bond occurs, but there is insufficient organotin hydride to hydrostannate all the olefin (43a). Both cis- and trans-β-deuteriostyrene, under similar conditions also show some cis-trans isomerization, but to a much smaller extent that found in the deuteriohexenes (43a).*

*The addition of an organotin radical to the β-position of styrene produces a benzylic radical. Therefore, although an organotin radical should add to styrene much more rapidly than to 1-hexene, the reverse reaction, or loss of the organotin radical from the benzylic radical, should be slowed by an even greater amount, relative to loss of the organotin radical from the hexyl radical. Therefore cis-trans isomerization is slower in styrene than 1-hexene (43a).

In a similar experiment, cis- and trans-piperylenes were found to undergo cis-trans isomerization in the presence of organotin radicals, through the reversible addition of the organotin radicals to the olefinic bonds (43b). This reversible addition of organotin radicals to olefinic is analogous to the previously-determined reversible additions of alkylthio- and arylthio radicals to olefins (44).

In the free-radical reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene, either olefinic starting material, or olefinic products, or both, will be present. Obviously, then, the reversible organotin radical addition could occur, leading to products other than those from the reductions of the bromides with the organotin hydrides. This could render product analysis data useless for purposes of determining the intermediates in the free-radical-reduction reaction.

(iii) Oxygen effects on organotin hydride reactions.

Another problem encountered in the use of organotin hydrides is the effect of oxygen upon the reactions. Kuivila and Menapace made a cursory study of the effects of the amount of oxygen in the atmosphere over the reduction of n-butyl bromide with tri-n-butyltin hydride in chlorobenzene (45). At room temperature, the reaction proceeded most rapidly in an atmosphere of about 10% oxygen, about half as fast in pure nitrogen, and more than an order of magnitude more slowly

in 20% oxygen or more in atmosphere. Fujimoto and Suzukawa have observed that the rate of reduction of alkyl halides is inhibited by oxygen, while under the same conditions, the hydrostannation of olefins is catalysed by oxygen (42). Carlsson and Ingold, in reference to the reduction of alkyl halides with organotin hydrides have noted that when carefully degassed reagents were added to a reaction cell,

> "A short induction period was occasionally observed with some of the less reactive chlorides, but never with the bromides. In contrast, methyl iodide, and some of the more reactive bromides sometimes exhibited an irreproducible, self-initiated reaction upon being added to the organotin hydrides" (46).

It is not clear whether this phenomenon is also related to oxygen, or previously-formed oxygen products, but it is certainly likely, because oxygen will react very readily with organotin hydrides, to produce several oxides and peroxides, which might readily serve as either radical initiators or inhibitors. The short duration of the induction period, and the small percent conversion which occurs during the self-initiated reaction imply that the phenomenon is due to the presence of a small amount of some material which is rapidly used up, making oxygen a likely culprit.

(iv) Disproportionation of organotin hydrides.

One additional problem in the use of organotin hydrides is their tendency to undergo a disproportionation to yield hydrogen and organoditins. The disproportionation reaction

appears to be unpredictable, and a recent review has listed some of the materials which catalyse it. They are amines, silicone grease, tin metal, aluminum halides, metal surfaces, diborane, and adventitious impurities * (39a).

In subsequent sections of this thesis, it will be shown that adequate consideration of the above problems in the use of organotin hydrides in the free-radical reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene has been given, and that none of them significantly affect the major results or conclusions.

The energetic parameters and kinetic parameters of organotin hydride reactions have been somewhat of a mystery until very recent years. In Appendix IV, the tin-hydrogen bond dissociation energy in tri-n-butyltin hydride has been calculated to be 71 Kcal/mole. When this value is combined with some other known and calculated energies, it becomes apparent that both chain-transfer steps in the free-radical reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride should be very exothermic. Therefore, the reductions should go via long-chain radical reactions. The result should be very "clean" reactions, with virtually no products

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*In a personal communication, Professor H. G. Kuivila recounted an example of disproportionation as a result of "adventitious impurities". He had filled ten tubes with a triorganotin hydride, degassed them, and sealed them, all under identical conditions. When they were opened, following storage for some time, nine of them still contained the pure organotin hydride under a vacuum. The tenth, however, virtually exploded when opened, from the hydrogen pressure buildup which resulted from extensive disproportionation.

other than the monomeric hydrocarbons, norbornene and nortricyclene.

Carlsson and Ingold recently determined the absolute-reaction-rate constants for the propagation and termination steps of several reductions of alkyl halides with organotin hydrides (46). These absolute reaction rates can be qualitatively extended to the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride. The rate-determining step in the reductions of alkyl bromides or alkyl iodides is the abstraction of hydrogen from the organotin hydride by the alkyl radical. In the reductions of alkyl chlorides, however, the rate-determining step is the abstraction of chlorine by the organotin radical. Some selected absolute reaction rates which are of interest in later calculations in this thesis are given in Table 5.

From Table 5, it can be seen that in the reductions of alkyl bromides with tri-n-butyltin hydride, the principal means of chain termination will be by alkyl radical-alkyl radical combination, unless the concentration of organotin hydride is at least several times the concentration of the alkyl bromide. Because of this recent work by Carlsson and Ingold (46), the reduction of alkyl halides with organotin hydrides is now a very well understood free-radical reaction. The rate constants for both chain-propagation steps, and the rate constants for alkyl-alkyl and organotin-organotin radical combinations are known. Only the rate for the cross-termination step involving alkyl radical-organotin radical combination is unknown, and Carlsson

Table 5. Absolute Reaction Rates in the Reductions of Alkyl Halides with Organotin Hydrides (46).

		k/Msec[a]
$\underline{t}\text{-}C_4H_9\cdot + (\underline{n}\text{-}C_4H_9)_3SnH \longrightarrow$	$\underline{t}\text{-}C_4H_{10} + (\underline{n}\text{-}C_4H_9)_3Sn\cdot$	$7.4\ (10^5)$
$\underline{t}\text{-}C_4H_9Br + (\underline{n}\text{-}C_4H_9)_3Sn\cdot \longrightarrow$	$\underline{t}\text{-}C_4H_9\cdot + (\underline{n}\text{-}C_4H_9)_3SnBr$	$8.5\ (10^7)$
$\underline{c}\text{-}C_6H_{11}\cdot + (\underline{n}\text{-}C_4H_9)_3SnH \longrightarrow$	$\underline{c}\text{-}C_6H_{11} + (\underline{n}\text{-}C_4H_9)_3Sn\cdot$	$1.2\ (10^6)$
$\underline{c}\text{-}C_6H_{11}Br + (\underline{n}\text{-}C_4H_9)_3Sn\cdot \longrightarrow$	$\underline{c}\text{-}C_6H_{11}\cdot + (\underline{n}\text{-}C_4H_9)_3SnBr$	$2.2\ (10^7)$
$\underline{n}\text{-}C_6H_{13}\cdot + (\underline{n}\text{-}C_4H_9)_3SnH \longrightarrow$	$\underline{n}\text{-}C_6H_{14} + (\underline{n}\text{-}C_4H_9)_3Sn\cdot$	$1.0\ (10^6)$
$\underline{n}\text{-}C_6H_{13}Br + (\underline{n}\text{-}C_4H_9)_3Sn\cdot \longrightarrow$	$\underline{n}\text{-}C_6H_{13}\cdot + (\underline{n}\text{-}C_4H_9)_3SnBr$	$1.9\ (10^7)$
		$2k$/Msec
$\underline{t}\text{-}C_4H_9\cdot + \underline{t}\text{-}C_4H_9\cdot$	$(CH_3)_3C\text{-}C(CH_3)_3$	$2.1\ (10^9)$
$\underline{c}\text{-}C_6H_{11}\cdot + \underline{c}\text{-}C_6H_{11}\cdot$	$\underline{c}\text{-}C_6H_{11}\text{-}\underline{c}\text{-}C_6H_{11}$	$2.7\ (10^9)$
$\underline{n}\text{-}C_6H_{13}\cdot + \underline{n}\text{-}C_6H_{13}\cdot$	$\underline{n}\text{-}C_{12}H_{26}$	$2.2\ (10^9)$
$(\underline{n}\text{-}C_4H_9)_3Sn\cdot + (\underline{n}\text{-}C_4H_9)_3Sn\cdot$	$(\underline{n}\text{-}C_4H_9)_3Sn\text{-}Sn(\underline{n}\text{-}C_4H_9)_3$	$1.4\ (10^9)$
$CH_3\cdot + CH_3\cdot$	C_2H_6	$8.9\ (10^9)$

[a] All values in hexane at 25°.

and Ingold have shown that this cross-termination cannot be very important, because concentration dependences show that the self-termination reactions are the principal means of termination in all the reactions studied (46).

If the rates of reduction of endo- and exo-5-bromonorbornene and 2-bromonortricyclene are compared to the reduction rates for some of the bromides in Table 5, then we should be able to obtain some good estimates of the absolute reaction rates for the propagation reactions in the reductions of these compounds. If we can obtain some values for the rates of the isomerization reactions of the intermediates, and some rate changes with temperature, we should be able to construct a reasonable energy diagram for the intermediates involved in the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride.

Part 3. Objectives of the Experimental Work

From the discussion in Part 1 of the Introduction, it is apparent that cyclopropylcarbinyl free radicals are unusual. Numerous examples of substantial rate enhancements provided by a cyclopropyl substituent on an incipient radical center were cited. Also, the esr spectra of several cyclopropylcarbinyl free radicals showed that these radicals prefer a "bisected" configuration, in which there is apparently substantial delocalization of the unpaired electron into an antibonding orbital of the γ-carbons. Allylcarbinyl free radicals do not appear to have corresponding unusual characteristics.

It appears, then, that cyclopropylcarbinyl free radicals meet Bartlett's definition that a "nonclassical" intermediate is one with delocalized sigma bonds in the ground state (21). Rationalizing the unusual characteristics of cyclopropylcarbinyl free radicals as those of "classical" free radicals, such as Cristol does (47), seems to be an oversimplification.

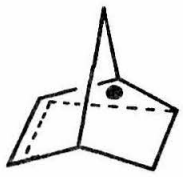
Recent studies have shown that rate enhancements are found for the abstraction of hydrogen from the position α to the cyclopropyl ring in the free-radical brominations of bicyclo[4.1.0]hept-3-ene, and cycloprop[2,3]indene with N-bromosuccinimide (48). Therefore, the characteristics found in unsubstituted or alkyl-substituted cyclopropylcarbinyl free radicals seem to extend to bicyclic cyclopropylcarbinyl radicals. It is probable, therefore, that the nortricyclyl free radical will be similar to these other cyclopropylcarbinyl

free radicals, and will therefore be best described as nonclassical. The norbornenyl free radical, by analogy with other allylcarbinyl free radicals, in which there don't appear to be any characteristics incompatible with classical free radicals, may very well be adequately described as classical.

In this thesis, our primary concern is not with the semantic classification of the norbornenyl- and nortricyclyl free radicals. We are interested mainly in the possibility of a third "bridged" radical as an intermediate between the norbornenyl- and nortricyclyl free radicals during their isomerization. We are also concerned with the products which can be formed from the norbornenyl- and nortricyclyl free radicals.

It is conceivable that delocalization in the norbornenyl- and nortricyclyl free radicals permits formation of "crossed" products. That is, some nortricyclene might arise from the norbornenyl free radical, or what is more plausible from previous discussion, some norbornene might arise from the nortricyclyl free radical.

Most of the effort in this thesis is oriented towards determining whether a third intermediate between the norbornenyl- and nortricyclyl free radicals during their isomerizations, is also present. Substantial overlap between the p-orbital at C_5 with the pi bond between C_1 and C_5 could result in the formation of a "bridged" radical, represented by (XXVIII). This "bridged" radical could presumably produce either norbornene or nortricyclene through abstraction of hydrogen by the appropriate position.



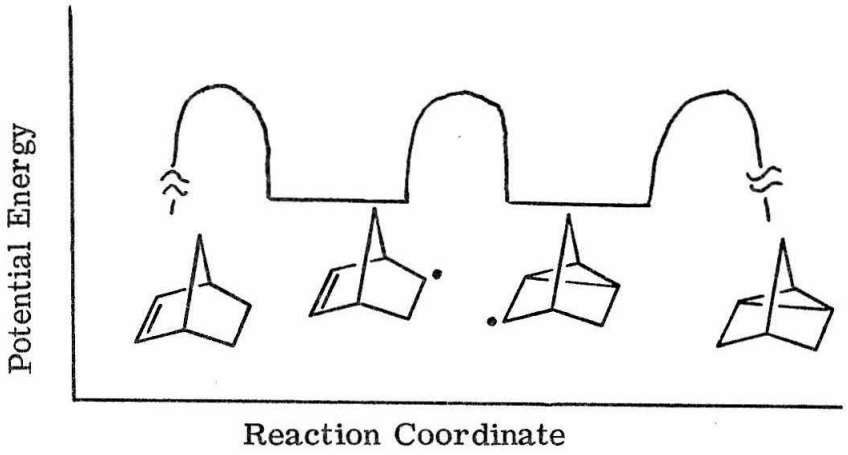
XXVIII

A simple comparison of the possible mechanisms discussed above is provided in Figure 4.

In the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride, the ratio of norbornene to nortricyclene is a function of the concentration of the hydrogen donor. The function will vary depending upon the mechanism. Kinetic equations can be used to predict the relationships between the product ratio and the concentration of the tri-n-butyltin hydride, and these relationships can be compared to the experimentally observed relationships. From this comparison, it should be possible to separate some of the hypothetical mechanisms into tenable or untenable categories.

In the free-radical reduction of endo-5-bromonorbornene-5, 6, 6-d_3 with tri-n-butyltin hydride, isomerization of the 5-norbornenyl-5, 6, 6-d_3 radical (XXV) can result in the formation of both norbornene-5, 6, 6-d_3 (NB_u) and norbornene-1, 7, 7-d_3 (NB_r), in addition to nortricyclene-5, 6, 6-d_3 (NT- d_3). The amount of rearranged

(a) Mechanism I – Simple reversible norbornenyl- and nortricyclyl radical isomerizations.



(b) Mechanism II – Complex reversible norbornenyl- and nortricyclyl radical isomerizations with crossed product formation.

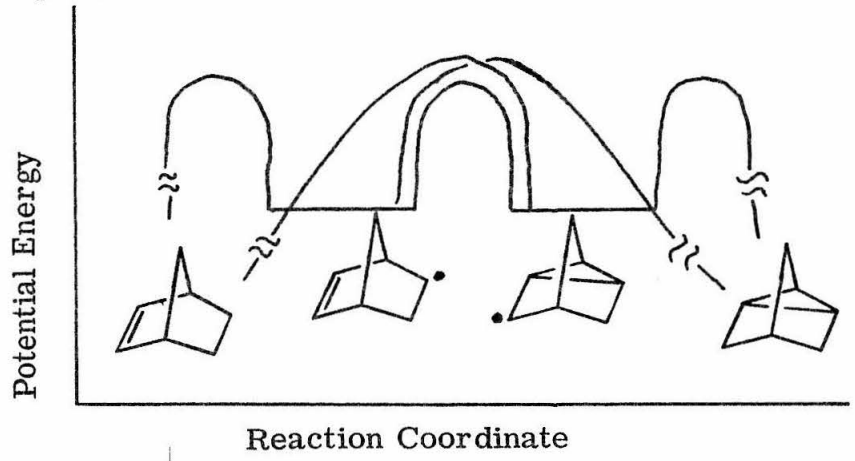
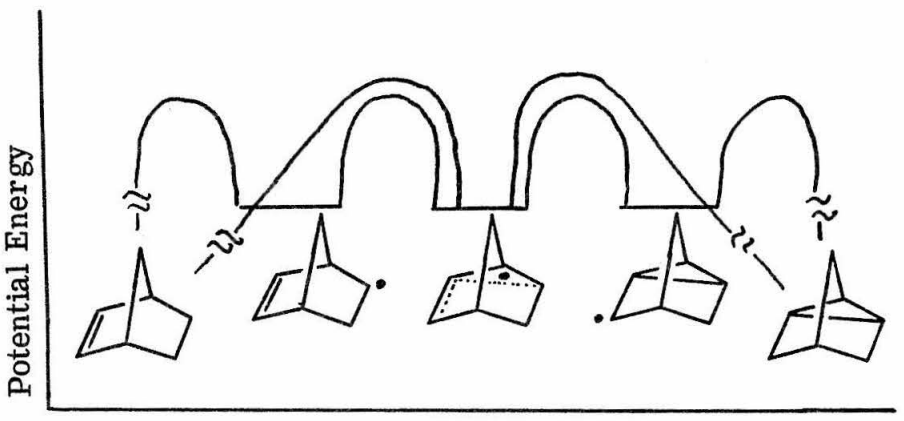


Figure 4. A Schematic Energy Diagram Comparing Mechanisms.*

(c) Mechanism III – Bridged radical participation.



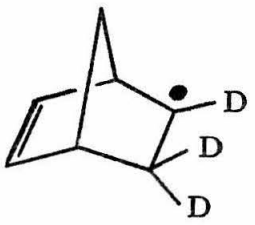
*Figures 4a-c are schematic representations only, and are not intended to show the correct relative potential energies along the reaction coordinate.

product (NB_r), will depend upon the rate at which the initially-generated radical (XXV) goes through a transition state, or an intermediate in which the C_3–C_4 and C_3–C_5 bonds are chemically equivalent.

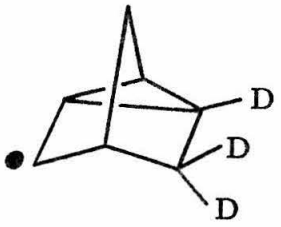
It is obviously important to know whether the 2-nortricyclyl-5, 6, 6-d_3 radical (XXVI) would be expected to have chemically-equivalent C_3–C_4 and C_3–C_5 bonds. To do so would require that this intermediate adopt a "bisected" geometry. Because this "bisected" geometry is the preferred geometry in simpler cyclopropylcarbinyl free radicals discussed earlier, it seems reasonable to expect a similar geometry in the nortricyclyl free radical unless evidence to the contrary arises. It is certainly possible that this expectation could prove to be incorrect, however.

Then in an isomerization of the intermediates which goes through a nortricyclyl free radical, it is expected that reopening of (XXVI) would occur equally in two ways, except for secondary deuterium isotope effects, to produce equal amounts of the 5-norbornenyl-5, 6, 6-d_3 radical (XXV) and the 5-norbornenyl-1, 7, 7-d_3 radical (XXVII).

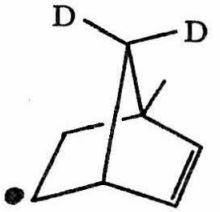
If the isomerization of (XXV) goes through a "bridged" intermediate, there exist two possibilities. The "bridged" intermediate might have either chemically-equivalent or chemically-nonequivalent C_3–C_4 and C_3–C_5 bonds. In the former case, it would behave like the presumably "bisected" nortricyclyl radical in that it would lose its stereochemistry and produce equal amounts of both (NB_u) and (NB_r).



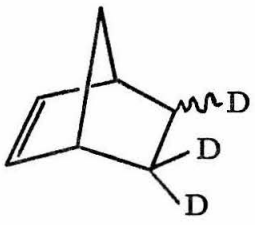
XXV



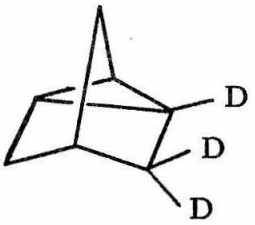
XXVI



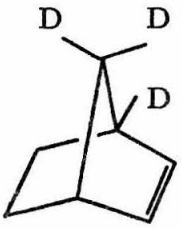
XXVII



NB_u



$NT\text{-}d_3$



NB_r

In the latter case, however, it should preserve its stereochemistry, and produce only (NB_u).

Kinetic equations enable us to predict the extent of rearrangement expected on the basis of the different postulated mechanisms, and symmetries of the intermediates. The predicted ratios of unrearranged trideuterionorbornene (NB_u) to rearranged trideuterionorbornene (NB_r) can be compared to the experimentally observed

ratios, to determine which mechanisms or intermediates are tenable.

If endo- and exo-5-bromonorbornene and 2-bromonortricyclene are reduced with tri-n-butyltin deuteride, there will be a primary deuterium isotope effect on the abstraction reactions of the intermediates. In the reduction of endo-5-bromonorbornene-5, 6, 6-d_3, there will be secondary deuterium isotope effects possible in both the isomerizations of the intermediates, and in the abstraction reactions of the intermediates. From the magnitude and direction of these isotope effects, we can speculate about the geometry and orbital hybridization at the free-radical center in some of the transition states and intermediates.

Section II. RESULTS AND DISCUSSION

Part 1. The Ratio of Norbornene to Nortricyclene as a Function of the Concentration of the Hydrogen Donor in the Free-Radical Reductions of endo- and exo-5-Bromonorbornene and 2-Bromonortricyclene with Tri-n-butyltin Hydride

Although it is possible to postulate many possible intermediates and mechanisms in the free-radical reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride, this part of the thesis is concerned with trying to differentiate between three possible mechanisms.

Mechanism I: The norbornenyl- and nortricyclyl free radicals are the only intermediates present, and they undergo a reversible isomerization, each to the other. All norbornene is produced exclusively from the norbornenyl free radical, and all nortricyclene is produced exclusively from the nortricyclyl free radical.

Mechanism II: The norbornenyl- and nortricyclyl free radicals are the only intermediates present, and they undergo a reversible isomerization, each to the other, but "crossed" products are formed. That is, some norbornene arises from the nortricyclyl free radical, and/or nortricyclene arises from the norbornenyl free radical.

Mechanism III: There is a "bridged" intermediate formed either irreversibly or reversibly from the norbornenyl- and nortricyclyl free radicals. This intermediate must form products to be distinguishable from Mechanism I or Mechanism II on the basis of the product ratio as a function of the concentration of tri-n-butyltin hydride. Otherwise, it would be kinetically indistinguishable from a transition state. The norbornenyl radical is assumed to produce only norbornene and the nortricyclyl radical is assumed to produce only nortricyclene, but the "bridged" radical may produce norbornene, nortricyclene, or both.

A comparison of the plots of product ratio against the concentration of tri-n-butyltin hydride in Graphs 1-8 shows that there is no obvious deviation from linearity. However, from these graphs, and from Table 6, it is obvious that there is often an appreciable difference between the experimentally observed plots, and those predicted from the data obtained in the reductions of the isomeric bromide or bromides, assuming Mechanism I. Before discussing the possibility that one of the other mechanisms might account for these differences, errors which might bring the results into agreement with Mechanism I will be discussed.

In some reactions, where the reductions were initiated by irradiating sealed, degassed tubes containing the reactants, internal standards indicated that when the tubes were opened and analyzed, the total norbornene plus nortricyclene was too low, particularly at higher

Mechanism I

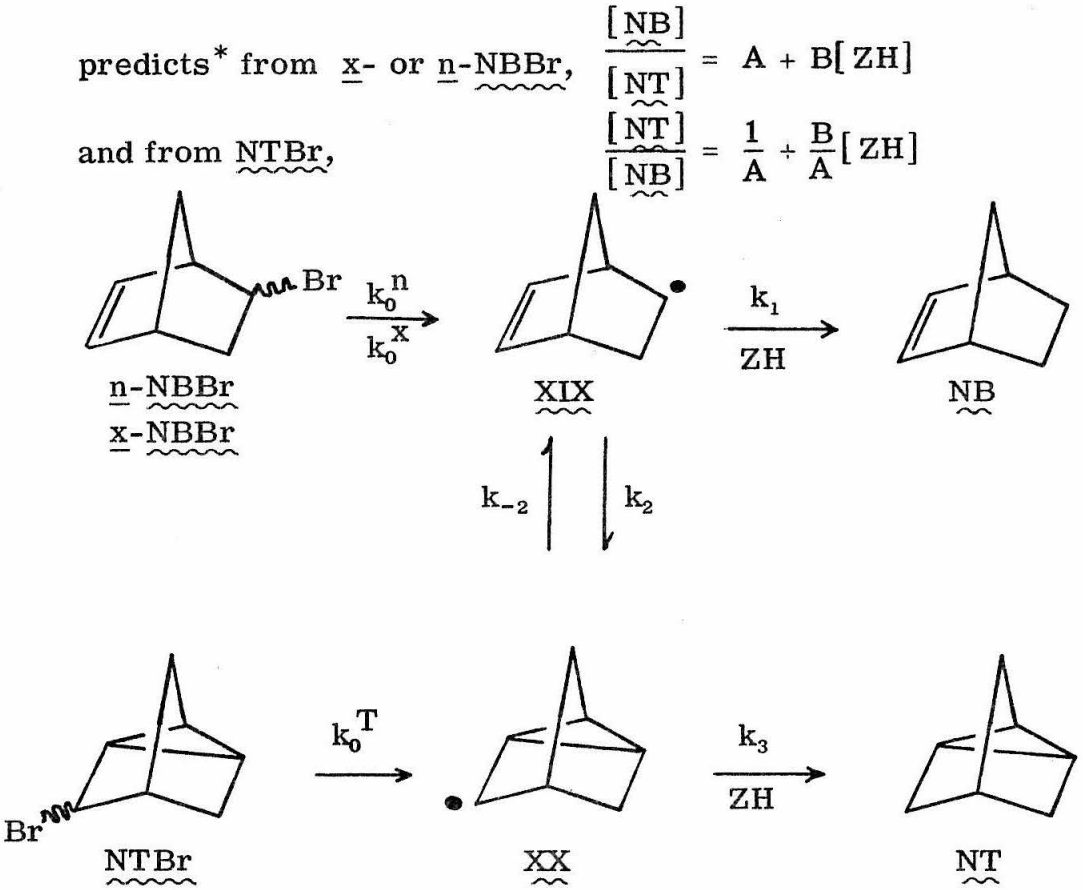


Figure 5. Reversible Isomerization of the Norbornenyl- and Nortricyclyl Free Radicals with no "crossed" Product Formation.

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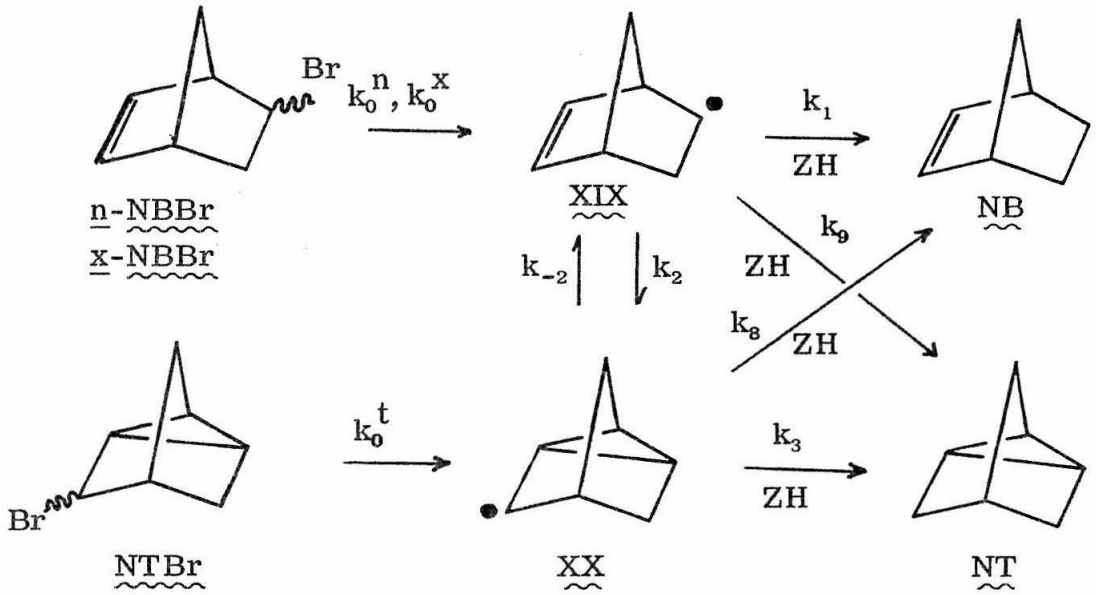
*Equations (A. I. 6) and (A. I. 7) in Appendix I.

Mechanism II

A. $k_9 = 0$

B. $k_8 = 0$



Predicted ratios* of NB to NT are not simple funtions of the concentration of hydrogen donor from both n- or x-NBBr and NTBr.

Figure 6. Reversible Isomerization of the Norbornenyl- and Nortricyclyl Free Radicals with Crossed Product Formation.

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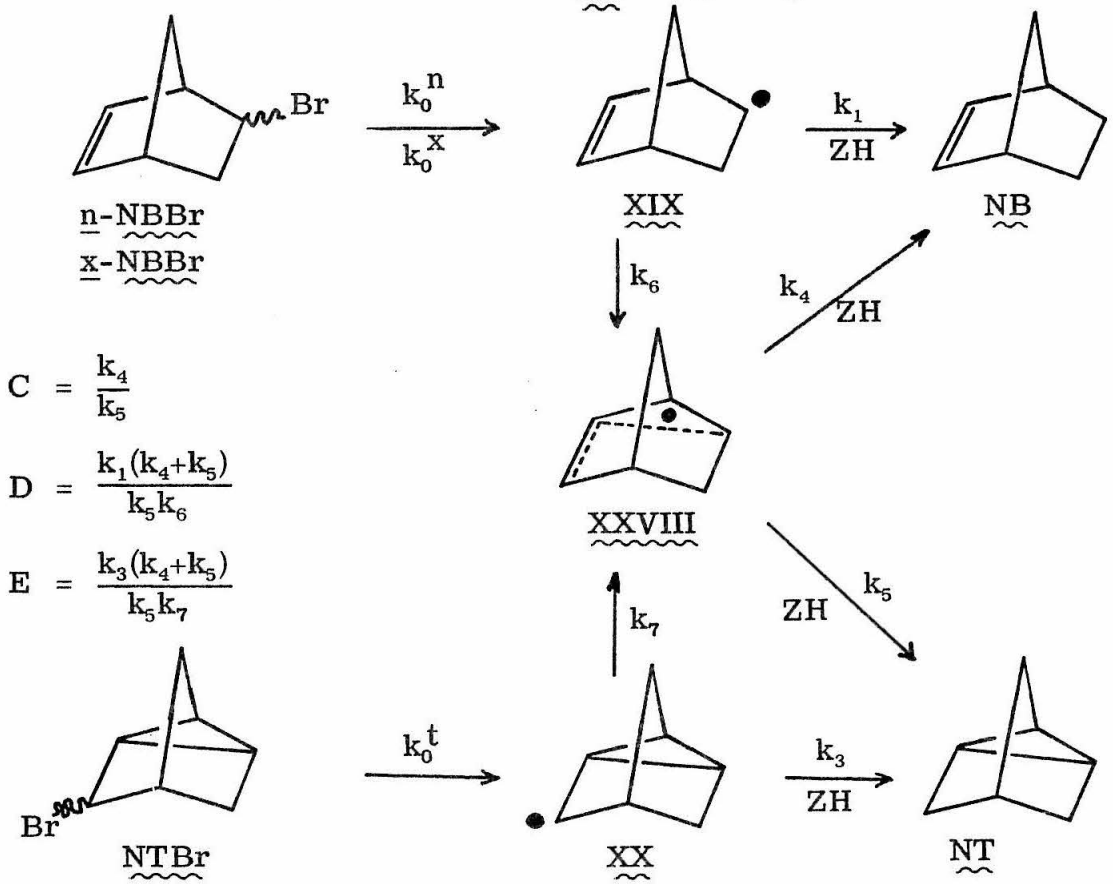
*Equations (A. II. 6), (A. II. 7), (A. II. 10), and (A. II. 11) in Appendix II. It has been assumed for calculations that either $k_8 = 0$ or $k_9 = 0$ to get workable equations.

Mechanism III

A. Irreversible bridged radical formation predicts, *

from x- or n-NBBr $\quad \frac{NB}{NT} = C + D[ZH]$

from NTBr $\quad \frac{NT}{NB} = \frac{1}{C} + \frac{E}{C}[ZH]$



$C = \frac{k_4}{k_5}$

$D = \frac{k_1(k_4+k_5)}{k_5 k_6}$

$E = \frac{k_3(k_4+k_5)}{k_5 k_7}$

For D = E, $\frac{k_1}{k_3} = \frac{k_6}{k_7}$ then it predicts the same as Mechanism I.

Figure 7. Irreversible Isomerization of the Norbornenyl- and Nortricyclyl Free Radicals to a Bridged Intermediate.

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* Equations (A. III. 6) and (A. III. 7) in Appendix III.

Mechanism III

B. Reversible bridged radical formation predicts,* from either bromide, a non-linear plot of product ratio against hydride donor concentration should result.

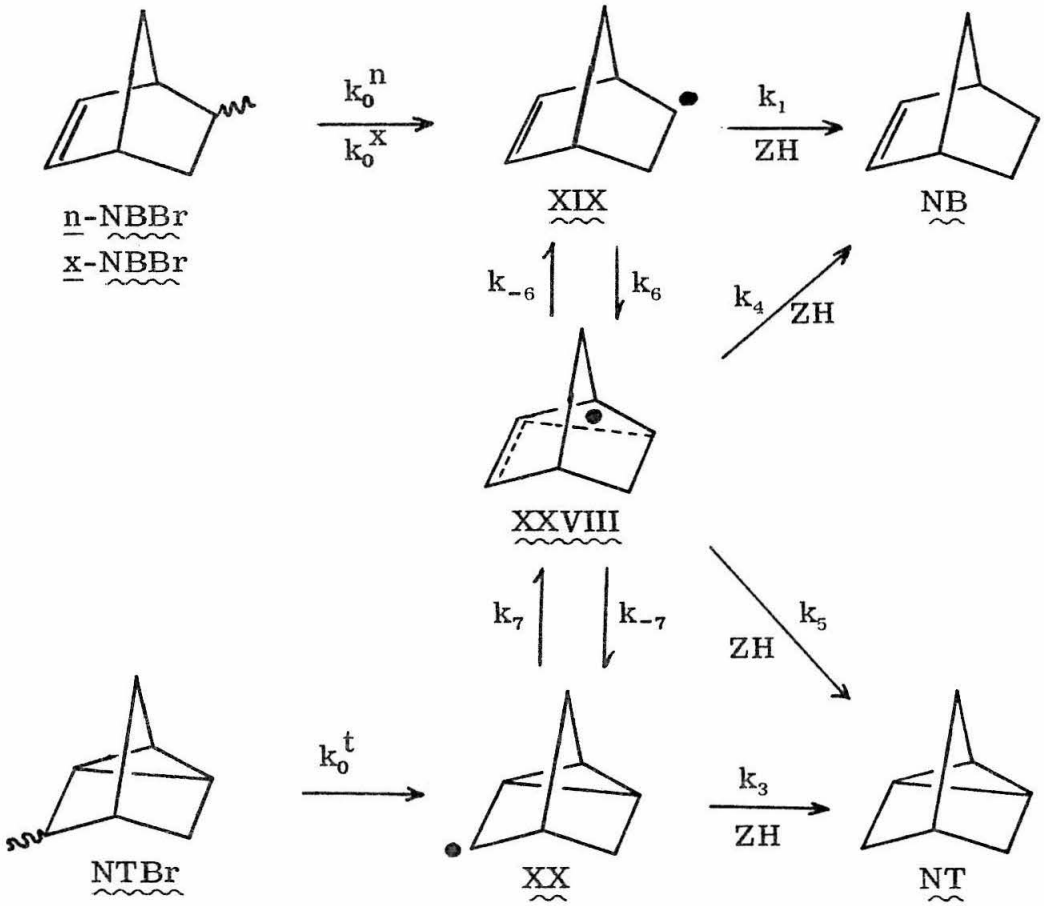

Figure 8. Reversible Isomerization of the Norbornenyl- and Nortricyclyl Free Radicals through a Bridged Intermediate.

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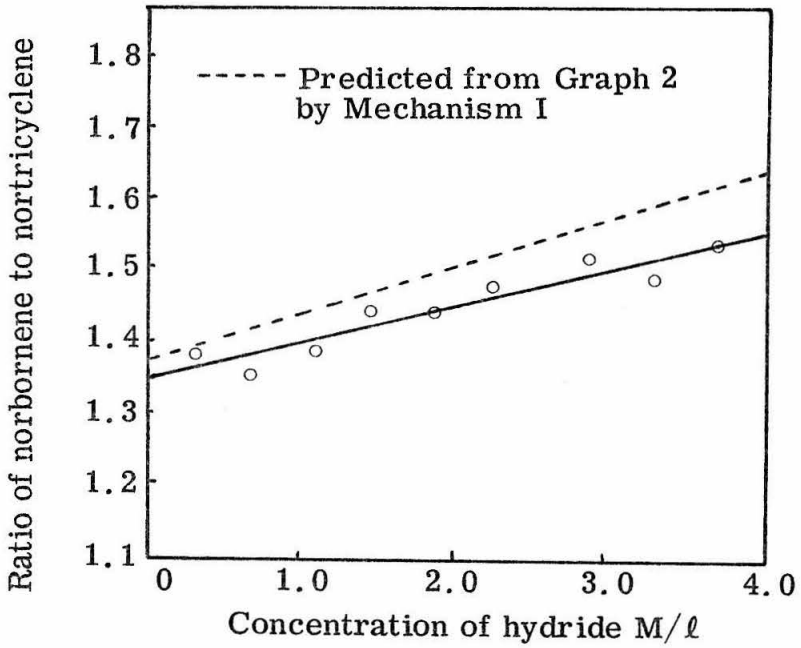
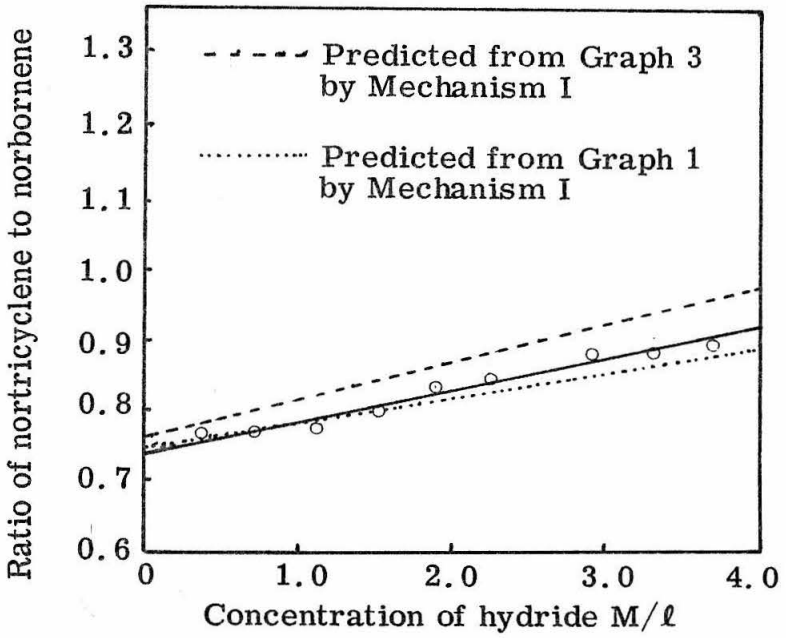
*Equations (A. III. 27) and (A. III. 29) in Appendix III.

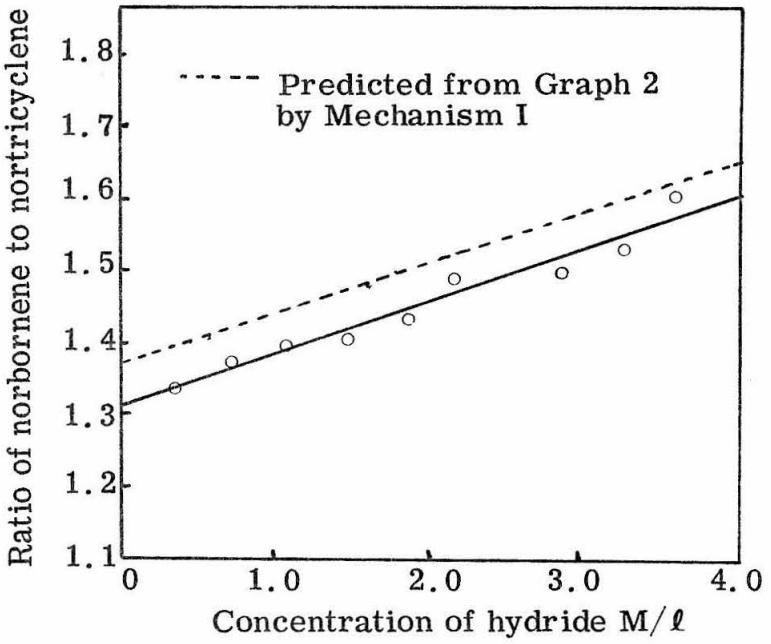
Graph 1. The reduction of endo-5-bromonorbornene with tri-n-butyltin hydride at 22°.
Product ratio versus donor concentration



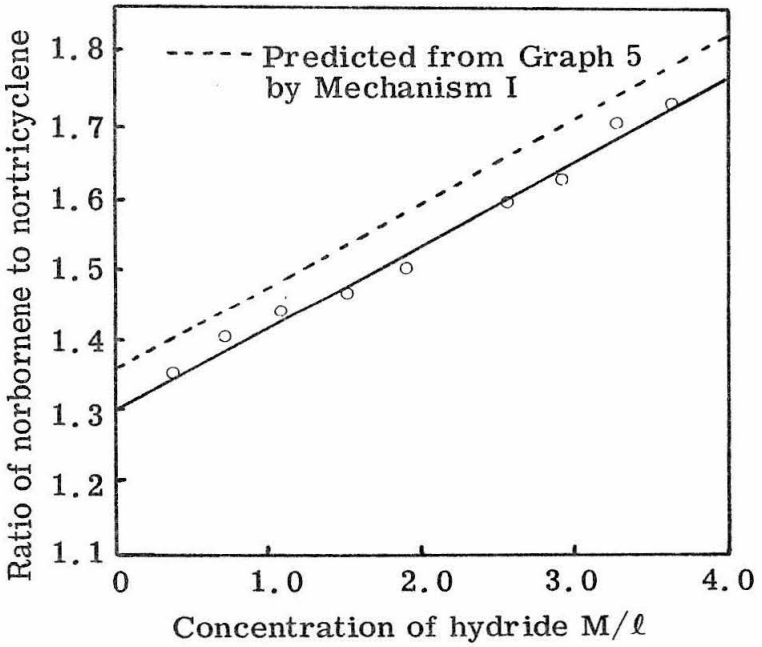
Graph 2. The reduction of 2-bromonortricyclene with tri-n-butyltin hydride at 22°.
Product ratio versus donor concentration



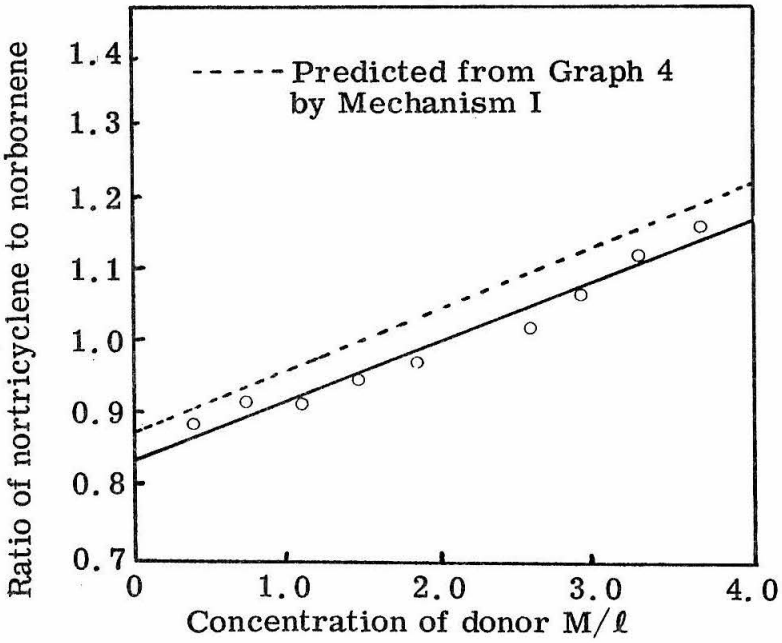
Graph 3. The reduction of exo-5-bromonorbornene with tri-n-butyltin hydride at 22°.
Product ratio versus donor concentration



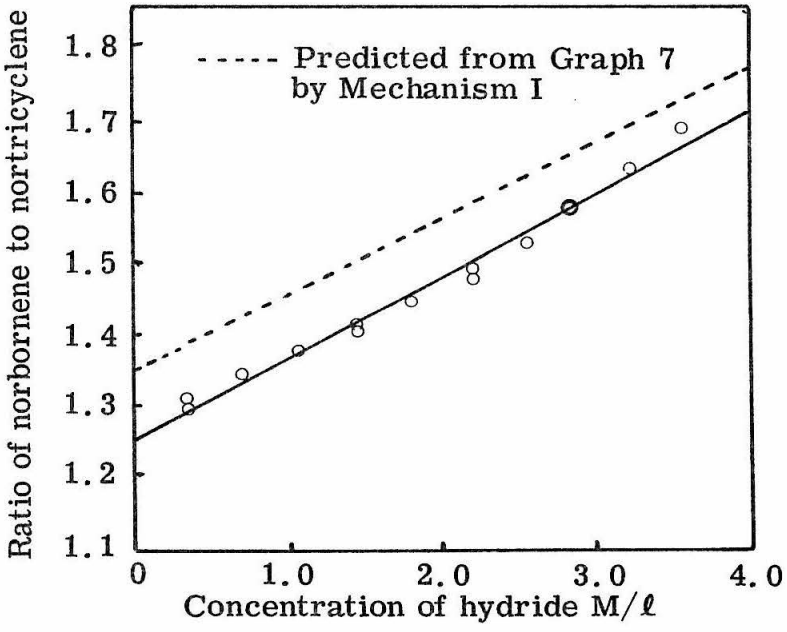
Graph 4. The reduction of endo-5-bromonorbornene with tri-n-butyltin hydride at -5°.
Product ratio versus donor concentration



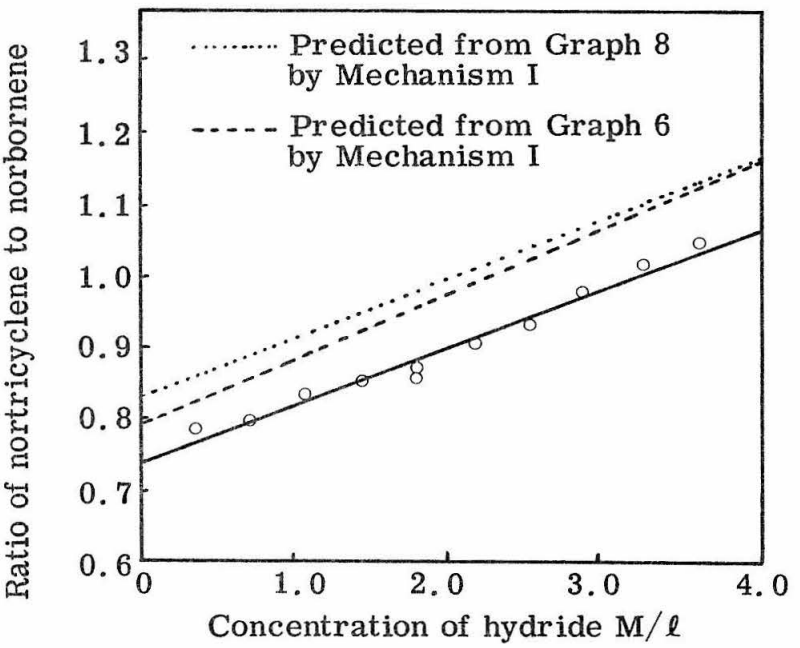
Graph 5. The reduction of 2-bromonortricyclene with tri-n-butyltin hydride at -5°.
Product ratio versus donor concentration



Graph 6. The reduction of endo-5-bromonorbornene with tri-n-butyltin hydride at -10°.
Product ratio versus donor concentration



Graph 7. The reduction of 2-bromonortricyclene with tri-n-butyltin hydride at -10°.
Product ratio versus donor concentration



Graph 8. The reduction of exo-5-bromonorbornene with tri-n-butyltin hydride at -8°.
Product ratio versus donor concentration

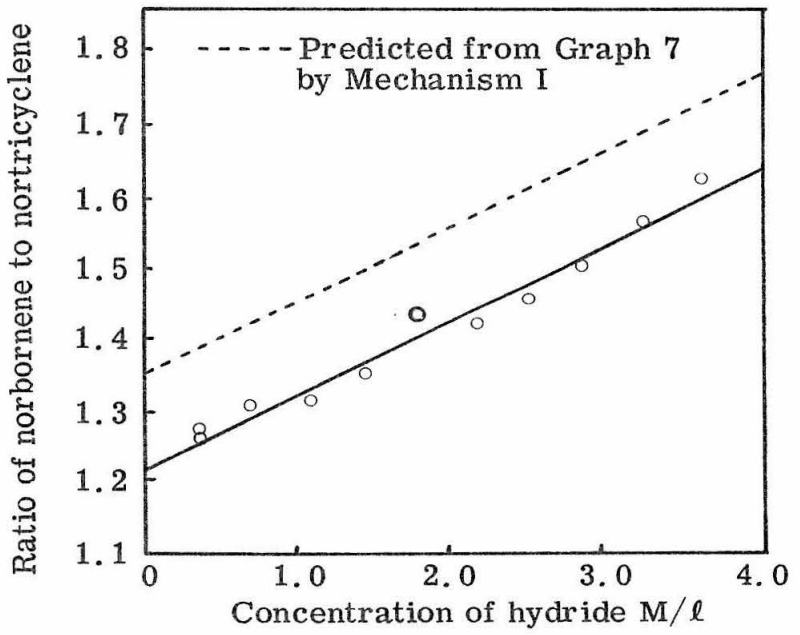


Table 6. Product Ratio as a Function of Hydrogen Donor Concentration in the Reductions of endo- and exo-5-Bromonorbornene and 2-Bromonortricyclene with Tri-n-butyltin Hydride.[a] Least-Squares Fit.

Bromide	temp. °C	observed slope[d] ℓ/M	observed intercept[b]	predicted[c] slope ℓ/M	predicted[c] intercept[b]
n-NBBr[e,g]	22 ±1	0.047 ±0.008	1.349	0.066	1.373
NTBr[e]	22 ±1	0.048 ±0.004	0.728	0.035 0.055	0.742[h] 0.763[j]
x-NBBr[e]	22 ±1	0.073 ±0.011	1.31	0.066	1.373
n-NBBr[e,g]	-4 ±1	0.077 ±0.015	1.27	0.096	1.277
NTBr[e]	-4 ±1	0.075 ±0.007	0.783	0.061	0.787
n-NBBr[e]	-5 ±1	0.116 ±0.011	1.300	0.107	1.364
NTBr[e]	-5 ±1	0.083 ±0.011	0.732	0.089	0.769
n-NBBr[f]	-9 ±2	0.113 -----	1.265	-----	-----
n-NBBr[f]	-10 ±1	0.117 ±0.005	1.257	0.110	1.349
NTBr[f]	-10 ±1	0.081 ±0.007	0.741	0.087 0.093	0.823[m] 0.795[h]
x-NBBr[f]	-8 ±1	0.106 ±0.011	1.213	0.110	1.349[k]

Table 6. (Cont'd)

[a] See Graphs 1-8 for plotted examples.

[b] The intercept is the ratio NB/NT from endo- or exo-5-bromonorbornene, and the reciprocal, NT/NB from 2-bromonortricyclene.

[c] Predicted by Mechanism I, equations (A.I. 6) and (A.I. 7).

[d] The error in the slope is the 90% confidence limit.

[e] Reductions done in sealed, degassed tubes.

[f] Reductions done in tubes flushed with nitrogen and capped at atmospheric pressure.

[g] Irradiated longer than necessary, some norbornene probably lost through hydrostannation.

[h] Predicted from n-NBBr.

[j] Predicted from x-NBBr.

[k] Predicted from NTBr at -10°, ignoring 2° difference.

[m] Predicted from x-NBBr at -8°, ignoring 2° difference.

concentrations of tri-n-butyltin hydride, although no unreacted bromide remained. It is believed that in these cases, a substantial amount of norbornene has been lost through hydrostannation, because the samples have been irradiated for much longer than necessary to complete the reductions of the bromides. Because hydrostannation should be approximately first order in tri-n-butyltin hydride, the loss of norbornene should be greatest at the highest concentration of the hydrogen donor, if irradiation times are identical. The result should be a plot with a slope which is too low in the reductions of endo- and exo-5-bromonorbornene, and too high in the reduction of 2-bromonortricyclene (see Graph 1, for example).

Even in the reductions where samples were analyzed as the reaction proceeded, so that they were irradiated just a sufficient time to result in nearly complete reduction of the respective bromides, there is a substantial difference between the observed and predicted plots of the product ratio as a function of the concentration of tri-n-butyltin hydride. In these plots, however, the slopes agree quite well, and the main disagreement between the observed and predicted plots appears to result from a "vertical shift" along the product-ratio axis. This "vertical shift" may result partially from non-identical vpc conditions during the analyses of the products of the reductions of the different isomeric bromides.* The ratio of norbornene to

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*See p. 136 in the Experimental Section for a more detailed discussion of vpc analyses in these reactions.

nortricyclene in standard samples does change several percent under different vpc conditions.

There is a persistent phenomenon in the "vertical shift" difference between the observed and predicted plots. The predicted plot is almost always above the observed plot. Any mechanism under consideration here would predict that the intercepts of the plots of the ratio of NB/NT as a function of the concentration of tri-n-butyltin hydride, in the reductions of the bromonorbornenes, must be the reciprocals of the intercepts of the plots of the ratio of NT/NB as a function of the concentration of tri-n-butyltin hydride in the reduction of 2-bromonortricyclene. This is obvious, because the intercepts reflect the product ratios from intermediates which are completely equilibrated. Whether the phenomenon that the predicted plot is almost always above the observed plot is just coincidental, and a result of the analytical vpc "vertical shift" error discussed on preceding pages is not known. If it is not, then it is indeed difficult to explain. It would require a mechanism in which bromonorbornenes prefer to produce nortricyclene, and bromonortricyclenes prefer to form norbornenes, relative to each other.

In considering Mechanism I, some mention should be made of the effect of errors in the slope and intercept upon the predicted values for the isomeric bromides. For example, if there should be a five per cent change in the vpc sensitivity ratio for norbornene and nortricyclene (e. g., if the injection port temperature decreased, resulting in a slight overlap of the tail of one peak with the other),

then all the points on the plot would be shifted by five per cent. This would then change both the slope and the intercept by five per cent. It can be seen from equations (A. I. 6) and (A. I. 7) that the predicted slope for the bromide or bromides of opposite structure will not be changed, but the predicted intercept will be changed by the five per cent factor. It should also be mentioned that a very few per cent difference in the predicted and observed intercepts is very prominent, but that a ten per cent difference in the predicted and observed slopes appears to be small, and is usually within the ninety per cent confidence limits of the slope of the least-squares best fit line used in the plots.

From the preceding discussion, it is apparent that the experimental results are somewhat uncertain. However, within several per cent, they can be accounted for by Mechanism I, in which only the norbornenyl- and nortricyclyl free radicals are present, and each produces only the product of the same structure. Also, the differences between observed and predicted results can be reasonably attributed to errors. However, the uncertainty in the results and possible errors increases the extent to which the results can also be accounted for by other mechanisms.

Assuming Mechanism IIA, with the nortricyclyl free radical producing twenty per cent as much norbornene as nortricyclene, the slope of the plot of nortricyclene to norbornene, in the reduction of 2-bromonortricyclene is predicted to be about twenty per cent lower

than the slope predicted by Mechanism I.* This seems to be outside the limits of reasonable error. Similar results would be arrived at in considering Mechanism IIB, where nortricyclene would be produced from the norbornenyl free radical. However, no conclusion can be drawn about the possibility of just a few per cent of "crossed" product formation from either of the radicals.

Assuming Mechanism IIIA, in which either the norbornenyl- or nortricyclyl free radical isomerizes irreversibly to a "bridged" intermediate, the slopes of the plots obtained from the reductions of the bromonorbornenes should have a different relationship to the slope of the plot obtained from the reduction of 2-bromonortricyclene than predicted by Mechanism I. However, as the ratio k_1/k_3 becomes equal to the ratio k_6/k_7, the relationships between the plots become identical to those in Mechanism I. Therefore, all we can say about Mechanism IIIA, from these product ratio plots, is that k_1/k_3 is not greatly different from k_6/k_7 if the reaction goes by Mechanism IIIA.

From Mechanism IIIB, where the formation of the "bridged" radical is reversible, equations (A. III. 27) and (A. III. 29) show that there should be a nonlinear relationship between the product ratio and the concentration of tri-n-butyltin hydride. However, unless there is

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*This is done by substituting the numerical values obtained for the slope and intercept from the observed plot of NB/NT as a function of the concentration of tri-n-butyltin hydride into equation (A. II. 6). These values are then put into equation (A. II. 7), and points calculated for several concentrations of tri-n-butyltin hydride. This calculated plot is then compared to the observed plot for the reduction of 2-bromonortricyclene, and the predicted plot based on Mechanism I.

substantial product formation from the "bridged" intermediate, the nonlinearity of the plot would not be great, and the precision of the experimental plots would probably be insufficient to detect it. No attempt was made to fit the points to a nonlinear equation, because none of the plots shows any significant deviation from linearity. As in Mechanism IIIA, increasing inequality between the ratios k_1/k_3 and k_6/k_7 would lead to increasing disagreement between the experimentally observed plots and those predicted by Mechanism I. Therefore, little can be said about excluding the possibility of even a considerable amount of product formation from a "bridged" intermediate in Mechanism IIIB from the product ratio plots.

Part 2. The Ratio of Norbornene-d_1 to Nortricyclene-d_1 as a Function of the Deuterium Donor Concentration in the Free-Radical Reductions of endo- and exo-5-Bromonorbornene and 2-Bromonortricyclene with Tri-n-butyltin Deuteride, and Primary Kinetic Deuterium Isotope Effects.

When endo- and exo-5-bromonorbornene and 2-bromonortricyclene are reduced with tri-n-butyltin deuteride, the abstraction reactions of the intermediates will have a primary deuterium isotope effect, relative to the analogous abstractions of hydrogen from tri-n-butyltin hydride. Carlsson and Ingold found this kinetic isotope effect to be 2.7 (k_H/k_D), for the abstractions of hydrogen or deuterium by the cyclohexyl radical from tri-n-butyltin hydride or tri-n-butyltin deuteride, respectively (46). In the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin deuteride, an isotope effect even close to this value of 2.7 should substantially alter the plots of product ratio as a function of donor concentration, because the abstraction reactions will be slowed considerably, thereby allowing more time for the intermediate radicals to equilibrate, before forming products.

From equations (A.I.10) and (A.I.11), in Appendix I, it can be seen that Mechanism I predicts that the plots of the ratio of norbornene to nortricyclene, in the reductions of endo- and exo-5-bromonorbornene, and the ratio of nortricyclene to norbornene in the reduction of 2-bromonortricyclene, as a function of the concentration

of the deuterium donor, tri-n-butyltin deuteride will be substantially different from those obtained in analogous reductions with tri-n-butyltin hydride. The slopes will be changed by a factor equal to the primary deuterium isotope effect on the abstraction reaction of the norbornenyl radical in the reductions of the bromonorbornenes, and the primary deuterium isotope effect on the abstraction reaction of the norbornenyl free radical in the reduction of 2-bromonortricyclene. The intercept in either case will be changed by a factor equal to the ratio of the kinetic isotope effects for the abstraction reactions of the norbornenyl- and nortricyclyl free radicals.

From equations (A. II. 8) and (A. II. 9), Mechanism II predicts that both the slopes and intercepts of the product ratio plots will be changed by factors dependent upon the primary deuterium isotope effects for the formation of norbornene from the norbornenyl free radical, the formation of nortricyclene from the nortricyclyl free radical, and the formation of the "crossed product".

For Mechanism IIIA, where a "bridged" radical is formed irreversibly, equations (A. III. 8) and (A. III. 9) show that in the reductions with tri-n-butyltin deuteride, the intercepts of the plots of product ratio as a function of donor concentration should be changed by a factor equal to the ratio of the primary deuterium isotope effects in the abstraction reactions leading to norbornene and nortricyclene from the "bridged" intermediate. The slopes of the plots should be changed by a more complex factor including the isotope effects for all the abstraction reactions. For Mechanism IIIB, both the slopes and

intercepts of the plots of the product ratio as a function of the donor concentration will be changed by complex factors involving the primary deuterium isotope effects for all four abstraction reactions, when tri-n-butyltin deuteride is the donor instead of tri-n-butyltin hydride.

It is apparent from Graphs 9-11, that the intercepts for the plots of product ratio as a function of the donor concentration change little in the reductions of any of the three isomeric bromides when tri-n-butyltin deuteride is used instead of tri-n-butyltin hydride.* However, the slopes are reduced by a substantial factor. From mass spectra of the norbornene and nortricyclene produced in a mixture of tri-n-butyltin hydride and tri-n-butyltin deuteride, accurate values for the primary kinetic deuterium isotope effect in the abstraction reactions leading to norbornene and nortricyclene can be determined. Values for the primary deuterium isotope effects determined from the product ratio plots and the equations developed in the appendices can then be compared to these values determined by mass spectra.

Table 7 lists the primary deuterium isotope effects determined by mass spectra. Table 8 lists the primary deuterium isotope effects calculated from the slopes of the plots obtained in the reductions with

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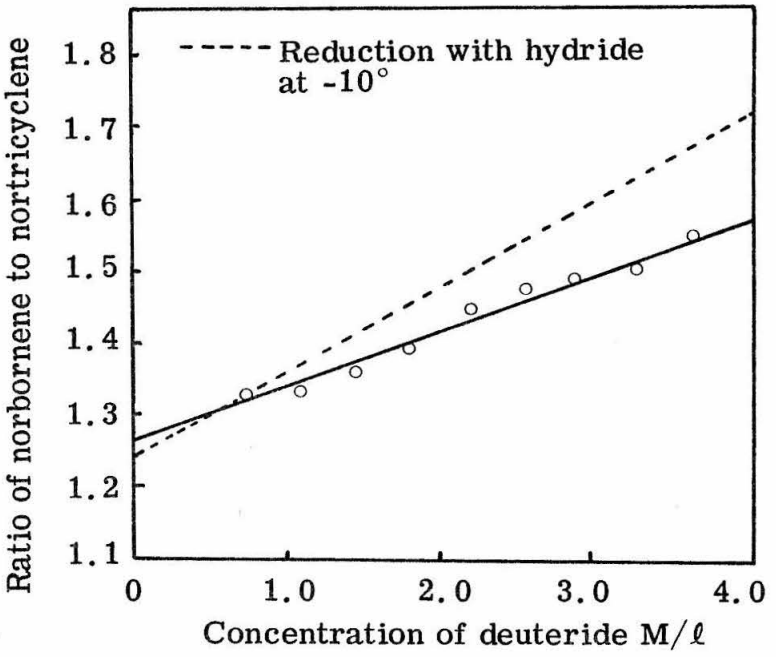
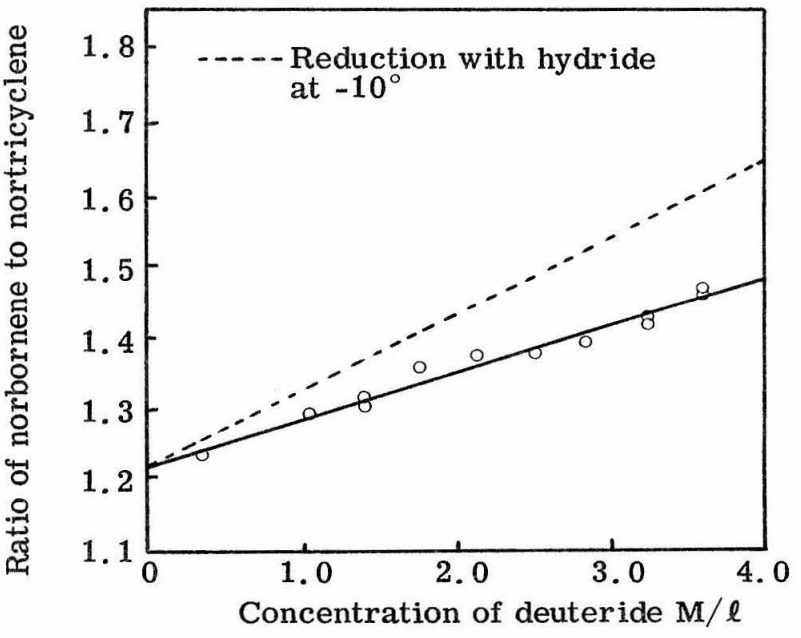
*The reductions of a given bromide with both tri-n-butyltin hydride and tri-n-butyltin deuteride were conducted simultaneously, under identical conditions, and samples from both reductions were analyzed alternately, under identical vpc conditions. Therefore, relatively, the plots for the reductions with tri-n-butyltin hydride and tri-n-butyltin deuteride should be very accurate. This procedure eliminates the problem of changes in the relative sensitivity of the vpc towards the two products, which was discussed earlier (see p. 64).

Graph 9. The reduction of endo-5-bromonorbornene with tri-n-butyltin deuteride at -10°.
Product ratio versus donor concentration



Graph 10. The reduction of exo-5-bromonorbornene with tri-n-butyltin deuteride at -8°.
Product ratio versus donor concentration



Graph 11. The reduction of 2-bromonortricyclene with tri-n-butyltin deuteride at -10°.

Product ratio versus donor concentration

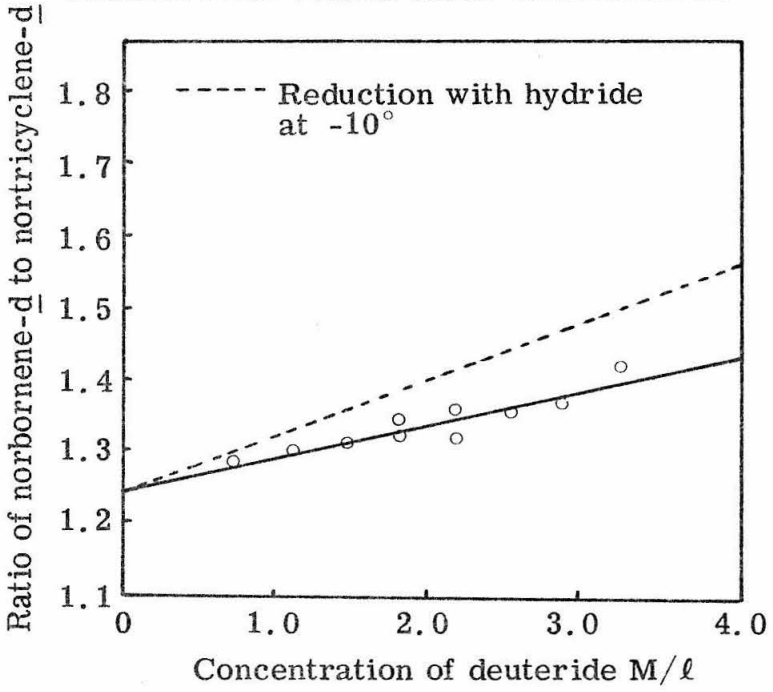


Table 7. Mass Spectral Determination of the Kinetic Primary Deuterium Isotope Effect in the Abstraction Reactions at -10° Leading to Norbornene and Nortricyclene.[a]

Bromide[b] reduced	Donor[c] concentration M/ℓ	Ratio[d] NB/NB-d_1	k_H/k_D[e, f]
n-NBBr	1.20	1.045 ± 0.5	2.09 ± 0.05
n-NBBr	3.70	0.995	1.99 ± 0.05
x-NBBr	1.20	1.055	2.11 ± 0.1
x-NBBr	3.70	1.06	2.12 ± 0.05
NTBr	1.20	1.16	2.32 ± 0.2
NTBr	3.70	1.08	2.16 ± 0.05
		Approximate mean	2.1

Bromide[b] reduced	Donor[c] concentration M/ℓ	Ratio[d] NT/NT-d_1	k_H/k_D[f, g]
n-NBBr	1.20	1.245	2.49 ± 0.2
n-NBBr	3.70	1.125	2.25 ± 0.05
x-NBBr	1.20	1.175	2.35 ± 0.1
x-NBBr	3.70	1.095	2.19 ± 0.15
NTBr	1.20	1.165	2.33 ± 0.2
NTBr	3.70	1.175	2.35 ± 0.05
		Approximate mean	2.3

Table 7. (Cont'd)

[a] The donor is a 2:1 v/v solution of tri-n-butyltin deuteride and tri-n-butyltin hydride.

[b] The molar ratio of donor to bromide is 14.5 for the reactions at 1.20 M donor concentration, and 51.5 for the reactions at 3.70 M donor concentration.

[c] The solvent is toluene, which does not compete as a hydrogen donor under the reaction conditions.

[d] The ratios of undeuterated and monodeuterated products were determined from mass spectra of the isolated products.

[e] The isotope effect in the abstraction reaction leading to norbornene.

[f] Errors in the isotope effects are approximate, and are based on the probable accuracies of the mass spectra.

[g] The isotope effect in the abstraction reaction leading to nortricyclene.

Table 8. The Kinetic Primary Deuterium Isotope Effect in the Abstraction Reactions Leading to Norbornene and Nortricyclene Determined from Product Ratio Plots.[a]

Bromide reduced	Reduction temperature	Donor	Slope[b, c] 1/M	k_H/k_D[d, e]
n-NBBr	-10°	$(n\text{-}C_4H_9)_3SnH$	0.117 ± 0.005	1.56
n-NBBr	-10°	$(n\text{-}C_4H_9)_3SnD$	0.075 ± 0.0075	
x-NBBr	-8°	$(n\text{-}C_4H_9)_3SnH$	0.106 ± 0.011	1.58
x-NBBr	-8°	$(n\text{-}C_4H_9)_3SnD$	0.067 ± 0.007	

Bromide reduced	Reduction temperature	Donor	Slope[c, f] 1/M	k_H/k_D[d, g]
NTBr	-10°	$(n\text{-}C_4H_9)_3SnH$	0.081 ± 0.007	1.72
NTBr	-10°	$(n\text{-}C_4H_9)_3SnD$	0.047 ± 0.011	

[a] From the slopes of the plots of the product ratio as a function of the concentration of tri-n-butyltin hydride or tri-n-butyltin deuteride, and assuming Mechanism I, equations (A. I. 10) and (A. I. 11) can be used to determine primary deuterium isotope effects in the abstraction reactions leading to norbornene and nortricyclene.

[b] The slope of the plot of the ratio of norbornene to nortricyclene as a function of the concentration of tri-n-butyltin hydride or tri-n-butyltin deuteride.

Table 8. (Cont'd)

[c] Errors in the slopes are statistical 90% confidence limits.

[d] The isotope effect is the ratio of the slope for the reduction with tri-n-butyltin hydride to that for the reduction with tri-n-butyltin deuteride.

[e] The isotope effect in the abstraction reaction leading to norbornene.

[f] The slope of the plot of the ratio of nortricyclene to norbornene as a function of the concentration of tri-n-butyltin hydride or tri-n-butyltin deuteride.

[g] The isotope effect in the abstraction reaction leading to nortricyclene.

tri-n-butyltin hydride and tri-n-butyltin deuteride using equations (A. I. 10) and (A. I. 11), assuming that the reactions go via Mechanism I.

The primary kinetic deuterium isotope effects, k_H/k_D, of about 2.1 and 2.3, determined from mass spectra, for the abstraction reactions leading to norbornene and nortricyclene, respectively, are only slightly lower than the value of 2.7 determined by Carlsson and Ingold for the abstraction reaction of the cyclohexyl radical from the same donors, tri-n-butyltin hydride and tri-n-butyltin deuteride (46). Unfortunately, there are no other available data on the primary kinetic deuterium isotope effects for free-radical abstractions from organotin hydrides and deuterides. Normal primary kinetic deuterium isotope effects for the abstraction of deuterium from various donors by various free radicals are from just over 1.0 to about 10.0 (49). Generally, the isotope effect increases with increasing activation energy for the abstraction reaction (50). Superficially, at least, this can be simply explained. Hammond's Postulate (51) predicts that as the activation energy decreases, the transition state more closely resembles the reactants. Therefore, in an abstraction reaction, the lower the activation energy, the less the donor-hydrogen or donor-deuterium bonds have been stretched in the transition state. Therefore, the primary kinetic deuterium isotope effect should decrease with decreasing activation energy for the abstraction reaction.

The activation energies for the abstraction of hydrogen or deuterium from tri-n-butyltin hydride or tri-n-butyltin deuteride are a very few kcal/mole for the reactions leading to norbornene and nortricyclene. Also, the activation energy for formation of nortricyclene by the nortricyclyl free radical is believed higher than the activation energy for the formation of norbornene from the norbornenyl free radical, * so the values of about 2.1 and 2.3 for the abstraction reactions leading to norbornene and nortricyclene, respectively, are of reasonable magnitude for a mechanism based on formation of norbornene from the norbornenyl free radical, and nortricyclene from the nortricyclyl free radical.

Probably the most important observation concerning the primary kinetic deuterium isotope effects in Table 7 is that there is no discernible change in the values when the concentration of the donor is changed from 3.70 M to 1.20 M. The implications of this observation are very important. Either nearly all the norbornene must come from a single intermediate, and nearly all the nortricyclene come from a single intermediate, or else the primary kinetic deuterium isotope effects in the abstractions by more than one intermediate leading to a single product must be almost identical. An obvious extension of this inference is that in Mechanism III, where a "bridged"

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*See p. 116, where calculations evolve activation energies of approximately 3.0 kcal/mole for formation of norbornene from the norbornenyl free radical and 3.5 kcal/mole for the formation of nortricyclene from the nortricyclyl free radical, in the abstractions of hydrogen from tri-n-butyltin hydride.

intermediate contributes to the formation of both norbornene and nortricyclene, the ratio of the primary kinetic deuterium isotope effects in the formation of norbornene and nortricyclene from the "bridged" intermediate must be approximately equal to the ratio of the isotope effects in the formation of norbornene and nortricyclene from the norbornenyl- and nortricyclyl free radicals, respectively.

Unfortunately, there is no precedent for the primary kinetic deuterium isotope effects one might expect for the abstraction reactions of a "bridged" radical which has two positions capable of abstracting hydrogen or deuterium from a donor to yield two different products.

Some ad hoc reasoning may be applied to determine whether it is reasonable to expect a "bridged" radical to have primary kinetic deuterium isotope effects essentially equal to the primary kinetic deuterium isotope effects in the abstraction reactions of either the norbornenyl- or nortricyclyl free radicals which lead to the same products as the abstraction reactions of either the norbornenyl- or nortricyclyl free radicals which lead to the same products as the abstractions by the "bridged" intermediate. In Mechanism IIIA, where the "bridged" radical is formed irreversibly, the irreversibility implies that the potential energy of the "bridged" intermediate is substantially below that of the norbornenyl- or nortricyclyl free radicals. It is reasonable, therefore, to expect the activation energy for hydrogen abstraction by the "bridged" intermediate to be higher than the activation energies for the abstraction reactions of

the norbornenyl- and nortricyclyl free radicals. This effect would be manifested by a change in the experimentally determined isotope effects in Table 7 with changes in the concentration of the donor, because as the concentration of the donor decreases, more of the product is being formed from the "bridged" intermediate, and less from "trapping" of the initially generated radical before it isomerizes to the "bridged" intermediate. To within small error limits, Table 7 shows the primary kinetic deuterium isotope effects leading to norbornene and nortricyclene to be invariant with concentration. Mechanism IIIA, where the "bridged" radical is formed irreversibly, therefore seems untenable.

In Mechanism IIIB, the "bridged" intermediate should be of comparable potential energy to the norbornenyl- and nortricyclyl free radicals. It is quite probable, therefore, that the primary kinetic deuterium isotope effects in the abstraction reactions of the "bridged" intermediate would be comparable to those of the norbornenyl- and nortricyclyl free radicals, because activation energies for these processes are likely to be similar. However, from reasoning analogous to that applied to the preceding discussion of Mechanism IIIA, we can surmise that if a large percentage of either product were formed from the "bridged" intermediate, then differences between the isotope effects for the "bridged" radical and the norbornenyl- and nortricyclyl free radicals would be likely. However, in the absence of a very large difference between the primary kinetic deuterium isotope effects for the abstraction

reactions of the "bridged" intermediate and the norbornenyl- and nortricyclyl free radicals, we could not detect a small contribution to the products by a "bridged" intermediate in Mechanism IIIB.

Mechanism II is subject to similar arguments advanced in the discussion of Mechanisms IIIA and IIIB. Here again, there are abstraction reactions by two intermediates leading to a single product. Therefore, because the relative amounts of the single product formed from the two intermediates changes with the donor concentration, a difference in the primary kinetic deuterium isotope effect for formation of that product would be expected with changes in the donor concentration. The exceptions would be if the isotope effects are nearly identical for the abstraction reactions of either intermediate which lead to the same product, or where the contribution of one of the two processes leading to the same product is very small relative to the contribution of the other.

The primary deuterium isotope effects in Table 8, calculated from the slopes of the plots of the product ratios of the reduction of n-NBBr, x-NBBr, and NTBr, assuming Mechanism I, as a function of the concentration of tri-n-butyltin hydride and tri-n-butyltin deuteride, are substantially lower than the values determined by mass spectroscopy, in Table 7. There are two possible reasons. Mechanism I may be incorrect, or the slopes of the plots of the product ratios in the reductions with tri-n-butyltin hydride and tri-n-butyltin deuteride may be incorrect.

Another problem is that the intercepts in Graphs 9-11 for the plots of product ratio as a function of the concentration of donor are identical for the reductions with both tri-n-butyltin deuteride and tri-n-butyltin hydride. From the isotope effects in Table 7, however, we would expect the intercepts of the plots of the ratio of norbornene to nortricyclene as a function of the donor concentration in the reductions of n-NBBr and x-NBBr to be higher by a factor of 2.3/2.1 (the ratio of the isotope effects in the abstractions leading to nortricyclene and norbornene, respectively) when the reducing agent is tri-n-butyltin deuteride instead of tri-n-butyltin hydride. Analogously, the intercept of the plot of the ratio of nortricyclene to norbornene as a function of the donor concentration in the reduction of NTBr should be lower by a factor of 2.1/2.3 when the reducing agent is tri-n-butyltin deuteride instead of tri-n-butyltin hydride. These factors come from substitution of the isotope effects into equations (A.I.10) and (A.I.11) assuming Mechanism I.

From preceding discussion, we have determined that if two abstraction reactions each contribute substantially to the formation of a single product, then the primary kinetic deuterium isotope effects for both abstraction reactions must be similar. By substituting isotope effects of 2.1 for any abstraction reaction leading to norbornene and 2.3 for any abstraction reaction leading to nortricyclene into appropriate equations from Appendices I-III, we can determine whether Mechanisms II or III offer better agreement with the results in Table 8 than Mechanism I does.

For Mechanism II, assuming that "crossed" product formation is limited to a maximum of 20% of the product formed from either the norbornenyl- or nortricyclyl free radical, as was inferred from previous discussion,* then equations (A. II. 8) and (A. II. 9) predict approximately the same changes in both the slopes and intercepts of the plots of the product ratio as a function of the donor concentration, when the donor is tri-n-butyltin deuteride instead of tri-n-butyltin hydride, as are predicted by Mechanism I.

Equations (A. III. 8) and (A. III. 9) for Mechanism IIIA, and equations (A. III. 27) and (A. III. 29) for Mechanism IIIB, upon substitution of isotope effects of 2. 1 and 2. 3 for abstraction reactions leading to norbornene or nortricyclene, respectively, also result in approximately the same changes in the slopes and intercepts of the plots of the product ratio as a function of the concentration of the donor, when the donor is tri-n-butyltin deuteride instead of tri-n-butyltin hydride.

The disagreement between the apparent isotope effects calculated in Table 8 and the more accurately determined values in Table 7 would appear to result from experimental errors in the plots used to calculate the values in Table 8.

Although the disagreement between the primary kinetic deuterium isotope effects in Table 8 and those determined by mass spectroscopy in Table 7 looks large, we can show that a small systemic error could readily account for the difference. The apparent errors in the intercepts are factors of less than 10% (2. 1/2. 3 or the

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*See p. 66.

reciprocal), and if the errors in the isotope effects determined by mass spectroscopy are in a direction which brings the values of 2.1 and 2.3 closer together, the errors in the intercepts of the plots of the product ratio as a function of the donor concentration could be almost negligible in the reductions with tri-n-butyltin deuteride. The error in the isotope effects calculated from the slopes of the plots of the product ratio as a function of the donor concentration would become very small if the slopes of plots from the reductions with tri-n-butyltin deuteride were reduced by about 15%, which is just slightly more than the usual statistical errors of about ±10% in the slopes for 90% confidence limits. This would bring the isotope effects calculated from the slopes of the plots of the product ratio as a function of the donor concentration listed in Table 8 into very good agreement with the values determined by mass spectroscopy in Table 7.

The only difference in the experimental conditions between the reductions with tri-n-butyltin hydride and tri-n-butyltin deuteride is that samples containing tri-n-butyltin deuteride are irradiated for longer periods of time than samples containing identical concentrations of tri-n-butyltin hydride, because of the slower reaction of the former. This has apparently resulted in ratios of norbornene to nortricyclene which are too low at low concentrations of tri-n-butyltin deuteride in the reductions of n-NBBr and x-NBBr, and ratios of nortricyclene to norbornene that are too high at low concentrations of tri-n-butyltin deuteride in the reduction of NTBr. This could readily be accounted for by the loss of a very few per cent of the norbornene through

hydrostannation, or some other secondary reaction, of increasing importance at lower concentrations of donor.* An error of this type could partially reconcile the difference between the observed and predicted plots of the product ratio as a function of the concentration of tri-n-butyltin hydride given in Table 6, and discussed previously.

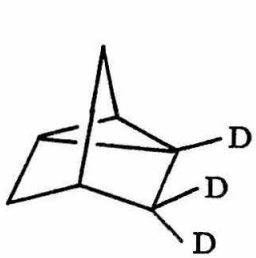
The agreement between the primary kinetic deuterium isotope effects apparently present in the abstraction reactions leading to norbornene and nortricyclene, and determined from the slopes and intercepts of the plots of the product ratio as a function of the concentration of the donor in the reductions of n-NBBr, x-NBBr, and NTBr with tri-n-butyltin hydride and tri-n-butyltin deuteride, and the primary kinetic deuterium isotope effects determined by mass spectroscopy for these reactions is not as precise as might be hoped for. However, the disagreement can be reasonably explained on the basis of relatively small experimental errors, and does not alter the conclusion that the results are consistent with Mechanism I. The results are compatible with Mechanism II or Mechanism IIIB only if fortuitous relationships between the primary kinetic deuterium isotope

*Experiments have shown that prolonged irradiation of a solution of norbornene and nortricyclene in tri-n-butyltin hydride results in gradual disappearance of the norbornene, probably through hydrostannation. The rate of this reaction is about two orders of magnitude slower than the rate of reduction of the bromides with tri-n-butyltin hydride. Where irradiation times of several hours are required to get nearly complete reduction of the bromide, such as with low concentrations of tri-n-butyltin deuteride, this reaction may cause loss of a very few per cent of the norbornene produced in the reduction reactions. Nortricyclene is unaffected by prolonged irradiation in the presence of tri-n-butyltin hydride, at least relative to norbornene.

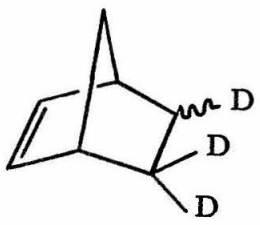
effects exist in the abstraction reactions leading to either norbornene or nortricyclene by more than one reaction, or else the contributions of "crossed" product formation in Mechanism II, or product formation from the "bridged" radical in Mechanism IIIB are small. Mechanism IIIA appears to be untenable.

Part 3. The Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride and Tri-n-butyltin Deuteride, and Secondary Kinetic Deuterium Isotope Effects.

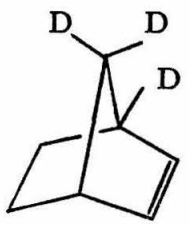
When endo-5-bromonorbornene-5, 6, 6, -d_3 (NBBr-d_3) is reduced with tri-n-butyltin deuteride, isomerization of the intermediates may result in three products being formed. They are nortricyclene-5, 6, 6-d_3 (NT-d_3), unrearranged norbornene-5, 6, 6-d_3 (NB_u), and skeletally rearranged norbornene-1, 7, 7-d_3 (NB_r). Figure 9 shows the reduction assuming that it goes via Mechanism I.



NT-d_3



NB_u



NB_r

Similarly, when (NBBr-d_3) is reduced with tri-n-butyltin deuteride, three products may be formed. They are nortricyclene-2, 5, 6, 6-d_4 (NT-d_4), unrearranged norbornene-5, 5, 6, 6-d_4 (NBD_u) and and skeletally rearranged norbornene-1, 6, 7, 7-d_4 (NBD_r)

Predicts in the absence of secondary deuterium isotope effects:

$$\frac{NB_u}{NB_r} = A + 2(B+\frac{B}{A})[ZH] + \frac{2B^2}{A}[ZH]^2 \qquad (A.I.21)$$

(assuming (XXVI) has chemically equivalent C_3-C_5 and C_3-C_4 bonds)

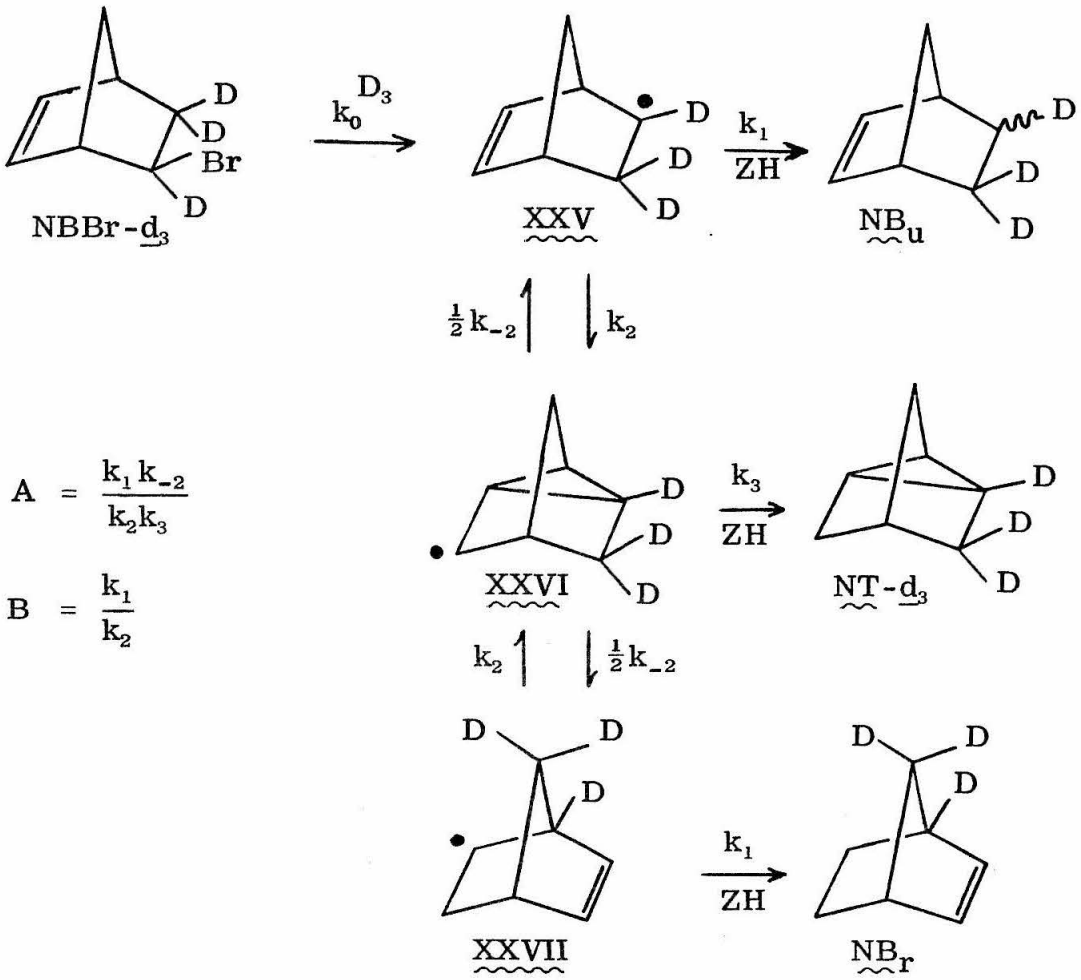
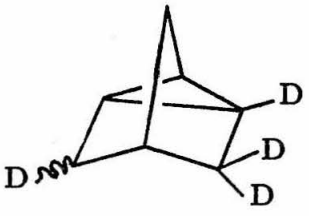
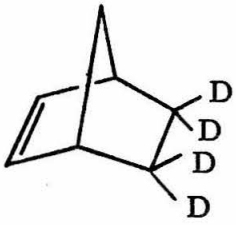


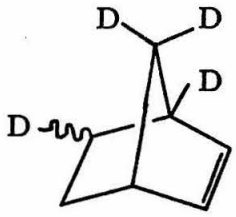
Figure 9. Rearrangement in the Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride via Mechanism I in the Absence of Secondary Deuterium Isotope Effects.



NT-d_4



NBD_u



NBD_r

In order to form the skeletally rearranged norbornenes, the intermediate must at some time prior to formation of products have the C_3-C_4 and C_3-C_5 bonds of the original radical, (XXV), essentially chemically equivalent.

To produce rearranged norbornenes via Mechanism I or Mechanism II, intermediate (XXVI) must have a "bisected" geometry, or go through an analogous transition state, which would result in isomerization equally to (XXV) and (XXVII) assuming that secondary deuterium isotope effects are negligible.

To produce rearranged norbornenes via Mechanism III would require that the "bridged" intermediate, or a transition state in its formation or isomerization, have the C_3-C_4 and C_3-C_5 bonds of the original radical, (XXV), essentially chemically identical.

If we assume that the reductions go via Mechanism I, then equation (A. I. 21) will enable us to use data previously presented in Tables 6, 7, and 8 to predict the ratios of unrearranged norbornenes to rearranged norbornenes in the reductions of (NBBr-$\underline{d}_3$) with various concentrations of tri-n-butyltin hydride and tri-n-butyltin deuteride, assuming that secondary deuterium isotope effects are negligible.

Formation of little or no rearranged norbornene in the reductions would be good evidence that the nortricyclyl free radical does not have the "bisected" geometry preferred by the unsubstituted- and alkyl-substituted cyclopropylcarbinyl free radicals, or that the isomerization goes through a "bridged" radical which does not have a "bisected" geometry.

The ratios of rearranged norbornene to unrearranged norbornene can be determined by mass spectrometry. In the mass spectrometer isatron, norbornene undergoes a retro Diels-Alder fragmentation to cyclopentadiene and ethylene fragments, resulting in the largest peak in the mass spectrum being at m/e 66, for the cyclopentadiene ion. The same process in the mass spectrum of the rearranged norbornenes results in a corresponding peak at m/e 69 for the cyclopentadiene-$\underline{d}_3$ ion.* Then from the ratios of the peaks in the mass spectrum at

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*The mass spectrum of norbornene-5, 5, 6, 6-$\underline{d}_4$ which was synthesized from ethylene-$\underline{d}_4$ and cyclopentadiene, and shown by nmr to have all the deuterium in the 5, 5, 6, 6-positions, gives a mass spectrum almost identical to that of norbornene in the region m/e 64 through m/e 72. No peak from m/e 68 through m/e 72 is greater than 2% of the peak at m/e 66 in the mass spectrum of norbornene-5, 5, 6, 6-$\underline{d}_4$. Therefore, the peaks at m/e 66 and m/e 69 should be a reliable means of determining the ratios of unrearranged to rearranged norbornenes.

Table 9. The Ratio of Unrearranged Norbornene ($\underset{\sim}{NB}_u$) to Rearranged Norbornene ($\underset{\sim}{NB}_r$) in the Reduction of endo-5-Bromonorbornene5, 6, 6-d_3 with Tri-n-butyltin Hydride at -10°.

Concentration of $(n\text{-}C_4H_9)_3SnH$ M/ℓ	Ratio of[a] $\underset{\sim}{NB}_u/\underset{\sim}{NB}_r$	Predicted[b,c] Ratio
3.67	2.43 ± 0.1	2.75 ± 0.2
3.67	2.19 ± 0.1	2.75 ± 0.2
3.16	2.12 ± 0.02	2.49 ± 0.16
2.93	1.79 ± 0.1	2.37 ± 0.15
2.18	1.525 ± 0.05	1.99 ± 0.11
1.08	1.11 ± 0.02	1.47 ± 0.06
0.34	0.855 ± 0.02	1.14 ± 0.02

[a] Determined by mass spectrometry. Errors are approximate errors expected from the mass spectra, and do not include other sources of error. No allowance has been made for the possibility that deuterium isotope effects might significantly alter the fragmentation patterns for the unrearranged or rearranged norbornenes. Although this might be significant, discussion in the text will show that it is not the most important contributor to the differences between the observed and predicted ratios above.

[b] Calculated from equation (A. I. 21), with B = 0.117 l/M, the slope of Graph 6, and A = 1.26, the intercept of Graph 6.

[c] Errors are calculated assuming the error in B is ±10% and the error in A is ±0.05.

Table 10. The Ratio of Unrearranged Norbornene (NBD_u) to Rearranged Norbornene (NBD_r) in the Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Deuteride at -10°.

Concentration of[a] $(n\text{-}C_4H_9)_3SnD$ M/ℓ	Ratio of[b] NBD_u/NBD_r	Predicted[c,d] Ratio
≅ 3.6	1.20 ± 0.02	1.76 ± 0.09
3.30	1.29 ± 0.1	1.70 ± 0.09
≅ 2.0	0.93 ± 0.05	1.39 ± 0.05
≅ 1.2	0.868 ± 0.02	1.24 ± 0.03
≅ 0.30	0.838 ± 0.02	1.07 ± 0.01

[a] Tests have shown that the tri-n-butyltin deuteride is effectively 100% deuteride, and adds 1.00 deuteriums/molecule to the abstraction products under the conditions in these reductions.

[b] Determined by mass spectrometry. Errors are approximate errors expected from the mass spectra, and do not include other possible sources of error. No allowance has been made for possible differences in the fragmentation patterns as a result of secondary deuterium isotope effects, between the unrearranged and rearranged norbornenes. Although this might be significant, discussion in the thesis text will show that it is not the most important contributor to the differences between the observed and predicted ratios here.

[c] Calculated from equation (A.I.21) with B = 0.117/2.1 1/M (from discussion in Part 2 of the Results and Discussion Section of this thesis, it seems more accurate to use the slope of Graph 6, divided by the primary kinetic deuterium isotope effect of 2.1, rather than the slope of 0.075 from Graph 9, for B). A = 1.26, the intercept of Graph 6.

[d] Errors are calculated assuming the error in B is ±10%, and the error in A is ±0.05.

m/e 66 and m/e 69, and the deuterium content of the compounds, we can obtain the ratios of unrearranged and rearranged norbornenes in a sample containing both.

In Table 9, the ratios of $\underset{\sim}{NB}_u$ to $\underset{\sim}{NB}_r$, determined by mass spectroscopy, in the norbornene produced in the reduction of ($\underset{\sim}{NBBr}$-$\underline{d}_3$) with tri-$\underline{n}$-butyltin hydride, and the ratios predicted by equation (A.I.21) assuming no significant secondary deuterium isotope effects are tabulated. In Table 10, an analogous tabulation is made for the norbornene produced in the reduction of ($\underset{\sim}{NBBr}$-$\underline{d}_3$) with tri-$\underline{n}$-butyltin deuteride.

It is apparent from Tables 9 and 10, that the rearranged norbornene in each case is apparently present in even greater amounts than predicted by Mechanism I in the absence of secondary deuterium isotope effects, assuming that ($\underset{\sim}{XXVI}$) has a "bisected" geometry or goes through a "bisected" transition state. Therefore, the initially generated 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical must isomerize through a "bisected" intermediate or transition state. However, the concentration dependence of the ratios of unrearranged to rearranged norbornenes means that we are "trapping" some of the initially generated radical before the C_3-C_4 and C_3-C_5 bonds become chemically equivalent.

The observation of more rearrangement than predicted could be a result of either of two fundamental causes. The retro Diels-Alder fragmentation in the mass spectrometer might be substantially affected by secondary deuterium isotope effects, resulting in incorrect values

for the ratios of unrearranged to rearranged norbornene. The fragmentation would be expected to go more easily in the rearranged ($\underset{\sim}{NB}_r$) or ($\underset{\sim}{NBD}_r$), where there are only one and two deuteriums $\underline{\alpha}$ to the C–C bonds being broken in ($\underset{\sim}{NB}_r$) and ($\underset{\sim}{NBD}_r$), respectively, than in the unrearranged ($\underset{\sim}{NB}_u$) or ($\underset{\sim}{NBD}_u$) where there are three and four deuteriums $\underline{\alpha}$ to the C–C bonds being broken, respectively. This could result in an apparently greater extent of rearrangement than actually occurred when mixtures of rearranged and unrearranged norbornenes are analyzed by mass spectroscopy. In our calculations, we have assumed that the retro Diels-Alder fragmentations occur with equal frequency for both unrearranged and rearranged norbornenes, because we have no means of accurately determining any correction factor if this is not true.

The second possible fundamental cause of the differences between the ratios determined by mass spectroscopy and those predicted in Tables 9 and 10, is obviously that there are secondary deuterium isotope effects during the reduction of ($\underset{\sim}{NBBr}$-$\underline{d}_3$), and that these isotope effects are in a direction which favors formation of the rearranged norbornenes.

Normal secondary $\underline{\alpha}$ deuterium isotope effects, where $k_H/k_D > 1.0$, occur when there is a decrease in the C–$\underline{d}$ bond force in the transition state of a reaction, and inverse secondary $\underline{\alpha}$ deuterium isotope effects, where $k_H/k_D < 1.0$, occur when there is an increase in the C–$\underline{d}$ bond force constant in the transition state of a reaction (52). Although there are some exceptions, there is generally a remarkably

consistent k_H/k_D of between 1.10 and 1.20 per deuterium for secondary $\underline{\alpha}$ deuterium isotope effects in reactions where a C–$\underline{d}$ bond changes from sp^3 to sp^2 hybridization. This is attributed mainly to the out-of-plane bending vibration of the deuterium atom in the transition state as the hybridization of the C–$\underline{d}$ bond changes to sp^2 (53). Numerous examples in free-radical-forming reactions are available (54).

Conversely, reactions in which the hybridization of a C–$\underline{d}$ bond changes from sp^2 to sp^3 are usually accompanied by any inverse secondary kinetic $\underline{\alpha}$ deuterium isotope effect, k_H/k_D, between about 0.87 and 0.92 per deuterium (55).

Secondary $\underline{\beta}$ deuterium isotope effects in free-radical-forming reactions are usually about 1.02 per $\underline{\beta}$ deuterium atom (56) if there is no significant change in the hybridization of the $\underline{\beta}$ C–$\underline{d}$ bonds during the reaction. However, in the thermolysis of pyrazolines, Al-Sader and Crawford found that the secondary $\underline{\beta}$ deuterium isotope effect in the cyclization of the trimethylene-2,2-$\underline{d}_2$ diradical was 1.13 per deuterium (57). The $\underline{\alpha}$ secondary deuterium isotope effect in the same cyclization reaction, but with deuterium at the terminal positions of the trimethylene diradical, is negligible. However, in the cyclization of the trimethylene diradical to cyclopropane, the terminal C–H bonds retain their sp^2 hybridization, while the $\underline{\beta}$ C–H bonds change from sp^3 to sp^2, at least to a good approximation. Therefore, when substantial changes in the hybridization of $\underline{\beta}$ C-$\underline{d}$ bonds in a reaction, then substantial secondary kinetic $\underline{\beta}$ deuterium isotope effects should be

expected.

An examination of Figure 9 shows that the isomerizations and abstraction reactions of the intermediates, assuming Mechanism I, during the reductions of NBBr-$\underline{d}_3$ involve major changes in the hybridization of C–$\underline{d}$ bonds in some cases.

In the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical (XXV), the C_5–$\underline{d}$ bond changes from approximately sp^2 to approximately sp^3 hybridization. Therefore, an inverse secondary $\underline{\alpha}$ deuterium isotope effect, which would cause an increase in the rate of formation of unrearranged norbornene seems to be a reasonable expectation.

In the isomerization of the 2-nortricyclyl-5, 6, 6-$\underline{d}_3$ radical (XXVI) to the 2-norbornenyl-1, 7, 7-$\underline{d}_3$ radical (XXVII), the C_5–$\underline{d}$ bond of (XXVI) changes from approximately sp^2 to approximately sp^3 as it becomes the C_1–$\underline{d}$ bond of (XXVII), and conversely in the reverse isomerization of (XXVII) to (XXVI). Then as (XXVI) isomerizes to (XXVII) as inverse secondary deuterium isotope effect would be expected, and in the reverse isomerization of (XXVII) to (XXVI), a normal secondary deuterium isotope effect would be expected. The cumulative effect of these two secondary deuterium isotope effects should be to increase the rate of formation of the rearranged norbornenes. At this juncture, then, the explanation of the differences between the observed and predicted ratios of unrearranged and rearranged norbornenes in Tables 9 and 10 would be expected to be found in the isomerizations of (XXVI) and (XXVII) because they give

effects in the right direction.

In Graphs 12 and 13, the ratios of norbornene to nortricyclene as a function of the donor concentration in the reductions of endo-5-bromonorbornene with tri-n-butyltin hydride and tri-n-butyltin deuteride are compared to the ratios of norbornene to nortricyclene as a function of the donor concentration in the simultaneous reductions of exo-5-bromonorbornene with tri-n-butyltin hydride and tri-n-butyltin deuteride. Previous discussion concerning the precision of plots of product ratio as a function of the donor concentration, especially when the slopes are low, and reaction times long, such as is found in the reductions with tri-n-butyltin deuteride, requires a cautious quantitative interpretation of Graphs 12 and 13. Qualitatively, however, in both graphs the slopes and intercepts for the reductions of endo-5-bromonorbornene-5, 6, 6-d_3 are substantially smaller than the corresponding slopes and intercepts for the reductions of exo-5-bromonorbornene with the same donor.

The most reasonable explanation for the lower slopes and intercepts in the reductions of (NBBr-d_3) compared to those in the analogous reductions of (x-NBBr) is a substantial (but normal) secondary kinetic deuterium isotope effect in the abstraction reactions of the 5-norbornenyl-5, 6, 6-d_3 radical (XXV).* If secondary deuterium isotope effects in the isomerizations of (XXVI) and (XXVII) were

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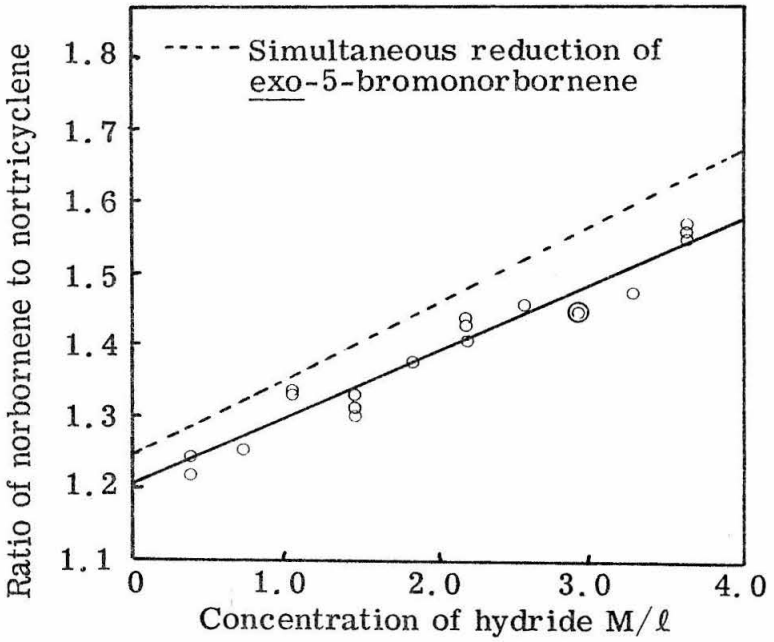
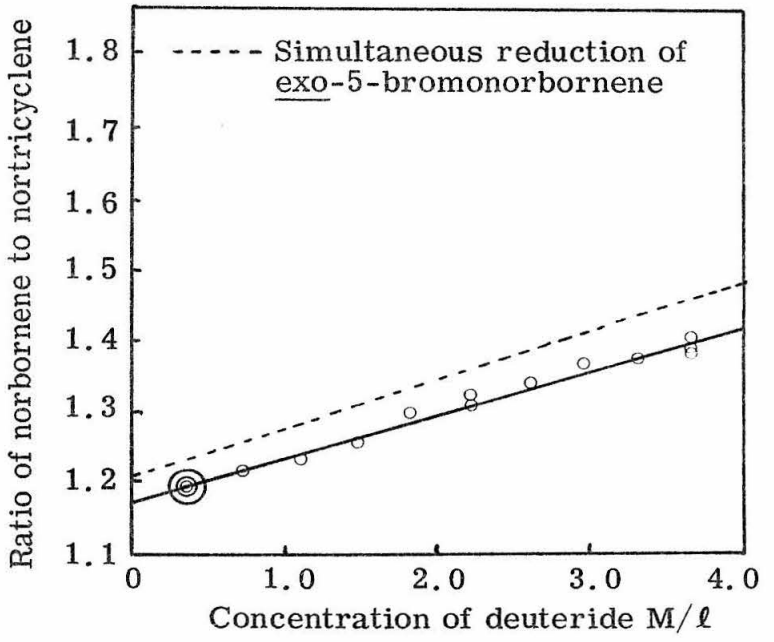
*Experiments have shown that the radicals generated from both (x-NBBr) and (n-NBBr) form identical products, so the results should not be attributable in any way to differences in the stereochemistry of the starting bromides.

Graph 12. The reduction of endo-5-bromonorbornene-5, 6, 6-d_3 with tri-n-butyltin hydride at -8°.
Product ratio versus donor concentration



Graph 13. The reduction of endo-5-bromonorbornene-5, 6, 6-d_3 with tri-n-butyltin deuteride at -8°.
Product ratio versus donor concentration



causing the disagreement between the observed and predicted ratios of unrearranged and rearranged norbornenes in Tables 9 and 10, then equation (A. I. 29) shows that there should be little effect on the slopes in Graphs 12 and 13, and an increase in the intercepts. A substantial secondary deuterium isotope effect in the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical would also bring the predicted and observed ratios of unrearranged to rearranged norbornenes in Tables 9 and 10 into closer agreement.

If a normal secondary deuterium isotope effect of $k_H/k_D = 1.25$ is assigned to the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical (XXV) (i.e., $k_1 = 1.25\ k_1^{D_3}$, or $\underline{\alpha} = 1.25$ in equation (A. I. 23)), then the differences in the slopes and intercepts for the plots of product ratio as a function of donor concentration for the reductions of (NBBr-$\underline{d}_3$) and ($\underline{x}$-NBBr) are reasonably well accounted for. Then the predicted ratios of unrearranged to rearranged norbornenes in Tables 9 and 10 are altered by equation (A. I. 23) to those in Table 11. The agreement between the ratios of unrearranged to rearranged norbornene predicted, allowing for the normal secondary deuterium isotope effect of 1.25 in the abstraction reactions of (XXV), and those obtained by mass spectroscopy is excellent, considering the limitations of the accuracy of the numbers used in calculating the predicted ratios.

The possibility that there is some contribution to the disagreement between the ratios of unrearranged to rearranged norbornene obtained by mass spectroscopy and those predicted by equation

Table 11. The Ratio of Unrearranged Norbornene to Rearranged Norbornene in the Reductions of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride and Tri-n-butyltin Deuteride at -10°.

Donor	Concentration M/ℓ	Ratio[a] NB_u/NB_r	Predicted ratios NB_u/NB_r $k_H/k_D = 1.0$[b]	$k_H/k_D = 1.25$[c, d]
$(n\text{-}C_4H_9)_3SnH$	3.67	2.43	2.75	2.20 ± 0.15
"	3.67	2.19	2.75	2.20 ± 0.15
"	3.16	2.12	2.49	1.99 ± 0.13
"	2.93	1.79	2.37	1.89 ± 0.12
"	2.18	1.525	1.99	1.59 ± 0.09
"	1.08	1.11	1.47	1.18 ± 0.04
"	0.34	0.855	1.14	0.91 ± 0.01

Donor	Concentration M/ℓ	Ratio[e] NBD_u/NBD_r	Predicted ratios NBD_u/NBD_r $k_H/k_D = 1.0$[b]	$k_H/k_D = 1.25$[c, d]
$(n\text{-}C_4H_9)_3SnD$	≅3.6	1.20	1.76	1.41 ± 0.07
"	3.30	1.29	1.70	1.36 ± 0.06
"	≅2.0	0.93	1.39	1.11 ± 0.03
"	≅1.2	0.868	1.24	0.99 ± 0.02
"	≅0.30	0.828	1.07	0.86 ± 0.01

Table 11. (Cont'd)

[a] Determined by mass spectroscopy; from Table 9.

[b] Calculated from equation (A. I. 21) assuming there are no secondary deuterium isotope effects; see Tables 9 and 10.

[c] Calculated from equation (A. I. 23) assuming $\underline{\alpha} = 1.25$.

[d] Errors are calculated assuming that the errors in B is ±10%, and the error in A is ±0.05.

[e] Determined by mass spectroscopy; from Table 10.

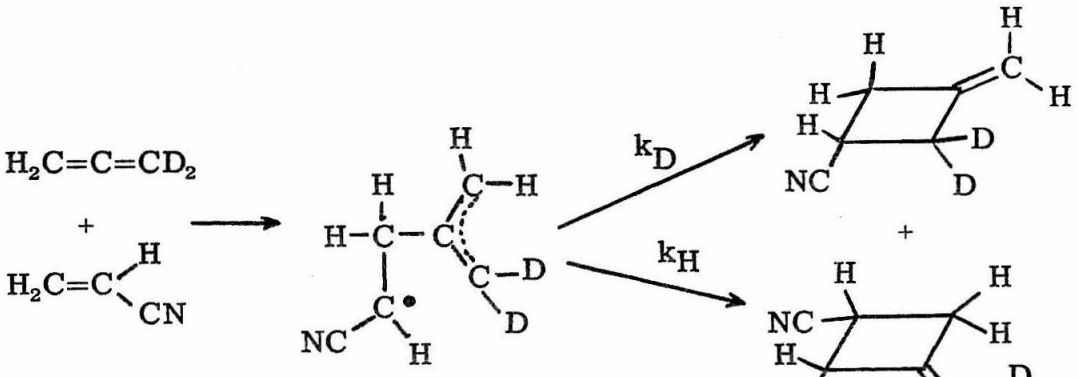
(A. I. 21) still exists. However, although no quantitative comparison will be made, there does not appear to be any substantial difference in the relative peak heights in the parent regions and at m/e 66 between the mass spectra of norbornene and norbornene-5, 5, 6, 6-$\underline{d}_4$. It seems reasonable, therefore, to expect any inaccuracies from this source to be minimal.

Although the value of 1.25 for the apparent secondary deuterium isotope effect in the abstraction reaction of (XXV) is only approximate, it is very close to that which would be expected for an average normal secondary $\underline{\alpha}$ deuterium isotope effect of about 1.15 plus the superimposed effect of two secondary $\underline{\beta}$ deuterium isotope effects of about 1.02 each, which would be the effects expected if C_5 in the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical were sp^3, and became closer to sp^2 in the transition state of the abstraction reactions. More generally, this would be the direction of the isotope effect expected if the transition state for the abstraction reactions of 5-norbornenyl radicals has a lower C_5–H out-of-plane bending force constant than the 5-norbornenyl radical. However, free radicals are expected to have a very "loose" C–H out-of-plane bending vibration, and the transition state of an abstraction reaction by a free radical would be expected to result in an increase in the C–H out-of-plane bending force constant in the transition state, and an inverse secondary $\underline{\alpha}$ deuterium isotope effect (58). Our results are opposite to this expectation.

There is a possibility that the 5-norbornenyl radical is non-planar, or has a "bridging" interaction between the unpaired electron at the radical center and the olefinic bond. This might result in the 5-norbornenyl radical having unusually strong C_5–H force constants

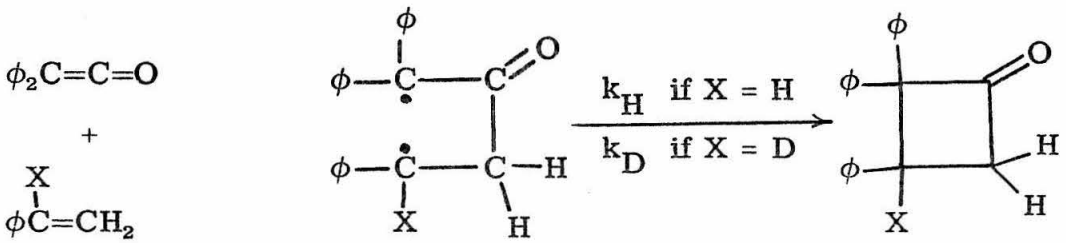
for a radical, which in turn results in a transition state in the abstraction reaction in which the C_5–H force constants decrease, providing the normal secondary $\underline{\alpha}$ deuterium isotope effect apparently observed in the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical. However, until more evidence is obtained, this must be considered as only a very speculative explanation of an apparently surprising secondary deuterium isotope effect.

Recently, in stepwise 2 + 2 addition reactions, large normal secondary $\underline{\alpha}$ deuterium isotope effects have been observed for formation of the second carbon-carbon bond, after an inverse secondary $\underline{\alpha}$ deuterium isotope effect has been observed in the formation of the first carbon-carbon bond (55). In analogous 2 + 4 additon reactions, however, only inverse secondary $\underline{\alpha}$ deuterium isotope effects are found (55a). These results have been interpreted on the basis of an unsymmetrical transition state in the 2 + 2 additions, where concerted 1,2-cis-addition is prohibited, but a symmetrical transition state in 2 + 4 additions, where a concerted reaction is permitted, on the basis of the Woodward-Hoffman rules (59). In the addition of acrylonitrile to allene-1, 1-$\underline{d}_2$ the unsymmetrical transition state requires rotation of a terminal methylene group before formation of the second carbon-carbon bond can occur, and the slower rotation of the terminal $C\underline{d}_2$ group relative to the terminal CH_2 group should result in preferential formation of the carbon-CH_2 bond rather than the carbon-$C\underline{d}_2$ bond. The secondary deuterium isotope effect is from 1.13 to 1.21 per deuterium for this second carbon-carbon bond formation (55a).



$$\frac{k_H}{k_D} = 1.13 - 1.21 \text{ per deuterium}$$

In the analogous addition of styrene to diphenylketene, the secondary deuterium isotope effect of about 1.23 for deuterium in the $\underline{\alpha}$-position of styrene has been attributed to the twisting of the $\underline{\alpha}$-carbon of styrene out of conjugation with the p orbital of the $\underline{\beta}$-carbon of styrene as a prerequisite to formation of the second carbon-carbon bond in the cycloaddition (55b).



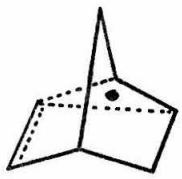
X = D, H

$$\frac{k_H}{k_D} = 1.23$$

Although it is not our intention to try to draw any close parallel between these reactions and the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical, it does seem relevant that these reactions involve normal secondary deuterium isotope effects in reactions in which the C-$\underline{d}$ bond has sp^2 hybridization initially. Secondary kinetic deuterium isotope effects are not sufficiently well documented or understood to exclude the possibility, therefore, that further investigations might show that our results are really in the expected direction.

The study of the products of the reduction of endo-5-bromo-norbornene-5, 6, 6-$\underline{d}_3$ with tri-$\underline{n}$-butyltin hydride and tri-$\underline{n}$-butyltin deuteride showed that the radical generated isomerizes through an intermediate or transition state with a symmetrical "bisected" geometry. These results can be adequately explained by Mechanism I, involving the intervention of only the norbornenyl and nortricyclyl free radicals, with the former producing only norbornene and the latter producing only nortricyclene in their respective abstraction reactions. The nortricyclyl free radical must have the "bisected" geometry shown by esr to be the preferred configuration for the cyclopropylcarbinyl radical and several alkyl-substituted cyclopropyl-carbinyl radicals, or else pass through a transition state of this geometry. A normal secondary deuterium isotope of approximately 1.25 must accompany the abstraction reactions of the 5-norbornenyl-5, 6, 6-$\underline{d}_3$ radical. The results do not preclude the possibility of the reduction going via Mechanism II, because a "bisected" nortricyclyl

radical would produce the same results via this mechanism as via Mechanism I. The important conclusion which can be drawn with respect to Mechanism III is that the results can not be attributed to the intervention of a "bridged" radical unless it possesses a "bisected" geometry, such as that in (XXIX), or is formed by way of a transition



XXIX

state with the same symmetry, in which the C_3-C_4 and C_3-C_5 bonds are chemically equivalent.

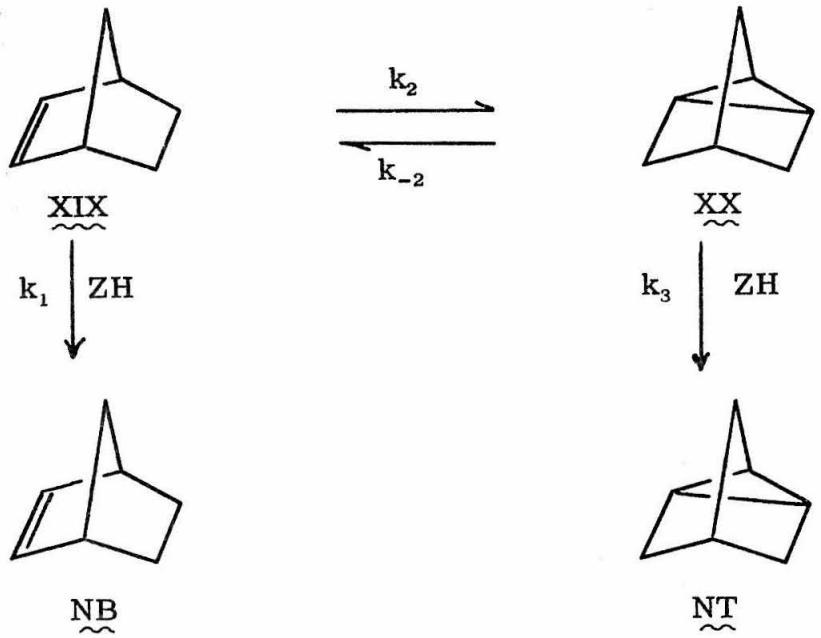
Part 4. Approximate Arrhenius Parameters in the Isomerizations and Abstraction Reactions of the Norbornenyl- and Nortricyclyl Free Radicals.

If we continue to assume that the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene go via Mechanism I, then we can obtain some approximate values for the A factors and activation energies for the rate constants expressed by the Arrhenius equation,

$$k = A e^{-\frac{E}{RT}} \qquad \text{(II. 4. 1)}$$

for both the isomerizations and the abstraction reactions of the intermediates involved in these reductions. The absolute accuracy of some of the data used in the following calculations will not be good, resulting in the quantitative accuracy of the results of these calculations being suspect. Qualitatively, however, a reasonable picture should emerge.

From equations (A. I. 6) and (A. I. 7), the slope of the plot of the ratio of NB/NT as a function of the concentration of tri-n-butyltin hydride equals the rate constant ratio k_1/k_2, in the reductions of n-NBBr and x-NBBr, and the slopes of the plots of the ratio of NT/NB as a function of the concentration of tri-n-butyltin hydride equals the rate constant ratio k_3/k_{-2}, in the reductions of NTBr.



From Table 6, k_1/k_2 is approximately 0.11 ℓ/M at -10° and 0.07 ℓ/M at 22°. Approximate values for k_3/k_{-2} are 0.08 ℓ/M at -10° and 0.05 ℓ/M at 22°. Using these values, we can calculate the differences in the activation energies of the abstraction and isomerization reactions for each of the two radicals, (XIX) and (XX).

$$\frac{k_1}{k_2} = 0.11 \pm 0.1 \text{ ℓ/M at } -10° \qquad \text{(II. 4. 2)}$$

$$\frac{k_1}{k_2} = 0.07 \pm 0.007 \text{ ℓ/M at } 22° \qquad \text{(II. 4. 3)}$$

$$\frac{k_1}{k_2} = \frac{A_1 e^{-\frac{E_1}{RT}}}{A_2 e^{-\frac{E_2}{RT}}} \qquad \text{(II. 4. 4)}$$

Substitution of (II. 4. 2) and (II. 4. 3) into (II. 4. 4) gives

$$E_2 = E_1 + 2.2 \pm 0.9 \text{ kcal/mole} \qquad \text{(II. 4. 5)}$$

and

$$\frac{k_1}{k_2} = 1.7\,(10^{-3.0 \pm 0.7})\, e^{\frac{+2.2 \pm 0.9}{RT}} \ \ell/M. \qquad \text{(II. 4. 6)}$$

Similarly,

$$\frac{k_3}{k_{-2}} = 0.08 \pm 0.008 \ \ell/M \text{ at } -10° \qquad \text{(II. 4. 7)}$$

$$\frac{k_3}{k_{-2}} = 0.05 \pm 0.005 \ \ell/M \text{ at } 22° \qquad \text{(II. 4. 8)}$$

$$\frac{k_3}{k_{-2}} = \frac{A_3\, e^{-\frac{E_3}{RT}}}{A_{-2} e^{-\frac{E_{-2}}{RT}}} \ . \qquad \text{(II. 4. 9)}$$

Substitution of (II. 4. 7) and (II. 4. 8) into (II. 4. 9) gives,

$$E_{-2} = E_3 + 2.3 \pm 0.9 \text{ kcal/mole} \qquad \text{(II. 4. 10)}$$

and,

$$\frac{k_3}{k_{-2}} = 1.0\,(10^{-3.0 \pm 0.7})\, e^{\frac{+2.3 \pm 0.9}{RT}} \ \ell/M. \qquad \text{(II. 4. 11)}$$

The intercepts of Graphs 6-8 show that the ratio of norbornene to nortricyclene from the reductions of n-NBBr, x-NBBr, and NTBr in tri-n-butyltin hydride at -10° is approximately 1.25 when the intermediate radicals should be at equilibrium. The intercepts of Graphs 1-3 show that the ratio of norbornene to nortricyclene from the same reductions at 22° is approximately 1.35, when the radicals are at equilibrium at this temperature. These values are in reasonably good agreement with the values of 55/45 at 25° and 60/40 at 90-100° for the ratio of norbornene to nortricyclene determined by Warner, Strunk, and Kuivila, in the reductions of endo-5-bromonorbornene, endo-5-chloronorbornene, 2-bromonortricyclene, and 2-chloronortricyclene with tri-n-butyltin hydride under conditions where the intermediates should be at equilibrium (14a).

The concentration independent terms in equations (A.I.5) or (A.I.6) give the ratio of norbornene to nortricyclene as a function of the isomerization- and abstraction rate constants, when the intermediate radicals, (XIX) and (XX) should be in equilibrium,

$$\left(\frac{[NB]}{[NT]}\right)_{[ZH]=0} = \frac{k_1 k_{-2}}{k_3 k_2} .$$

Then,

$$\frac{k_1 k_{-2}}{k_3 k_2} = \frac{A_1 A_{-2}}{A_3 A_2} e^{\frac{-(E_1 + E_{-2}) + (E_3 + E_2)}{RT}} \qquad (II.4.12)$$

and,

$$\frac{k_1 k_{-2}}{k_3 k_2}^{*} = 1.25 \pm 0.05 \text{ at } -10^\circ \qquad \text{(II. 4. 13)}$$

$$\frac{k_1 k_{-2}}{k_3 k_2} = 1.50 \pm 0.05 \text{ at } 100^\circ. \qquad \text{(II. 4. 14)}$$

Substitution of (II. 4. 13) and (II. 4. 14) into (II. 4. 12) gives,

$$(E_1 + E_{-2}) = (E_3 + E_2) + 0.3 \pm 0.1 \text{ kcal/mole} \qquad \text{(II. 4. 15)}$$

and,

$$\frac{A_1 A_{-2}}{A_3 A_2} = 6.6 (10^{-1.0 \pm 0.1}) \qquad \text{(II. 4. 16)}$$

$$\frac{k_1 k_{-2}}{k_3 k_2} = 6.6 (10^{-1.0 \pm 0.1}) e^{-\frac{(0.3 \pm 0.1)}{RT}}. \qquad \text{(II. 4. 17)}$$

Equation (II. 4. 17) can also be derived by combining (II. 4. 6) and (II. 4. 11) to get,

$$\frac{k_1 k_{-2}}{k_3 k_2} = \frac{1.7 (10^{-3.0 \pm 0.7}) e^{\frac{+2.2 \pm 0.9}{RT}}}{1.0 (10^{-3.0 \pm 0.7}) e^{\frac{+2.3 \pm 0.9}{RT}}} \qquad \text{(II. 4. 18)}$$

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* From the slopes of the plots of the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride at -10°, $k_1/k_2 \approx 0.11$ and $k_3/k_{-2} \approx 0.8$. Substituting these values into (II. 4. 13) gives $\frac{k_1 k_{-2}}{k_3 k_2} \approx 1.35$, which is in reasonable agreement with the intercept of 1.25.

or,

$$\frac{k_1 k_{-2}}{k_3 k_2} = 1.7\,(10^{0 \pm 1.4})\, e^{-0.1 \pm 1.8}. \qquad \text{(II. 4. 19)}$$

Equation (II. 4. 19) is in reasonable agreement with (II. 4. 17), although the error limits on the A factor and activation energy sum in (II. 4. 19) are becoming prohibitive. Because the A factor and the activation energy sum are both very small, even small error limits result in both the A factor and the activation energy sum being uncertain by a sizable factor in (II. 4. 19).

Other studies have found that the rate of reduction of bromocyclohexane with tri-n-butyltin hydride at 45° is about 1. 5 times as rapid as the rate of reduction of endo-5-bromonorbornene under the same conditions (13a). We have found a similar relative rate factor of about 1. 5 in the same reductions at 0° or 25°.

Because the rate-determining step in the reductions of alkyl bromides with triorganotin hydrides is the abstraction of hydrogen from the triorganotin hydride by the alkyl radical (46), then if the rates of chain-initiation from both n-NBBr and NTBr are the same we can express the rate of reduction of n-NBBr and NTBr as a function of the

abstraction rates of (XIX) and (XX).* The absolute rate of abstraction of hydrogen from tri-n-butyltin hydride by the cyclohexyl radical at 25° is 1.0 (10^6) ℓ/M-sec (46). Therefore, by simply applying the factor of 1.5, for the differences in the reduction rates of bromocyclohexane and n-NBBr or NTBr to the rate constant for the abstraction of hydrogen from tri-n-butyltin hydride by the cyclohexyl radical at 25° we obtain equation (II. 4. 20).

$$\{0.67(10^6)\}\{[XIX] + [XX]\} \simeq k_1[XIX] + k_3[XX]. \qquad \text{(II. 4. 20)}$$

From the intercepts of the plots of the product ratio as a function of the concentration of tri-n-butyltin hydride in the reductions of n-NBBr and NTBr at 22°, we have equation (II. 4. 21), which will not be significantly different from the ratio at 25°.

$$\frac{k_1[XIX]}{k_3[XX]} \simeq 1.35 \text{ at } 22°. \qquad \text{(II. 4. 21)}$$

Now, if a reasonable estimate of either k_1 or k_3 can be made, then the other one, and the equilibrium ratio of the concentrations of (XIX)

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*x-NBBr is reduced at a rate approximately 3.5 times as rapid as the rates of reduction of either n-NBBr or NTBr. This probably results from a greater chain length for the reduction of x-NBBr than for n-NBBr through a lower activation energy for abstraction of the exo-bromine than for the abstraction of the endo-bromine or from more efficient chain initiation. However, the presence of this difference shows that there will be considerable uncertainty in calculations based on the assumption that the difference in the reduction rates of n-NBBr and NTBr, relative to the reduction rates of bromocyclohexane is a result solely of differences in the abstraction rates of the respective intermediate radicals.

and (XX) at 25° can be obtained.

In Table 19, in Appendix IV, the decomposition rates for endo- and exo-5-carbo-t-butylperoxynorbornene are compared with the decomposition rates for several other t-butyl peresters, at 110°. The decomposition rates for endo- and exo-5-carbo-t-butylperoxy-norbornene are only slightly slower than the decomposition rate for carbo-t-butylperoxycyclohexane, but about ten times faster than the decomposition rate for t-butyl peresters of n-alkyl carboxylic acids, and more than an order of magnitude slower than the decomposition rate for t-butyl 2,2-dimethylperpropanoate. These decomposition rates have been shown to involve a concerted reaction, in which the rate is dependent upon the stability of the alkyl radical generated when the alkyl radical is secondary or tertiary (8). Therefore, the stability of the 5-norbornenyl radical should be very close to the stability of the cyclohexyl radical. Therefore, we are not likely to be greatly in error if we assume that the rate of abstraction of hydrogen from tri-n-butyltin hydride by the 5-norbornenyl radical is equal to the same abstraction rate for the cyclohexyl radical.*

Therefore,

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*Obviously, this contention could be incorrect, but the fact that the rate of reduction of bromocyclohexane with tri-n-butyltin is only about 1.5 times as rapid as the rate of reduction of either n-NBBr or NTBr, where the major product is norbornene, presumably formed from the norbornenyl radical, makes it unlikely that the rate of abstraction of hydrogen by the norbornenyl radical is different from the rate of abstraction of hydrogen by the cyclohexyl radical by more than about 50%.

$$k_1 = (1.0 \pm 0.5)(10^6)\ \ell/\text{M-sec at } 25°. \qquad \text{(II. 4. 22)}$$

Substitution of (II. 4. 21) and (II. 4. 22) into (II. 4. 20) gives,

$$\frac{[\underset{\sim\sim}{XX}]}{[\underset{\sim\sim\sim}{XIX}]} = 1.6 \pm 1.2 \quad \text{at } 25° \qquad \text{(II. 4. 23)}$$

and,

$$k_3 = (0.46 \pm 0.3)(10^6)\ \ell/\text{M-sec at } 25°. \qquad \text{(II. 4. 24)}$$

It can be seen from the error limits placed upon the ratio of the concentrations of ($\underset{\sim\sim}{XX}$) and ($\underset{\sim\sim\sim}{XIX}$), and the rate constants, k_1 and k_3, that we can not ascertain for sure which radical is present in greater concentration or which abstraction rate, k_1 or k_3, is greater. The calculations do indicate, however, that there is not any great difference in either the relative concentration of ($\underset{\sim\sim}{XX}$) and ($\underset{\sim\sim\sim}{XIX}$) or between the abstraction rate constants, k_1 and k_3.

Halgren has calculated an activation energy of 2.6 kcal/mole for the abstraction of hydrogen from triethyltin hydride by the (γ, γ-diphenylallyl)carbinyl free radical (60). The activation energy for the same abstraction from tri-n-butyltin hydride should be close to, but slightly higher than, this value, because triethyltin hydride is a marginally better hydrogen donor than tri-n-butyltin hydride. Although we lack any quantitative comparative data for tri-n-butyltin hydride and triethyltin hydride, we can not be in error by more than about ±0.5 kcal/mole if we assume an activation energy of 3.0

kcal/mole for the abstraction of hydrogen from tri-n-butyltin hydride by the (γ, γ-diphenylallyl)carbinyl free radical.

From the data in Table 5, on the absolute reaction rates for abstraction of hydrogen from tri-n-butyltin hydride by alkyl radicals determined by Carlsson and Ingold (46), it is apparent that these rates are very "compressed". There is a factor of less than 8 between the abstraction rates for the methyl radical and that for the t-butyl radical at 25°. Therefore, there must be only a small change in the activation energies for the abstraction of hydrogen from tri-n-butyltin hydride by alkyl radicals with changes in the stability of the alkyl radical.* We cannot be greatly in error if we assume that the rates and activation energies for the abstraction of hydrogen by the (γ, γ-diphenylallyl)carbinyl radical and the n-hexyl radical are the same, because the former radical has been shown to have characteristics typical of a normal alkyl radical in its rate of formation and rates of abstraction (7).

The absolute reaction rates from Table 5, for the abstraction of hydrogen from tri-n-butyltin hydride by the cyclohexyl radical and

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*A difference by a factor of about 8 in rate constants at 25°, if the differences in A factors are negligible, requires a difference of about 1.25 kcal/mole in activation energies. While this is obviously a small change in activation energy, when applied to activation energies of only about 3.0 kcal/mole, it represents a relatively large change. Therefore, while the changes in the activation energy with changes in the alkyl radical must be absolutely small, they may be relatively quite large during the abstraction of hydrogen from tri-n-butyltin hydride by alkyl radicals. Obviously, too, part or all of the factor of 8 could be readily attributed to A factor differences.

the n-hexyl radical are 1.2 (10^6) ℓ/M-sec, and 1.0(10^6) ℓ/M-sec, respectively, at 25°. It is surprising to find the abstraction rate for the cyclohexyl radical higher than that for the n-hexyl radical, but Carlsson and Ingold noted that the differences between the rate constants for the abstraction reactions of these two radicals was within the range of experimental error (46). The similarity of these rates suggests that there can be little difference in the activation energies for the abstraction of hydrogen from tri-n-butyltin hydride by the n-hexyl- and cyclohexyl radicals. Therefore, the estimate of 3.0 kcal/mole for the activation energy for the abstraction of hydrogen from tri-n-butyltin hydride by the (γ, γ-diphenylallyl)-carbinyl radical should also be a good estimate for the activation energy for the abstraction of hydrogen from tri-n-butyltin hydride by either the n-hexyl- or cyclohexyl radical.

Combining analogous reasoning to that presented previously to estimate that the rate of abstraction of hydrogen from tri-n-butyltin hydride by the 5-norbornenyl radical should not be greatly different from the same abstraction by the cyclohexyl radical,* with the apparently small range of activation energies in the abstraction of hydrogen from tri-n-butyltin hydride by alkyl radicals enables us to estimate that the activation energy for abstraction of hydrogen from tri-n-butyltin hydride by the 5-norbornenyl radical should be almost equal to the activation energy for the same abstraction reaction by the

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*See page 113.

cyclohexyl radical, or 3.0 kcal/mole. Error limits of ±0.5 kcal/mole should be ample.

Substitution of the estimated activation energy for the abstraction of hydrogen from tri-n-butyltin hydride by the 5-norbornenyl radical into equation (II.4.22) gives,

$$A_1 = 1.6(10^{8\pm0.5})\ \ell/\text{M-sec} \qquad \text{(II.4.25)}$$

or,

$$k_1 = 1.6(10^{8\pm0.5})\, e^{\frac{-3.0\pm0.5}{RT}}\ \ell/\text{M-sec.} \qquad \text{(II.4.26)}$$

Substitution of (II.4.26) into (II.4.6) gives,

$$A_2 = 9.4(10^{10\pm1})/\text{sec} \qquad \text{(II.4.27)}$$

and,

$$E_2 = 5.2\pm1.0\ \text{kcal/mole} \qquad \text{(II.4.28)}$$

or,

$$k_2 = 9.4(10^{10})\, e^{\frac{-5.2}{RT}}/\text{sec.} \qquad \text{(II.4.29)}$$

Unfortunately, we have now reached a point where we lack any comparative information from which we might calculate the activation energies and A factors for the rate constants k_3 and k_{-2}. However, it is likely that most of the difference between the rate constants k_3 and k_{-2} results from differences in activation energy, rather than

differences in A factors. In almost all reactions involving the abstraction of hydrogen by an alkyl radical, the A factors are between 10^8 and 10^9 ℓ/M-sec (61). The 5-norbornenyl and 2-nortricyclyl radicals are both secondary radicals, with quite similar functional groups attached to the radical carbon, so it is reasonable to expect no major differences in the entropy changes in the transition states for the abstraction reactions of the two radicals, with the subsequent result that the A factors should be nearly identical for the two abstraction reactions. However, it must again be emphasized that we have no quantitative basis for attributing the differences in k_1 and k_3 entirely to activation energy differences. However, if,

$$A_1 = A_3 = 1.6(10^8)\ \ell/\text{M-sec} \qquad \text{(II. 4. 30)}$$

then,

$$E_3 = 3.5\ \text{kcal/mole} \qquad \text{(II. 4. 31)}$$

and,

$$k_3 = 1.6\ (10^8)\ e^{\frac{-3.5}{RT}}\ . \qquad \text{(II. 4. 32)}$$

Then from equation (II. 4. 11),

$$E_{-2} = -5.8\ \text{kcal/mole} \qquad \text{(II. 4. 33)}$$

and,

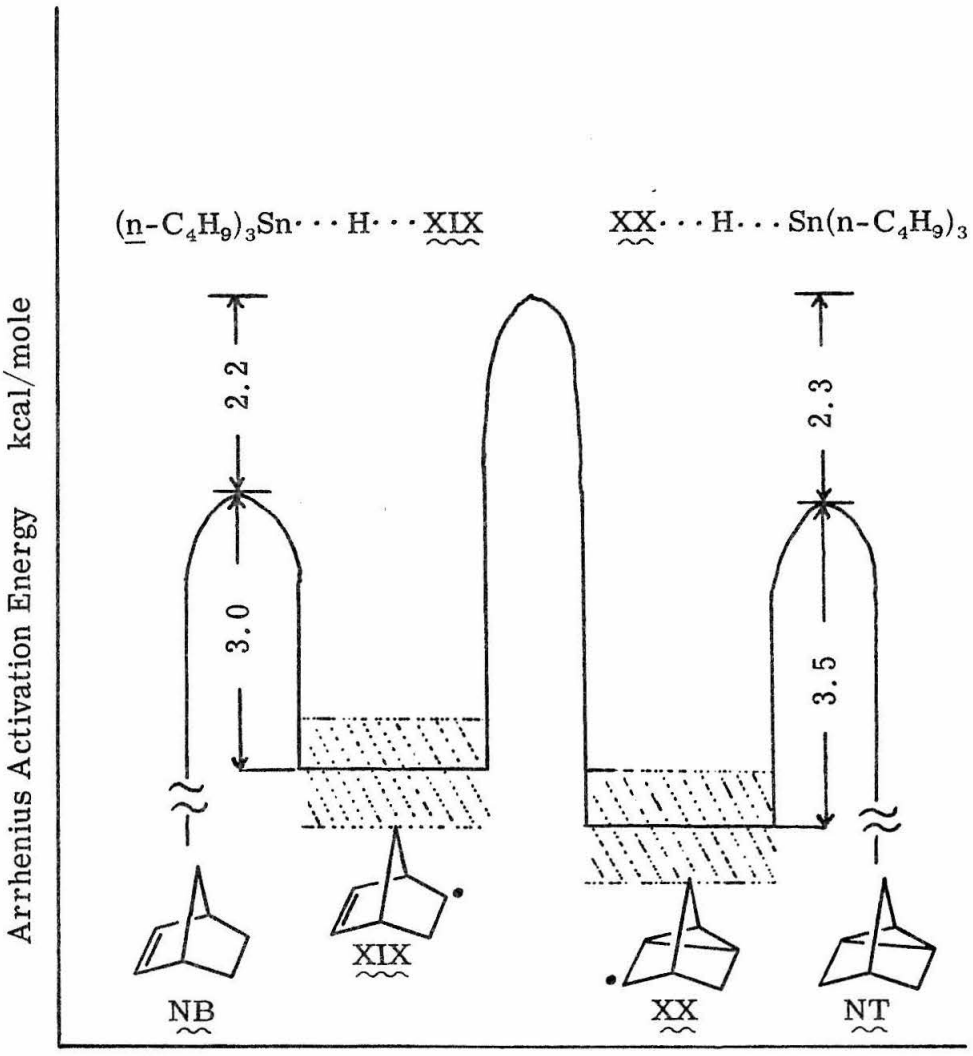
$$A_{-2} = 1.6(10^{11})/\text{sec} \qquad \text{(II. 4. 34)}$$

or

$$k_{-2} = 1.6(10^{11})\, e^{\frac{-5.8}{RT}} \quad \ell/\text{mole-sec.} \qquad \text{(II. 4. 35)}$$

The activation energies for rate constants k_1 and k_2 were estimated to be accurate only to about ±0.5 and ±1.0 kcal/mole, respectively. It can be seen that even if we had assumed that the difference between rate constants k_1 and k_3 had come entirely from differences in the respective A factors, the activation energies which would be calculated for k_3 and k_{-2} would not differ from 3.5 and 5.8 kcal/mole by more than 0.5 and 1.0 kcal/mole, respectively, and the values calculated for the activation energies for k_3 and k_{-2} are at least as uncertain as those for k_1 and k_2, respectively. Therefore, regardless of the relative contributions to the difference between k_1 and k_3 from differences in A factors or differences in activation energies, the resulting activation energies will still be within the probable error limits. In Fig. 10, the activation energies are shown along the reaction coordinate.

In assessing the results of our calculations, we are naturally drawn to the much more rigorous treatment given to the analogous isomerization and abstraction reactions of the ($\underline{\gamma}$,$\underline{\gamma}$-diphenylallyl)-carbinyl radical and the diphenylcyclopropylcarbinyl radical by Halgren (7). The diphenylcyclopropylcarbinyl radical was found to be about 8 kcal/mole more stable than the isomeric ($\underline{\gamma}$,$\underline{\gamma}$-diphenylallyl)-carbinyl radical, but there was a preponderance of 1,1-diphenylbutene



Shaded areas indicate probable limits of uncertainty on relative energies of XIX and XX.

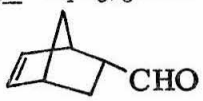
Figure 10. Arrhenius activation energies along the reaction coordinate in the reactions of the 5-norbornenyl radical and the 2-nortricyclyl radical in tri-n-butyltin hydride.

over diphenylcyclopropylmethane even when highly reactive and unselective triethyltin hydride was used as the hydrogen donor. As successively less reactive hydrogen donors were used, the ratio of 1,1-diphenylbutene to diphenylcyclopropylmethane increased substantially. Therefore, as expected, the activation energy for abstraction by the more stable radical increased more than the activation energy for abstraction of hydrogen by the less stable radical, as less active, or more selective, hydrogen donors were used.

Some ratios of norbornene to nortricyclene at different temperatures, and with different hydrogen donors, under conditions where the intermediate radicals should be at equilibrium are given in Table 11. The difference in the activation energies for abstraction of hydrogen by (XIX) and (XX) are calculated from the equations derived previously for rate constants k_1, k_2, k_{-2}, and k_3. The small differences in the activation energies for abstraction of hydrogen from donors of considerably different activity by (XIX) and (XX) are consistent with our calculations showing only a small difference in the relative potential energies of (XIX) and (XX) along the reaction coordinate. By analogy with the results calculated by Halgren, and discussed in the preceding paragraph, it would be difficult to rationalize the small changes in the product ratio with large changes in the hydrogen donor activity otherwise.

One pertinent observation revealed by a cursory examination of Table 11 is that the ratio of norbornene to nortricyclene decreases

Table 11. The Ratio of Norbornene to Nortricyclene with Different Donors at Different Temperatures.

Temperature	Hydrogen donor	Approximate abstration E kcal/mole	$[NB]/[NT]^a$	E_1-E_3 [b] kcal/mole
22°	$(n\text{-}C_4H_9)_3SnH$	3.0	1.25 [c]	-0.5
35°	$(C_2H_5)_2O$	10.0	0.49 [d]	+0.17
90-100°	$(C_6H_5)_3SnH$	2.0	1.50 [e]	+0.30
90-100°	$(n\text{-}C_4H_9)_3SnH$	3.0	1.50 [e]	+0.30
130°		8.0	0.89 [f]	+0.04

[a] The ratio of norbornene to nortricyclene formed under conditions where the 5-norbornenyl and 2-nortricyclyl radicals should be at equilibrium.

[b] Calculated from equations (II. 4. 26), (II. 4. 29), (II. 4. 32), and (II. 4. 35), assuming only E_1 and E_3 vary with donor.

[c] This work.

[d] Reference 13b.

[e] Reference 14a.

[f] Reference 13c.

with decreasing donor activity at similar temperatures. Again by analogy with the results calculated by Halgren, this implies that the 5-norbornenyl radical should be slightly lower in energy along the reaction coordinate than the 2-nortricyclyl radical. Although our calculations implied the opposite, the error limits on the accuracy of the calculations can readily accommodate the 5-norbornenyl radical being slightly lower in energy along the reaction coordinate than the 2-nortricyclyl radical. At least there are no experimental observations presently available which are incompatible with our calculations within reasonably small error limits.

The most interesting qualitative conclusion from the calculations is probably that there are substantially higher activation energies for the isomerizations of (XIX) and (XX), than for their abstraction reactions. However, the activation energies of 5-6 kcal/mole for the isomerizations of (XIX) and (XX) are lower than the activation energies of about 10 kcal/mole normally found for the abstraction of hydrogen from organic molecules by organic free radicals. Coupled with the much higher A factors for the isomerization reactions than for the bimolecular abstraction reactions, this explains the failure to "intercept" the radicals before they reach equilibrium with any but the most reactive of hydrogen donors. The general insensitivity of the product ratios to temperature changes results from the small difference in the activation energies for the abstraction reactions of (XIX) and (XX) and the small difference in the activation energies for the isomerizations of (XIX) and (XX), which results in little change either

in the relative concentrations of (XIX) and (XX) or their relative abstraction rates with large changes in temperature.

Certainly the results of the calculations are consistent with the results of other workers, where comparisons can be made, and none of the A factors or activation energies are inconsistent with reasonable expectations for Mechanism I. It is still conceivable that there could be intervention of a "bridged" intermediate of Mechanism III, or some "crossed product" formation via Mechanism II, but it is not necessary to invoke any deviations from Mechanism I to satisfactorily explain the results.

Section III. EXPERIMENTAL SECTION

Part 1. Apparatus

Analytical vapor phase chromatography was carried out on a Hewlett-Packard Model 5754B dual-flame/duel-thermoconductivity gas chromatograph equipped with a Moseley 7127A single-pen recorder and a disc integrator. Product ratios of norbornene and nortricyclene are the uncorrected results from the disc integrator. Some preliminary analytical vapor phase chromatography was carried out on a Perkin-Elmer Model 800 dual-flame gas chromatograph equipped with a Leeds & Northrup Model S-6000 recorder and a Perkin-Elmer Model 194 printing integrator.

Preparative vapor phase chromatography was carried out on an F & M Scientific Prepmaster 775 equipped with a Honeywell Class 18 recorder. Occasionally, some preparative vapor phase chromatography was carried out on an Aerograph Autoprep 700 equipped with Honeywell Model 15 recorder.

Several columns were used on the gas chromatographs. The most frequently used were:

Analytical TCP...16 ft. × 1/8 in. aluminum column packed with 6% tricresyl phosphate on 80/100 mesh acid-washed, dimethyldichlorosilane-treated Chromasorb G.

Preparative TCP...16 ft. × 3/8 in. aluminum column packed with 20% tricresyl phosphate on 40/50 mesh acid-washed,

dimethyldichlorosilane-treated Chromasorb G.

Preparative Carbowax...12 ft. × 3/4 in. stainless steel column packed with 20% Carbowax 20M on an unknown Chromasorb.

Nuclear magnetic resonance spectra were normally taken on Varian Models A-60, A-60A, and A-56/60 spectrometers. On some special occasions, the Varian A-56/60 spectrometer equipped with a Varian C-1024 Computer of Average Transients was used. Some spectra, particularly in deuterated compounds where standard 60 MHz spectra did not provide satisfactory resolution of similar resonance frequencies, were run on a Varian HR-220 spectrometer.

Mass Spectra were run on a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer, with a standard ionizing voltage of 70 volts.

Infrared spectra were taken on Perkin-Elmer Infracord Models 237 or 257.

Melting points were taken on a Mettler FP 1 melting point apparatus, usually from a simultaneous run in triplicate. Melting points and boiling points are uncorrected.

Ultraviolet irradiation of reaction mixtures was performed with a Hanovia 450 watt high-pressure mercury lamp in a pyrex well. In some cases, a uranium glass filter was used to remove most of the light of wavelength shorter than 3550Å.

Part 2. Materials Used.

Hexamethylethane. -- Hexamethylethane (Aldrich Chemical Co., Inc.) was sublimed once before being used as an internal standard in reaction mixtures to be analyzed by vapor phase chromatography.

Norbornene. -- Norbornene (Aldrich Chemical Co., Inc.) was used as received for most purposes, but was sublimed once before being used to obtain reference nmr spectra and mass spectra.

Toluene. -- Toluene (J. T. Baker Chemical Co., reagent grade) was purified by preparative gas chromatography with a Carbowax 20M column to 99.99% as estimated from an analytical vpc trace. This toluene was then used as a solvent in the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride.

Tri-n-butyltin Hydride. -- Tri-n-butyltin chloride (Aldrich Chemical Co., Inc.) was reduced with lithium aluminum hydride (Metal Hydrides, Inc., 95% minimum) in anhydrous ether (Mallinkrodt anhydrous analytical reagent grade), in a procedure developed by Kuivila (39a) and Neumann (63). The usual yields were 60-80%, bp 65-75° (0.1-2.0 mm); lit. (39a) bp 76-81° (0.7-0.9 mm). The product showed the characteristic strong ir Sn-H stretching absorption at 1810 cm^{-1}; lit. (39a) 1815 cm^{-1}.

Tri-n-butyltin Deuteride. -- Tri-n-butyltin chloride was reduced with lithium aluminum deuteride (E. Merck, 99% minimum

deuterium content, 90% lithium aluminum deuteride minimum) in the same procedure used in the preparation of tri-n-butyltin hydride. The usual yields were 60-70%, bp 70° (0.3 mm); lit. (39a) bp 76-81° (0.7-0.9 mm). The product showed a strong ir Sn-D stretching absorption at the calculated frequency of 1310 cm^{-1}. The nmr spectrum showed a maximum of approximately 0.1% tri-n-butyltin hydride.

endo- and exo-5-Bromonorbornene. -- In a procedure similar to that used by Roberts and co-workers (63), vinyl bromide (Aldrich Chemical Co., Inc.) and cyclopentadiene from freshly-cracked dicyclopentadiene (Matheson Coleman & Bell, practical grade, 95%) in approximately 1:1 molar ratios were heated in degassed, heavy-walled pyrex tubes at 160° for 12-20 hours. The product was distilled and the bromonorbornenes collected, bp 40-45° (4 mm); lit. (63) 63° (11.5 mm). The crude yield of bromonorbornenes was 35-50%, consisting of a mixture of endo/exo epimers in the ratio of about 60/40. The crude endo- and exo-5-bromonorbornenes were separated and purified by preparative gas chromatography on a Carbowax 20M column at 120-130°. The separated epimers were run through the chromatograph a second time to give endo-5-bromonorbornene of 99% minimum purity, and exo-5-bromonorbornene of 98% minimum

purity.*

2-Bromonortricyclene. -- Dr. J. B. Dence kindly supplied ample quantities of 2-bromonortricyclene, which he obtained as an undesired byproduct in the bromination of norbornene with N-bromosuccinimide (63). The crude 2-bromonortricyclene was purified by preparative gas chromatography on a Carbowax 20M column at 120-130°. The 2-bromonortricyclene so prepared had a minimum purity of 98%.**

1,2-Dibromoethane-d_4. -- In a procedure similar to that used by Leitch and Morse (64), 1,2-dibromoethane-d_4 was prepared by the addition of deuterium bromide to acetylene-d_2, with catalysis by ultraviolet light from a portable uv lamp. The acetylene-d_2 was generated from calcium carbide (Baker & Adamson, lump) and deuterium oxide (Columbia Organic Chemicals Co., 99.77% D). The deuterium bromide was prepared from phosphorus tribromide (Matheson Coleman & Bell, practical grade) and deuterium oxide.

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*exo-5-Bromonorbornene slowly isomerizes to 2-bromonortricyclene upon standing for periods of months or more, even when shielded from light and stored in a refrigerator. The same isomerization frequently occurs to the extent of up to 5% when exo-5-bromonorbornene is injected into a vpc injection port at temperatures above 140°. endo-5-Bromonorbornene is more stable, however, and shows no tendency to isomerize under similar conditions.

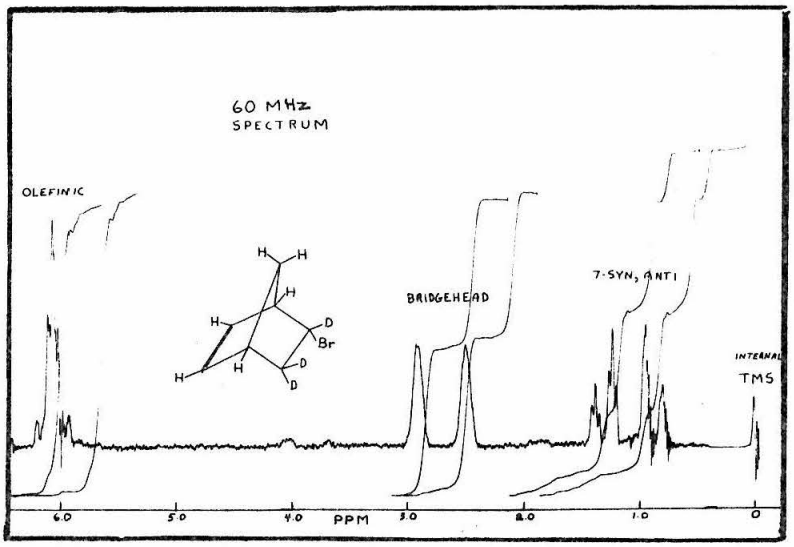
**2-Bromonortricyclene slowly isomerizes to exo-5-bromonorbornene upon standing for periods of months or more, even when shielded from light and stored in a refrigerator. The same isomerization frequently occurs to the extent of a very few per cent when 2-bromonortricyclene is injected into a vpc injection port at temperatures above about 140°.

A total of 65 g of 1,2-dibromoethane-$\underline{d}_4$ was prepared of bp 129-133°; lit. (64) bp 129.5°. The nmr spectrum of the product showed a deuterium content of approximately 96%.

Vinyl-$\underline{d}_3$ Bromide. -- By the procedure of Schaefer, Dagani, and Weinberg (65), 1,2-dibromoethane-$\underline{d}_4$ was dedeuterobrominated with potassium hydroxide in ethanol. Most of the product was distilled directly into a heavy-walled pyrex tube for the subsequent addition to cyclopentadiene. The nmr spectrum of the vinyl-$\underline{d}_3$ bromide showed a deuterium content of approximately 93%.

endo- and exo-5-Bromonorbornene-5,6,6-$\underline{d}_3$. -- From 9.0 ml (0.109 moles) of cyclopentadiene and 7.0 ml (0.095 moles) of vinyl-$\underline{d}_3$ bromide, in the procedure described for the preparation of endo- and exo-5-bromonorbornene, approximately 6 ml of a crude mixture of endo- and exo-5-bromonorbornene-$\underline{d}_3$ bp 40-45° at 2.0-4.0 mm was obtained. Preparative separation and purification of the epimeric bromides on a Carbowax 20M column gave about 2.5 ml (25% yield) of endo-5-bromonorbornene-$\underline{d}_3$ and 1.0 ml (9% yield) of exo-5-bromonorbornene-$\underline{d}_3$.

The endo-5-bromonorbornene-$\underline{d}_3$ prepared as described contained 2.5% of exo-5-bromonorbornene-$\underline{d}_3$ and 1.5% of 2-bromonortricyclene-$\underline{d}_3$. The mass spectrum showed a deuterium content of 2.88 deuteriums per molecule. The nmr spectrum showed that no deuterium scrambling had occured, and the product was deuterated 5,6,6.



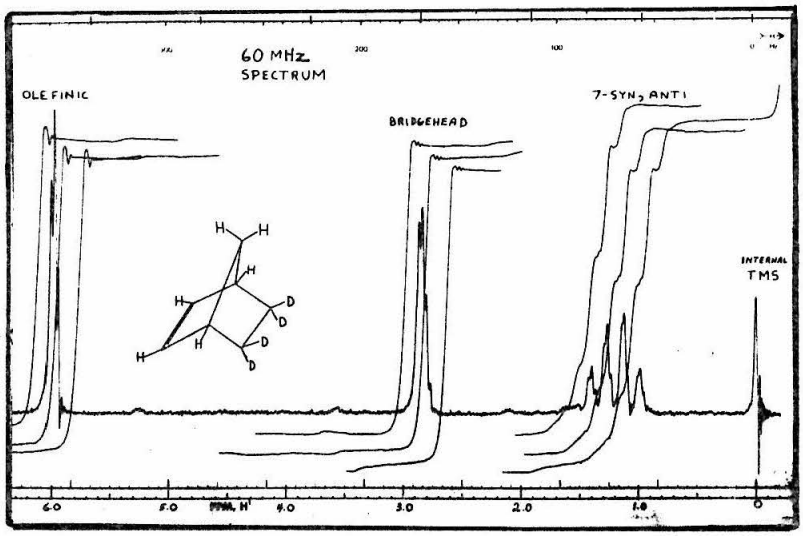
The nmr spectrum of endo-5-bromonorbornene-5, 6, 6-d_3.

The exo-5-bromonorbornene-d_3 was found to have a deuterium content of 2.86 deuteriums per molecule by mass-spectral analysis, but the nmr spectrum showed that substantial deuterium scrambling had occurred. This presumably occurred from a reversible isomerization of the exo-5-bromonorbornene-d_3 to 2-bromonortricyclene-d_3. The ^{13}C nmr spectrum of the exo-5-bromonorbornene-d_3, taken by Dr. John Grutzner, showed that the scrambling apparently came from skeletal rearrangement rather than proton or deuterium migrations, because there was no C-DH group in the scrambled product. Because

of the deuterium scrambling, the exo-5-bromonorbornene-d_3 was not used in any further studies.

Ethylene-d_4. -- In a procedure similar to that used by Leitch and Morse (64), 21.5 g (0.11 moles) of 1,2-dibromoethane-d_4 were debrominated with 30 g of zinc dust (Merck & Co., Inc., reagent grade, 94% minimum). The ethylene-d_4 was collected in a trap in liquid nitrogen, then used directly in the subsequent preparation of norbornene-5, 5, 6, 6-d_4.

Norbornene-5, 5, 6, 6-d_4. -- In a procedure used with minor modifications by several previous workers (66), the ethylene-d_4 from the preceding preparation and 7.0 ml (0.076 moles) of cyclopentadiene were added to a 50 ml stainless steel bomb and heated at 200° for 48 hours. The products were distilled from the bomb, and collected in a dry-ice-cooled trap acetone, the yield was 1.35 g. The crude product consisted of approximately 97% norbornene, 2% nortricyclene, and less than 1% cyclopentadiene, and no other volatile products in the vpc trace. The norbornene-d_4 was separated and purified by preparative gas chromatography with a tricresyl phosphate column at 80-90°. The mass spectrum showed 3.84 deuteriums per molecule. The nmr spectrum showed that no detectable scrambling of the deuteriums from the 5, 5, 6, 6-d_4 product expected had occurred.



The nmr spectrum of norbornene-5, 5, 6, 6-$\underline{d}_4$.

Part 3. Procedures.

The Reductions of endo- and exo-5-Bromonorbornene and 2-Bromonortricyclene with Tri-n-butyltin Hydride -

Procedure 1 - In Sealed Degassed Pyrex Tubes. -- In a typical reduction, the reactants and hexamethylethane internal standard were added to 8 mm heavy-walled pyrex tubes at room temperature. The tubes were then attached to a "cow" on a vacuum line, and freeze-thaw degassed at least twice to 10^{-2} to 10^{-4} torr, sealed, and placed in a turntable, or "merry-go-round", in an ethylene glycol/water bath at the appropriate reaction temperature. The samples were then irradiated at a distance of about 3 inches from the center of a pyrex well containing a Hanovia 450 watt high-pressure mercury lamp as the "merry-go-round" rotated to provide equal irradiation intensity to all samples. In some cases, a uranium glass filter was used to remove the irradiation of wavelength greater than 3550Å, resulting in substantially longer irradiation times being required to achieve nearly complete reduction * of the respective bromides than was

* Theoretically, it would be ideal to analyze samples after only a few per cent reduction. Unfortunately, however, there is often up to 1-2% reduction during the preparation of samples or in the heated injection port of the analytical vpc during product analyses when there is a substantial amount of unreacted bromide. Therefore, to minimize errors in the vpc analyses, it was necessary to take the reduction reactions to near completion before they were analyzed for the ratio of norbornene to nortricyclene.

required without the filter. After appropriate irradiation times, the tubes were removed from the "merry-go-round", opened, and their contents analyzed by vpc on the analytical TCP column with the injection port temperature at 70-80° and the column temperature at 80°. Samples were stored in dry ice in a stoppered dewar until analyzed if the analysis could not be done immediately following the irradiation period. Tables 12 and 13 list the reactants and analytical results for the reductions of endo-5-bromonorbornene and 2-bromonortricyclene, respectively, with tri-n-butyltin hydride at -5°.

Procedure 2 - Under Nitrogen at Atomospheric Pressure in Pyrex Tubes. -- In Procedure 1, if the samples were not irradiated for a sufficiently long time, the extent of reduction would be insufficient for accurate product ratio determination. If the samples were irradiated for longer times than were required for essentially complete reduction of the respective bromide, then the loss of norbornene, presumably by hydrostannation, became significant. It was desirable, therefore, to develop an experimental reduction technique in which the extent of reaction could be continuously monitored, and irradiation stopped at an appropriate time. This led to the adoption of Procedure 2.

In a typical reduction, each tube was flushed with dry nitrogen and placed in a bath at the temperature at which the reduction was to be performed. While the tube was kept flushed with nitrogen, the reactants were added, and the tube stoppered with a serum cap.

Table 12. The Reduction of endo-5-Bromonorbornene with Tri-n-butyltin Hydride at -5° in Sealed, Degassed Pyrex Tubes.

Tube No.	Bromide μℓ	Hydride mℓ	[Hydride] M/ℓ	Standard[a] μℓ	Toluene mℓ	Irradiation[b] min	[NB]/[NT][c]	Tot/HME[c, d]
1	10	1.0	3.67	10	0	240	1.73	3.50
2	10	0.9	3.30	10	0.1	270	1.72	3.19
3	10	0.8	2.93	10	0.2	300	1.63	3.56
4	10	0.7	2.55	10	0.3	330	1.59	3.66
5	10	0.6	2.18	10	0.4	broken during sealing		
6	10	0.5	1.81	10	0.5	360	1.485	3.68
7	10	0.4	1.45	10	0.6	390	1.455	3.69
8	10	0.3	1.07	10	0.7	420	1.44	3.54
9	10	0.2	0.70	10	0.8	450	1.40	3.67
10	10	0.1	0.34	10	0.9	430	1.34	2.65

[a] Standard solution of hexamethylethane in toluene, containing 0.2116 g of hexamethylethane per milliliter.

[b] A uranium glass filter was used to remove irradiation of wavelength less than 3550Å.

[c] Flame ionization vpc ratio.

[d] Tot/HME is the vpc ratio of norbornene plus nortricyclene to hexamethylethane. Theoretically, assuming 100% conversion of endo-5-bromonorbornene to norbornene and nortricyclene, the weight to weight ratio of the total to hexamethylethane should be 3.70.

Table 13. The Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride at -5° in Sealed, Degassed Pyrex Tubes.

Tube No.	Bromide μl	Hydride mℓ	[Hydride] M/ℓ	Standard[a] μl	Toluene mℓ	Irradiation[b] min	[NT]/[NB][c]	Tot/HME[c, d]
1	10	1.0	3.67	10	0	240	1.05	3.22
2	10	0.9	3.30	10	0.1	270	1.01	3.55
3	10	0.8	2.93	10	0.2	300	0.957	3.42
4	10	0.7	2.55	10	0.3	330	0.905	3.60
5	10	0.6	2.18	10	0.4	0- kept 5 days at 0°	0.85	1.86
6	10	0.5	1.81	10	0.5	360	0.86	3.31
7	10	0.4	1.45	10	0.6	390	0.835	3.81
8	10	0.3	1.07	10	0.7	420	0.81	3.80
9	10	0.2	0.70	10	0.8	450	0.813	1.94
10	10	0.1	0.34	10	0.9	480	0.773	2.28

[a] Standard solution of hexamethylethane in toluene, containing 0.2116 g of hexamethylethane per milliliter.

[b] A uranium glass filter was used to remove irradiation of wavelength less than 3550Å.

[c] Flame ionization vpc ratio.

[d] Tot/HME is the vpc ratio of norbornene plus nortricyclene to hexamethylethane internal standard. Theoretically, assuming 100% conversion of 2-bromonortricyclene to norbornene and nortricyclene, the weight to weight ratio of the total to hexamethylethane should be 3.85.

The filled tubes were then placed in the "merry-go-round" and irradiated as in Procedure 1. Samples were periodically removed from the tubes and analyzed by vpc to ensure that the irradiation was stopped after the reduction was near completion. The irradiated samples were stored in dry ice in a stoppered dewar until analyzed if analysis for norbornene and nortricyclene was not performed immediately following removal of the sample from the "merry-go-round", and for purposes of later comparison with other samples under identical vpc conditions. The reaction mixtures were analyzed by vpc on the analytical TCP column with the injection port temperature at 70-80°, and the column at 80°. Occasionally, where an nmr spectrum of the norbornene produced in a reduction reaction was desired, the reaction was done with larger quantities of reactants in a 10 mm standard-walled pyrex tube by the same procedure as outlined above. Tables 14 and 15 list the reactants and analytical results for the reductions of endo-5-bromonorbornene and 2-bromonortricyclene, respectively, with tri-n-butyltin hydride at -10°.

The Reductions of endo- and exo-5-Bromonorbornene and 2-Bromonortricyclene with Tri-n-butyltin Deuteride - All reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene were carried out by Procedure 2, in a manner analogous to the same reductions with tri-n-butyltin hydride.

Table 14. The Reduction of endo-5-Bromonorbornene with Tri-n-butyltin Hydride at -10° under Nitrogen at Atmospheric Pressure.

Tube No.	Bromide μl	Hydride mℓ	[Hydride] M/ℓ	Standard[a] μl	Toluene mℓ	Irradiation[b] min	[NB]/[NT][c]	Tot/HME[c, d]
1	10	1.0	3.67	10	0	260	1.71	2.43
2	10	0.9	3.30	10	0.1	267	1.65	3.55
3	10	0.8	2.93	10	0.2	193	1.60	2.85
4	10	0.7	2.55	10	0.3	112	1.545	4.23
5	10	0.6	2.18	10	0.4	180	1.50	4.15
6	10	0.5	1.81	10	0.5	227	1.46	3.28
7	10	0.4	1.45	10	0.6	300	1.42	2.20
8	10	0.3	1.07	10	0.7	580	1.385	4.60
9	10	0.2	0.70	10	0.8	580	1.35	4.52
10	10	0.1	0.34	10	0.9	3085	1.30	2.22

[a]Standard solution of hexamethylethane in toluene, containing 0.2116 g of hexamethylethane per milliliter.

[b]A uranium glass filter was used to remove irradiation with wavelength less than 3550 Å.

[c]Flame ionization vpc ratio.

[d]Tot/HME is the vpc ratio of norbornene plus nortricyclene to hexamethylethane internal standard. Theoretically, assuming 100% conversion of endo-5-bromonorbornene to norbornene and nortricyclene, the weight to weight ratio of the total to hexamethylethane should be 3.70. Apparently in some cases some internal standard has been lost.

Table 15. The Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride at -10° under Nitrogen at Atmospheric Pressure.

Tube No.	Bromide μℓ	Hydride mℓ	[Hydride] M/ℓ	Standard[a] μℓ	Toluene mℓ	Irradiation[b] min	[NT]/[NB][c]	Tot/HME[c, d]
1	10	1.0	3.67	10	0	10	1.050	2.17
2	10	0.9	3.30	10	0.1	25	1.022	3.69
3	10	0.8	2.93	10	0.2	25	0.984	3.65
4	10	0.7	2.55	10	0.3	25	0.940	4.05
5	10	0.6	2.18	10	0.4	25	0.904	2.92
6	10	0.5	1.81	10	0.5	50	0.876	3.95
7	10	0.4	1.45	10	0.6	50	0.857	3.34
8	10	0.3	1.07	10	0.7	170	0.835	3.31
9	10	0.2	0.70	10	0.8	170	0.800	3.37
10	10	0.1	0.34	10	0.9	170	0.785	3.27

[a]Standard solution of hexamethylethane in toluene, containing 0.2116 g of hexamethylethane per milliliter.

[b]No light filter was used.

[c]Flame ionization vpc ratio.

[d]Tot/HME is the vpc ratio of norbornene plus nortricyclene to hexamethylethane internal standard. Theoretically, assuming 100% conversion of 2-bromonortricyclene to norbornene and nortricyclene, the weight to weight ratio of the total to hexamethylethane should be 3.85.

The Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride or Tri-n-butyltin Deuteride - All reductions of endo-5-bromonorbornene-5, 6, 6-d_3 with tri-n-butyltin hydride or deuteride were carried out by Procedure 2, in a manner analogous to the reductions of undeuterated endo-5-bromonorbornene with tri-n-butyltin hydride or tri-n-butyltin deuteride.

Mass Spectral Analyses of the Undeuterated and Deuterated Norbornenes and Nortricyclenes Produced in the Reductions of endo- and exo-5-Bromonorbornene, 2-Bromonortricyclene, and endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride or Tri-n-butyltin Deuteride - The products of the respective reduction reactions were distilled at room temperature at pressures of about 1.0 torr. The volatiles were collected, and pentane added to the distillate from those samples which contained little or no toluene solvent. The distillate, or distillate/pentane solutions were then separated by preparative gas chromatography on the preparative TCP column at a column temperature of 80-90°. The norbornene and/or nortricyclene were collected in U-tubes made out of 8 mm standard-walled pyrex tubing, which were attached to the Prepmaster 775 manifold adapters with rubber sleeves. The U-tubes were then attached to a special "micro-cow" to which glass capillaries were connected. The system was evacuated to 10^{-1} - 10^{-2} torr while the norbornene or nortricyclene in the U-tube was kept in dry ice. The norbornene or nortricyclene was then distilled into the capillaries, which were then sealed off.

The mass spectra were taken by breaking the respective capillary in the inlet system of the mass spectrometer. Some mass spectral results are given in Table 16.

Table 16. Mass Spectra of Norbornene and Several Deuterated Norbornenes.[a]

m/e	Ref[b]	Norbornene[c]	Norbornene-5, 5, 6, 6-d_4	Norbornene-d_3[d]	Norbornene-d_4[e]
60	0.76	0.1	0.09	0.11	0.12
61	0.45	0.8	0.44	0.58	0.16
62	1.96	1.4	0.82	1.09	1.28
63	0.42	2.5	1.44	1.89	2.22
64	0.27	0.83	1.32	1.60	2.15
65	5.89	8.42	5.00	5.34	5.84
66	100.00	100.00	100.00	100.00	93.3
67	7.16	6.35	7.36	9.08	10.5
68	0.69	0.4	1.90	7.63	17.9
69	0.18	0.1	1.42	39.3	100.00
70	0.04	–	0.78	3.01	6.83
71	0.04	–	0.60	0.47	1.22
72	–	–	0.27	0.11	0.55
90	0.04	–	0.03	0.1	0.1
91	3.43	2.59	0.09	0.3	1.05
92	0.67	0.29	0.15	0.7	0.95
93	1.72	1.36	0.74	2.0	1.68
94	10.3	7.87	1.27	1.5	2.91
95	1.14	0.62	0.65	0.8	1.6
96	0.05	–	0.66	2.8	1.5
97	–	–	2.06	11.4	5.2
98	–	–	8.55	0.9	17.3
99	–	–	0.69	0.1	1.3
100	–	–	0.04	0.0	0.6

Table 16. (Cont'd)

[a] All spectra were taken at an ionizing voltage of 70 volts; all peaks are expressed in the usual manner as a percentage of the largest peak in the spectrum.

[b] From API reference tables (67).

[c] The norbornene was subjected to the usual reduction conditions, then separated by distillation and purified by vpc as an operating procedure checkout.

[d] From the reduction of endo-5-bromonorbornene-5, 6, 6, -$\underline{d}_3$ with 3.67 M tri-n-butyltin hydride; a mixture of norbornene-5, 6, 6-$\underline{d}_3$ and norbornene-1, 7, 7-$\underline{d}_3$.

[e] From the reduction of endo-5-bromonorbornene-5, 6, 6-$\underline{d}_3$ with 0.34 M tri-n-butyltin deuteride; a mixture of norbornene-5, 5, 6, 6-$\underline{d}_4$ and norbornene-1, 6, 7, 7-$\underline{d}_4$.

Part 4. Tests.

It was necessary to conduct several tests to confirm that the experimental results were being correctly interpreted, and that the results were not subject to major experimental errors. The tests were usually mentioned only in footnotes in earlier sections of the thesis text, but in most cases the results of the tests are vital to the conclusions reached in this thesis.

1. endo-5-Bromonorbornene and 2-Bromonortricyclene Do Not Isomerize Significantly under either Normal Reduction Conditions, or under Normal Analytical Vapor-Phase Chromatography Conditions -- After 765 minutes irradiation at -10°, through the uranium-glass filter, endo-5-bromonorbornene (minimum 99% with less than 1% of 2-bromonortricyclene as an impurity) in 0.34 M tri-n-butyltin hydride was found to retain a minimum purity of 99% endo-5-bromonorbornene, with the same original impurity of less than 1% of 2-bromonortricyclene. An identical test on a sample containing 2-bromonortricyclene (approximately 2% endo-5-bromonorbornene and exo-5-bromonorbornene) showed that the unreacted bromide was approximately 99% 2-bromonortricyclene with traces of endo- and exo-5-bromonorbornene present. An identical test on a sample containing endo-5-bromonorbornene-5, 6, 6-d_3 (approximately 1% exo-5-bromonorbornene-d_3 and 2% 2-bromonortricyclene-d_3) showed that the unreacted bromide was close to 99% endo isomer with traces

of the exo- and tricyclic isomers present. Although further quantitative tests were not conducted, the vpc charts from the analyses of samples for the ratio of norbornene to nortricyclene showed that there had been no appreciable isomerization of the unreacted bromide during the reductions of endo- or exo-5-bromonorbornene, 2-bromonortricyclene, or endo-5-bromonorbornene-5, 6, 6-d_3, even when the reductions were nearly complete, and only a small amount of unreacted bromide remains, in the reductions with either tri-n-butyltin hydride or tri-n-butyltin deuteride.

2. Unreacted endo-5-Bromonorbornene and 2-Bromonortricyclene in Tri-n-butyltin Hydride Do Not Undergo Significant Reduction under Normal Analytical Vapor-Phase Chromatography Conditions -- Samples of endo-5-bromonorbornene or 2-bromonortricyclene in neat tri-n-butyltin hydride, prepared by Procedure 2 at -10° show a maximum of less than 1% reduction when analyzed shortly after preparation and prior to any irradiation at an injection port temperature of 70-80°, and a column temperature of 80°.

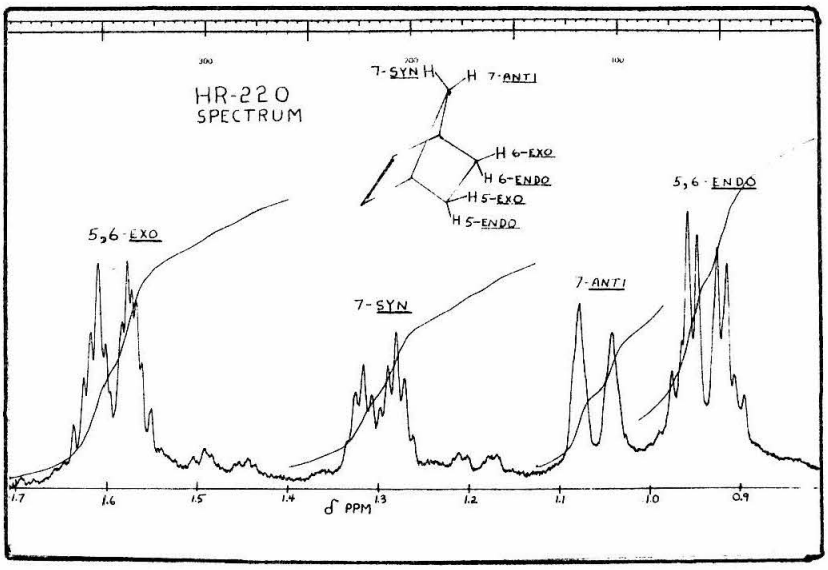
3. Loss or Rearrangement of Norbornene or Nortricyclene is Minor under Normal Reduction Conditions, or Normal Analytical Vapor-Phase Chromatography Conditions -- A standard solution containing norbornene and nortricyclene (w/w 1.22 ± 0.2) in toluene was prepared. The vpc ratio of norbornene to nortricyclene was 1.15 - 1.18 at injection port temperatures of 65-160° and a column temperature of 80°. Addition of 0.25 mole-percent of azoisobutyronitrile

resulted in no change in the ratio of norbornene to nortricyclene when the solution was analyzed at injection port temperatures of 65-160°. Addition of 50 mole-percent of bromocyclohexane plus a large molar excess of tri-n-butyltin hydride (with or without the azoisobutylronitrile initiator) to the standard solution resulted in no change in the ratio of norbornene to nortricyclene when this solution was analyzed at injection port temperatures of 65-160°, although the vpc chart showed that at 160°, most of the bromocyclohexane had been reduced to cyclohexane. However, when samples containing the standard solution, 50 mole-percent of bromocyclohexane, and a large excess of tri-n-butyltin hydride were irradiated without a filter for 10 minutes at 30°, the ratio of norbornene to nortricyclene had dropped to 1.13 (an internal standard indicated that the change was wholly due to loss of norbornene, presumably through hydrostannation), and the bromocyclohexane had been completely reduced. The loss of norbornene (presumably through hydrostannation) under the conditions used in the reductions of the 5-bromonorbornenes and 2-bromonortricyclene should not exceed the loss found in this test, except in reductions done by Procedure 1, where the samples might be irradiated long after essentially complete reduction because the extent of reaction was not monitored in this procedure. Therefore, in the reductions done by Procedure 2 there may be some error resulting from the loss of norbornene during the reduction, however, that error should be small.

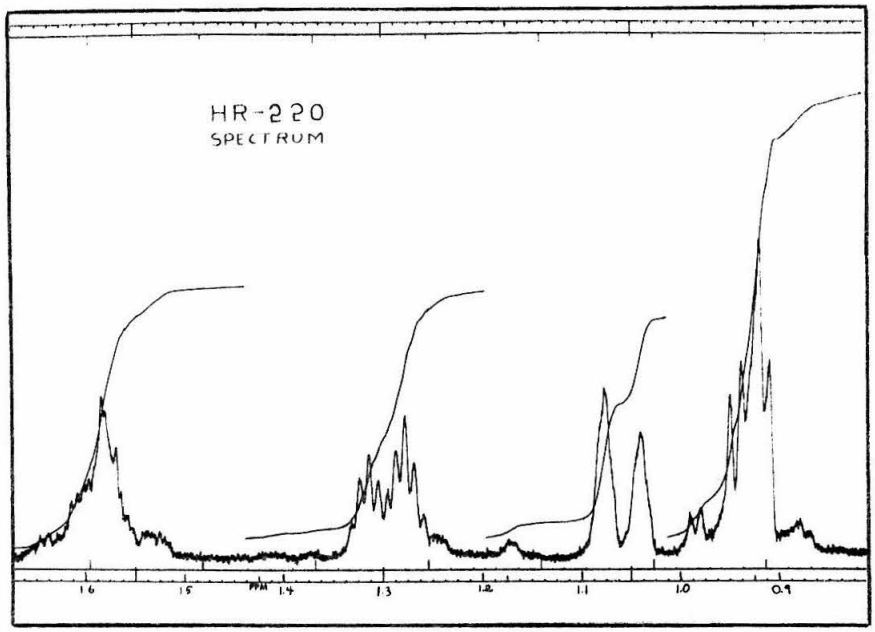
4. The Concentration of Tri-n-butyltin Hydride Does Not Decrease Significantly During the Reduction of endo-5-Bromonorbornene with Tri-n-butyltin Hydride at -10° -- 60 MHz nmr spectra of the reaction mixtures after the reduction of endo-5-bromonorbornene with various concentrations of tri-n-butyltin hydride at -10° was essentially complete were taken. From the hydride hydrogen of tri-n-butyltin hydride, which has a resonance frequency at δ 4.9, the final concentration of tri-n-butyltin hydride was unchanged from the original concentration (except for a small detectable loss in samples containing molar excesses of tri-n-butyltin hydride only several times that of the respective bromides being reduced, where the amount of tri-n-butyltin hydride lost was approximately equal to the number of moles of alkyl bromide reduced). Therefore, the pseudo-first-order kinetics employed throughout this thesis appear to be well founded.

5. endo- and exo-5-Bromonorbornene Form Stereochemically Identical Norbornene-d_1 upon Reduction with Tri-n-butyltin Deuteride at -10° -- Samples containing 0.1 ml of either endo- or exo-5-bromonorbornene in 2.6 ml of tri-n-butyltin deuteride were prepared by Procedure 2, and irradiated at -10° until the respective bromide was more than 90% reduced. The products were then distilled and the norbornene-d_1 from each sample was separated and purified by preparative gas chromatography on the preparative TCP column at an oven temperature of 80-90°. The 220 MHz nmr spectra of the region containing the resonance frequencies for protons in the 5-, 6-, and

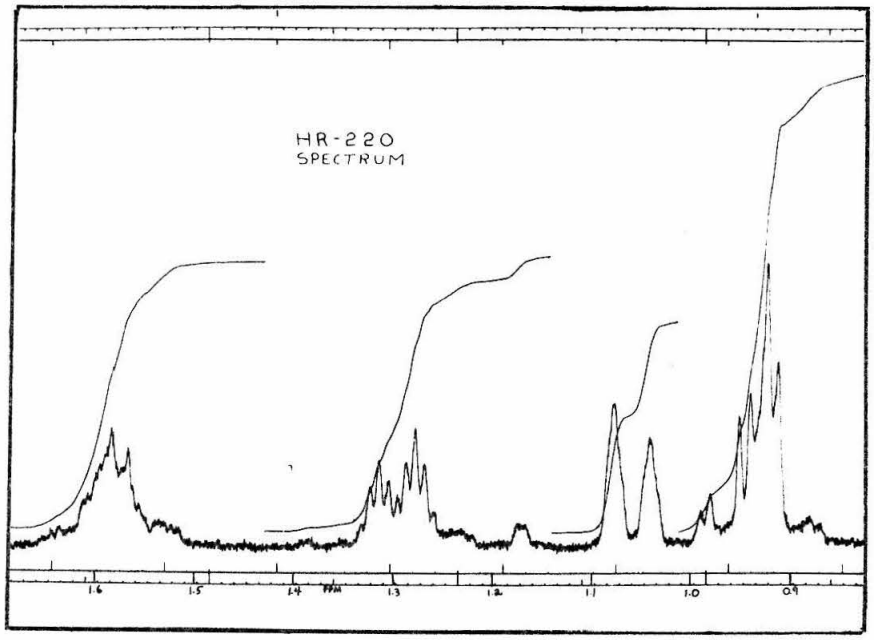
7-positions of norbornene show that the norbornene-$\underline{d}_1$ produced from the reductions of endo- and exo-5-bromonorbornene with tri-n-butyltin deuteride are stereochemically identical. Therefore, because there should be substantial "trapping" of the initially-generated 5-norbornenyl radicals before they isomerize to 2-nortricyclyl radicals under these reduction conditions, the 5-norbornenyl radicals generated from endo- and exo-5-bromonorbornene must be identical, or else interconvert rapidly relative to the isomerization of either to the 2-nortricyclyl radical. Table 17 compares the integrals from the 220 MHz nmr spectra of the 5-, 6-, and 7-protons of norbornene-$\underline{d}_1$ from the reductions of endo- and exo-5-bromonorbornene with tri-n-butyltin deuteride.



The 220 MHz nmr spectrum of the 5-, 6-, and 7-protons of norbornene.



The 220 MHz nmr spectrum of the 5-, 6-, and 7-protons of norbornene-$\underline{d}_1$ produced in the reduction of endo-5-bromonorbornene with neat tri-n-butyltin deuteride at -10°.



The 220 MHz nmr spectrum of the 5-, 6-, and 7-protons of norbornene-$\underline{d}_1$ produced in the reduction of exo-5-bromonorbornene with tri-n-butyltin deuteride at -10°.

Table 17. Proton Integrals from the 220 MHz nmr Spectra of the 5-, 6-, and 7-Positions of Norbornene-d_1 Produced in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Deuteride at -10°.

Position	Proton integral[a] Norbornene-d_1 (from n-NBBr)	Norbornene-d_1 (from x-NBBr)
5, 6-exo	1.16 ± 0.01	1.17 ± 0.01
5, 6-endo	1.95 ± 0.02	1.96 ± 0.01
7-syn	0.98 ± 0.01	0.97 ± 0.01
7-anti	0.91 ± 0.01	0.90 ± 0.01

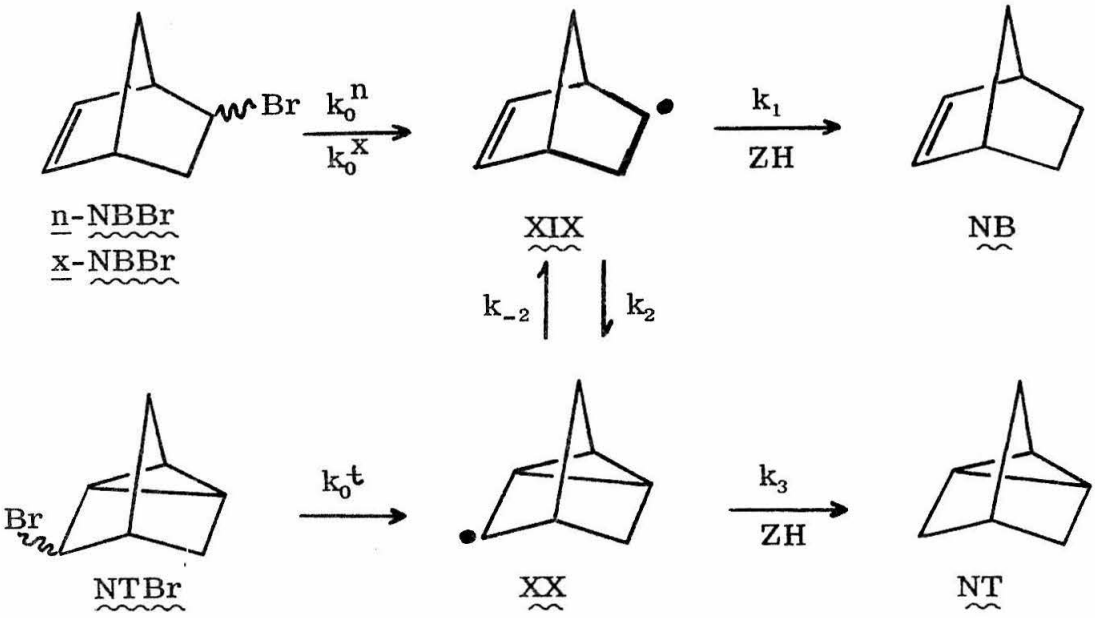
[a] Mass spectroscopy has shown that reduction of endo- and exo-5-bromonorbornene with tri-n-butyltin deuteride adds 1.00 deuteriums per molecule, so in the 5-, 6-, and 7-positions of the norbornene-d_1 there should be 5.00 hydrogens and 1.00 deuteriums per molecule. Errors in the integrals are the approximate errors expected assuming that the nmr spectral integrals are correct. Relatively, these are fair error limits, because the spectra were run under identical conditions. Absolutely, however, the errors in the integrals would be much greater than the errors listed, explaining the low values for the 7-protons and the high total for the 5- and 6-protons.

6. Norbornene-5, 5, 6, 6-$\underline{d}_4$ Does Not Undergo Any Deuterium Scrambling Prior to Undergoing a Retro Diels-Alder Fragmentation upon Ionization in the Mass Spectrometer -- From the mass spectrum of norbornene-5, 5, 6, 6-$\underline{d}_4$ listed in Table 16, it is apparent that the fragment at m/e 66 comes from the cyclopentadienyl ion formed in a retro Diels-Alder fragmentation process. The absence of any significant peaks at m/e 68-70 implies that the peaks at m/e 66 and m/e 69 should provide an accurate means of determining the ratios of norbornene 5, 6, 6-$\underline{d}_3$ to norbornene-1, 7, 7-$\underline{d}_3$ and norbornene-5, 5, 6, 6-$\underline{d}_4$ to norbornene-1, 6, 7, 7-$\underline{d}_4$ in our studies of skeletal rearrangement during the reduction of endo-5-bromo-norbornene-5, 6, 6-$\underline{d}_3$ with tri-n-butyltin hydride or tri-n-butyltin deuteride.

7. Norbornene-5, 5, 6, 6-$\underline{d}_4$ Does Not Undergo Any Significant Deuterium Scrambling under the Normal Conditions Used for the Reduction of endo-5-bromonorbornene-5, 6, 6-$\underline{d}_3$ with Tri-n-butyltin Hydride or Tri-n-butyltin Deuteride -- Samples of norbornene-5, 5, 6, 6-$\underline{d}_4$ in large excesses of tri-n-butyltin hydride or tri-n-butyltin deuteride, or 1/1 (v/v) hydride or deuteride in toluene, plus 10 mole-percent of bromocyclohexane were subjected to irradiation times up to several times longer than required to completely reduce the bromocyclohexane at -8°. The mass spectra of the norbornene isolated from these samples showed no significant changes from the mass spectrum of norbornene-5, 5, 6, 6-$\underline{d}_4$, even when the samples had been subjected to conditions sufficiently severe to result in the loss

of a considerable percentage of the norbornene initially present in the sample (again presumably through hydrostannation).

Appendix I. Mechanism I – Simple Reversible Isomerization of the 5-Norbornenyl Radical (XIX) and the 2-Nortricyclyl Radical (XX).



ZH represents the hydrogen donor, tri-n-butyltin hydride.

(a) The Ratio of Norbornene to Nortricyclene in the Free-Radical Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Hydride.

From (n-NBBr) or (x-NBBr),

$$\frac{d[NB]}{dt} = k_1[XIX][ZH] \qquad (A.I.1)$$

$$\frac{d[\underset{\sim}{NT}]}{dt} = k_3[\underset{\sim}{XX}][ZH]. \qquad (A.I.2)$$

From the stationary state hypothesis, *

$$\frac{d[\underset{\sim}{XX}]}{dt} = k_2[\underset{\sim}{XIX}] - k_2[\underset{\sim}{XX}] - k_3[\underset{\sim}{XX}][ZH] \simeq 0 \qquad (A.I.3)$$

then,

$$[\underset{\sim}{XX}] \simeq \frac{k_2[\underset{\sim}{XIX}]}{k_{-2} + k_3[ZH]}. \qquad (A.I.4)$$

Now,

$$\frac{\frac{d[\underset{\sim}{NB}]}{dt}}{\frac{d[\underset{\sim}{NT}]}{dt}} = \frac{k_1[\underset{\sim}{XIX}][ZH]}{k_3[\underset{\sim}{XX}][ZH]} \simeq \frac{[\underset{\sim}{NB}]}{[\underset{\sim}{NT}]}. \qquad (A.I.5)$$

Because the concentration of the hydrogen donor, tri-n-butyltin hydride is always much greater than the concentration of the alkyl halide being reduced, it may assumed to be constant throughout the reduction, allowing us to use pseudo-first-order kinetics.

Substitution of (A.I.4) into (A.I.5) gives,

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*Throughout the kinetic treatment in Appendices I-III, the stationary state hypothesis is used. From the absolute reaction rates determined by Carlsson and Ingold (46), and the equations developed by Benson (68), it can be shown that this hypothesis will introduce no significant errors in our results.

$$\frac{[\underset{\sim}{NB}]}{[\underset{\sim}{NT}]} \simeq \frac{k_1[\underset{\sim}{XIX}][ZH]}{k_3\left(\frac{k_2[\underset{\sim}{XIX}]}{k_{-2}+k_3[ZH]}\right)[ZH]}$$

$$\simeq \frac{k_1(k_{-2}+k_3[ZH])}{k_2k_3} \qquad \text{(A.I.6)}$$

$$\simeq \frac{k_1 k_{-2}}{k_2 k_3} + \frac{k_1}{k_2}[ZH]$$

$$\simeq A + B[ZH]$$

where,

$$A = \frac{k_1 k_{-2}}{k_2 k_3} \qquad B = \frac{k_1}{k_2}$$

(b) <u>The Ratio of Nortricyclene to Norbornene in the Free-Radical Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride.</u>

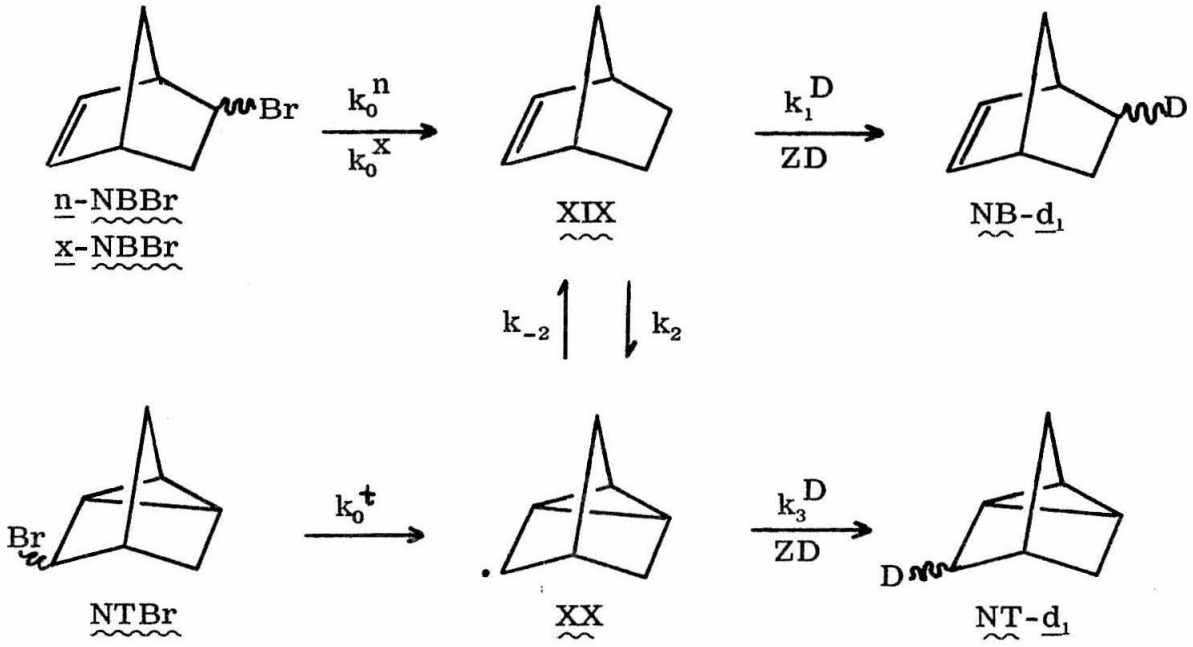
From steps analogous to those used in equations (A.I.1) through (A.I.6), it can be shown that from $\underset{\sim}{NTBr}$,

$$\frac{[\underset{\sim}{NT}]}{[\underset{\sim}{NB}]} \simeq \frac{k_2 k_3}{k_1 k_{-2}} + \frac{k_3}{k_{-2}}[ZH] \qquad \text{(A.I.7)}$$

$$\simeq \frac{1}{A} + \frac{B}{A}[ZH].$$

(c) The Ratio of Norbornene-d_1 to Nortricyclene-d_1 in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Deuteride.

In the reductions of (n-NBBr), (x-NBBr), and (NTBr) with tri-n-butyltin deuteride, the rates of deuterium abstraction by (XIX) and (XX) will be lower than k_1 and k_3 by factors equal to the primary kinetic deuterium isotope effect in each case.



ZD represents the deuterium donor, tri-n-butyltin deuteride, and,

$$k_1^D = \frac{k_1}{\epsilon_1} \qquad \text{(A. I. 8)}$$

and

$$k_3^D = \frac{k_3}{\epsilon_3} \qquad \text{(A. I. 9)}$$

where ϵ_1 and ϵ_3 are the primary kinetic deuterium isotope effects for the abstraction reactions of (XIX) and (XX), respectively. Then in the reductions of endo- and exo-5-bromonorbornene, substitution of (A. I. 8) and (A. I. 9) into (A. I. 6) gives,

$$\frac{[NB\text{-}d_1]}{[NT\text{-}d_1]} \simeq \frac{k_1 \epsilon_3 k_{-2}}{k_2 \epsilon_1 k_3} + \frac{k_1}{\epsilon_1 k_2}[ZD]. \qquad \text{(A. I. 10)}$$

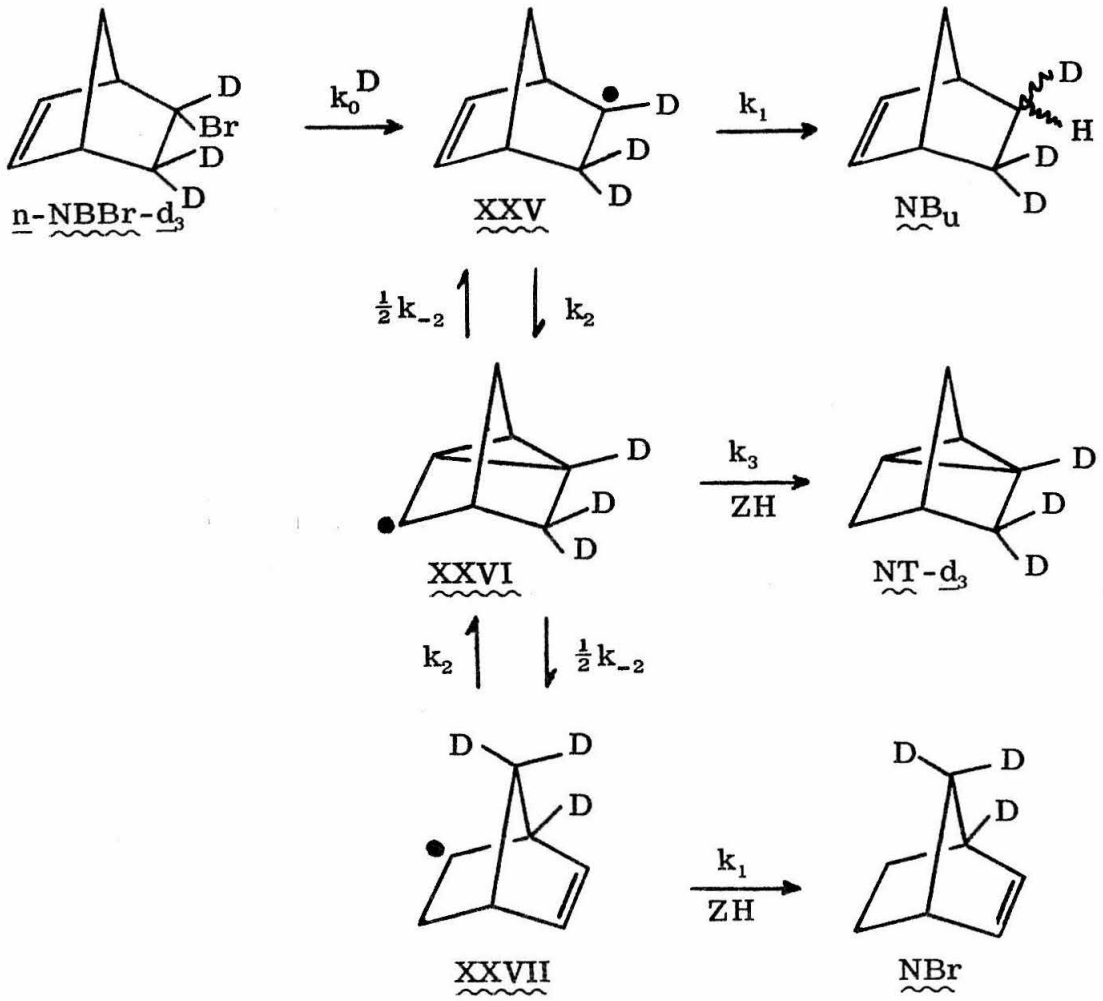
(d) The Ratio of Nortricyclene-d_1 to Norbornene-d_1 in the Reduction of 1-Bromonortricyclene with Tri-n-butyltin Deuteride.

Substitution of (A. I. 8) and (A. I. 9) into (A. I. 7) gives,

$$\frac{[NT\text{-}d_1]}{[NB\text{-}d_1]} = \frac{k_3 \epsilon_1 k_2}{k_1 \epsilon_3 k_{-2}} + \frac{k_3}{\epsilon_3 k_{-2}}[ZD]. \qquad \text{(A. I. 11)}$$

(e) Skeletal Rearrangement During the Reduction of endo-5-Bromonorbornene-5, 6, 6, -d_3 with Tri-n-butyltin Hydride.

(1) -- Assuming there are no significant secondary kinetic deuterium isotope effects present.



Now,

$$\frac{\frac{d[NB_u]}{dt}}{\frac{d[NB_r]}{dt}} = \frac{k_1[XXV][ZH]}{k_1[XXVII][ZH]} \simeq \frac{NB_u}{NB_r} \qquad \text{(A.I.12)}$$

but,

$$\frac{d[\underset{\sim}{\text{XXVII}}]}{dt} = \frac{1}{2} k_{-2}[\underset{\sim}{\text{XXVI}}] - k_2[\underset{\sim}{\text{XXVII}}] - k_1[\underset{\sim}{\text{XXVII}}][ZH] \simeq 0 \qquad \text{(A.I.13)}$$

or,

$$[\underset{\sim}{\text{XXVII}}] \simeq \frac{\frac{1}{2} k_{-2}[\underset{\sim}{\text{XXVI}}]}{k_2 + k_1[ZH]} \qquad \text{(A.I.14)}$$

and,

$$\frac{d[\underset{\sim}{\text{XXVI}}]}{dt} = k_2[\underset{\sim}{\text{XXV}}] + k_2[\underset{\sim}{\text{XXVII}}] - \tfrac{1}{2}k_{-2}[\underset{\sim}{\text{XXVI}}] - \tfrac{1}{2}k_{-2}[\underset{\sim}{\text{XXVI}}] - k_3[\underset{\sim}{\text{XXVI}}][ZH] \simeq 0. \qquad \text{(A.I.15)}$$

Substituting (A.I.14) into (A.I.15) gives,

$$k_2[\underset{\sim}{\text{XXV}}] - k_{-2}[\underset{\sim}{\text{XXVI}}] - k_3[\underset{\sim}{\text{XXVI}}][ZH] + \frac{\frac{1}{2}k_2 k_{-2}[\underset{\sim}{\text{XXVI}}]}{k_2 + k_1[ZH]} \simeq 0 \qquad \text{(A.I.16)}$$

or,

$$[\underset{\sim}{\text{XXVI}}] \simeq \frac{k_2[\underset{\sim}{\text{XXV}}]}{k_{-2} + k_3[ZH] - \left(\frac{\frac{1}{2}k_2 k_{-2}}{k_2 + k_1[ZH]} \right)}. \qquad \text{(A.I.17)}$$

Substitution of (A.I.14) into (A.I.12) gives,

$$\frac{[\underset{\sim}{\text{NB}_u}]}{[\underset{\sim}{\text{NB}_r}]} \simeq \frac{k_1[\underset{\sim}{\text{XXV}}][ZH]}{\left(\frac{\frac{1}{2}k_1 k_{-2}[\underset{\sim}{\text{XXVI}}][ZH]}{k_2 + k_1[ZH]} \right)} \qquad \text{(A.I.18)}$$

and substitution of (A.I.17) into (A.I.18) gives,

$$\frac{[\underset{\sim}{\sim}NB_u]}{[\underset{\sim}{\sim}NB_r]} \simeq \frac{k_1[\underset{\sim}{\sim}XXV][ZH]\,(k_2 + k_1[ZH])}{\frac{1}{2}k_1 k_{-2}[ZH]\left(\frac{k_2[\underset{\sim}{\sim}XXV](k_2 + k_1[ZH])}{(k_{-2}+k_3[ZH])(k_2+k_1[ZH]) - \frac{1}{2}k_2 k_{-2}}\right)}$$

$$\simeq \frac{(k_1k_2+k_1k_1[ZH])(k_{-2}k_2+k_1k_{-2}[ZH]+k_2k_3[ZH]-\frac{1}{2}k_2k_{-2}+k_1k_3[ZH]^2)}{\frac{1}{2}k_1k_2(k_2k_2 + k_1k_2[ZH])}$$

$$\simeq \frac{k_1 k_2 k_2 k_{-2} + (2 k_1 k_2 k_2 k_3 + 3 k_1 k_1 k_2 k_{-2})[ZH]}{k_1 k_2 k_2 k_{-2} + k_1 k_1 k_2 k_{-2}[ZH]}$$

$$+ \frac{(2 k_1 k_1 k_{-2} + 4 k_1 k_1 k_2 k_3)[ZH]^2 + 2 k_1 k_1 k_1 k_3[ZH]^3}{k_1 k_2 k_2 k_{-2} + k_1 k_1 k_2 k_{-2}[ZH]}. \qquad \text{(A.I.19)}$$

Division of (A.I.19) by $k_1k_2k_2k_{-2}$ gives,

$$\frac{[\underset{\sim}{\sim}NB_u]}{[\underset{\sim}{\sim}NB_r]} \simeq \frac{1+\left(\frac{2k_3}{k_{-2}}+\frac{3k_1}{k_2}\right)[ZH]+\left(\frac{2k_1k_1}{k_2k_2}+\frac{4k_1k_3}{k_2k_{-2}}\right)[ZH]^2+\frac{2k_1k_1k_3}{k_2k_2k_{-2}}[ZH]^3}{1 + \frac{k_1}{k_2}[ZH]}.$$

(A.I.20)

But, from (A.I.6),

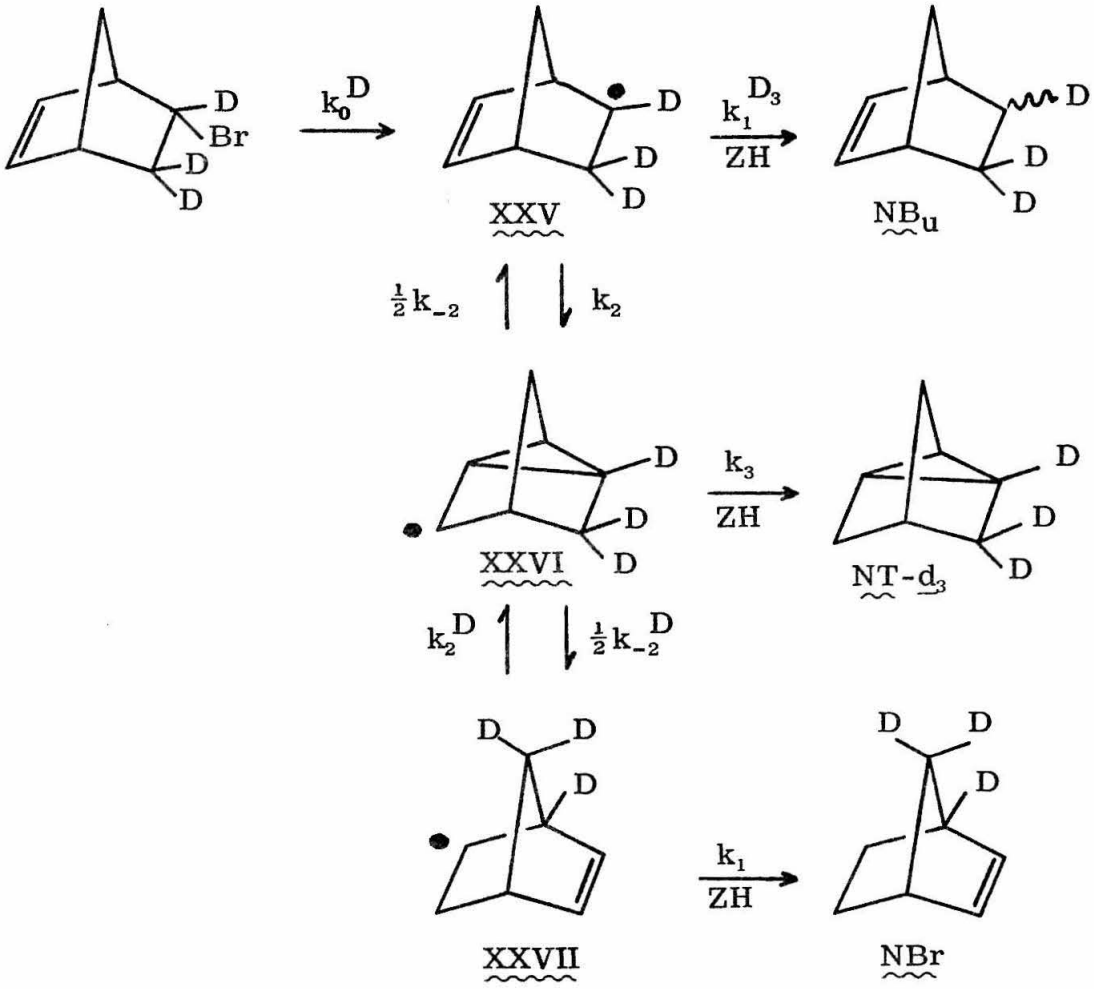
$$\frac{k_1}{k_2} = B \qquad \text{and} \qquad \frac{k_1 k_{-2}}{k_2 k_3} = A.$$

Substitution of A and B into (A.I.20), and rearrangement, gives,

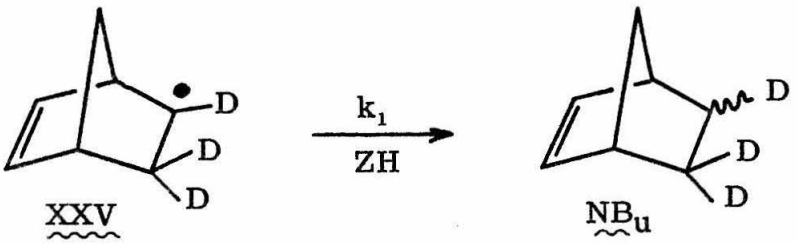
$$\frac{[\underset{\sim}{NBu}]}{[\underset{\sim}{NBr}]} \simeq \frac{1 + (3B + \frac{2B}{A})[ZH] + (2B^2 + \frac{4B^2}{A})[ZH]^2 + \frac{2B^2}{A}[ZH]^3}{1 + B[ZH]}$$

$$\simeq 1 + 2(B + \frac{B}{A})[ZH] + \frac{2B^2}{A}[ZH]^2. \qquad \text{(A.I.21)}$$

(2) -- Allowing for secondary kinetic deuterium isotope effects.

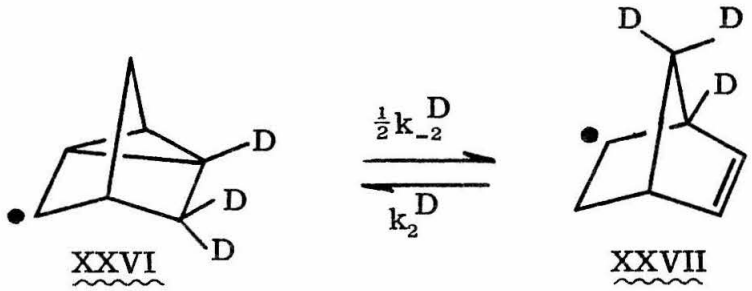


The hybridization of deuterium-bearing carbons changes substantially during two reactions. In the first,



XXV NBu

an $\underline{\alpha}$ secondary deuterium isotope effect for a C-$\underline{d}$ bond which should be approximately sp^2 that becomes approximately sp^2 in the product is expected. In the second,



XXVI XXVII

in the direction (XXVI) → (XXVII), a $\underline{\beta}$ secondary deuterium isotope effect for a C-$\underline{d}$ bond which should be approximately sp^2 in (XXVI) that becomes approximately sp^3 in (XXVII) is expected. In the direction (XXVII) → (XXVI), a $\underline{\beta}$ secondary deuterium isotope effect for a C-$\underline{d}$ bond which should be approximately sp^3 in (XXVII) that becomes approximately sp^2 in (XXVI) is expected.

(i) -- Assuming $k_1^{D_3} = \frac{k_1}{\alpha}$, and no other secondary deuterium isotope are significant.

Then from (A. I. 12), it can be seen that,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{k_1}{\alpha} \frac{[\underset{\sim}{XXV}][ZH]}{k_1[\underset{\sim}{XXVII}][ZH]} \qquad \text{(A. I. 22)}$$

so the constant α will follow through in equations analogous to (A. I. 13) through (A. I. 21) to give,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{1}{\alpha}\left(1 + 2\left(B + \frac{B}{A}\right)[ZH] + 2\frac{B^2}{A}[ZH]^2\right). \qquad \text{(A. I. 23)}$$

(ii) -- Assuming $\frac{1}{2}k_{-2}^D = \frac{1}{2}\frac{k_{-2}}{\beta}$ and $k_2^D = \beta k_2$ (i. e., the $\underline{\beta}$ secondary deuterium isotope effects are equal in magnitude,* but opposite in direction, in the reversible isomerization ($\underset{\sim}{XXVI}$) $\rightleftharpoons$ ($\underset{\sim}{XXVII}$)), and no other significant secondary deuterium isotope effects are present. Then, using equations analogous to (A. I. 12) through (A. I. 20), gives,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{\beta^2 + \left(2\beta^2\frac{k_3}{k_{-2}} + (2\beta+1)\frac{k_3}{k_{-2}}\right)[ZH]}{1 + \frac{k_1}{\beta k_2}[ZH]}$$

$$+ \frac{\left((1+\frac{1}{\beta})\frac{k_1k_1}{k_2k_2} + 4\beta\frac{k_1k_3}{k_2k_{-2}}\right)[ZH]^2 + 2\frac{k_1k_1k_3}{k_2k_2k_{-2}}[ZH]^3}{1 + \frac{k_1}{\beta k_2}[ZH]}. \qquad \text{(A. I. 24)}$$

---

* It would indeed be fortuitous if the effects should be exactly equal in magnitude. However, they are unlikely to be greatly different, so to simplify the equations, this assumption is being used.

Substitution of A and B from (A. I. 6) into (A. I. 24) gives,

$$\frac{[\underset{\sim}{\sim}NB_u]}{[\underset{\sim}{\sim}NB_r]} \simeq \beta^2 + (\beta+1)\,B[ZH] + 2\beta^2\frac{B}{A}[ZH] + 2\beta\frac{B^2}{A}[ZH]^2. \quad \text{(A. I. 25)}$$

(f) The Ratio of Norbornene-$\underline{d}_3$ to Nortricyclene-$\underline{d}_3$ in the Reduction of endo-5-Bromonorbornene-5, 6, 6-$\underline{d}_3$ with Tri-n-butyltin Hydride when Secondary Deuterium Isotope Effects are Considered.

(i) -- As in (e-2-i), where $k_1^{D_3} = \frac{k_1}{\alpha}$ and no other significant secondary deuterium isotope effects are present. Then steps analogous to (A. I. 12) through (A. I. 20) give,

$$\frac{[\underset{\sim}{\sim}NB_u]+[\underset{\sim}{\sim}NB_r]}{[\underset{\sim}{\sim}NT\text{-}\underline{d}_3]} \simeq \frac{\alpha-1}{2\alpha}\left(\frac{k_1k_{-2}}{k_2k_3+k_1k_3[ZH]}\right) + \frac{1}{\alpha}\left(\frac{k_1k_{-2}}{k_2k_3} + \frac{k_1}{k_2}[ZH]\right). \quad \text{(A. I. 26)}$$

Substitution of A and B from (A. I. 6) into (A. I. 26) gives,

$$\frac{[\underset{\sim}{\sim}NB_u]+[\underset{\sim}{\sim}NB_r]}{[\underset{\sim}{\sim}NT\text{-}\underline{d}_3]} \simeq \frac{\alpha-1}{\alpha}\left(\frac{A}{1+B[ZH]}\right) + \frac{1}{\alpha}(A+B[ZH]). \quad \text{(A. I. 27)}$$

(ii) -- As in (e-2-ii), where $\frac{1}{2}k_{-2}^{D} = \frac{1}{2}\frac{k_{-2}}{\beta}$ and $k_2^{D} = \beta k_2$ but no other significant secondary deuterium isotope effects are present. Then steps analogous to (A. I. 12) through (A. I. 20) give,

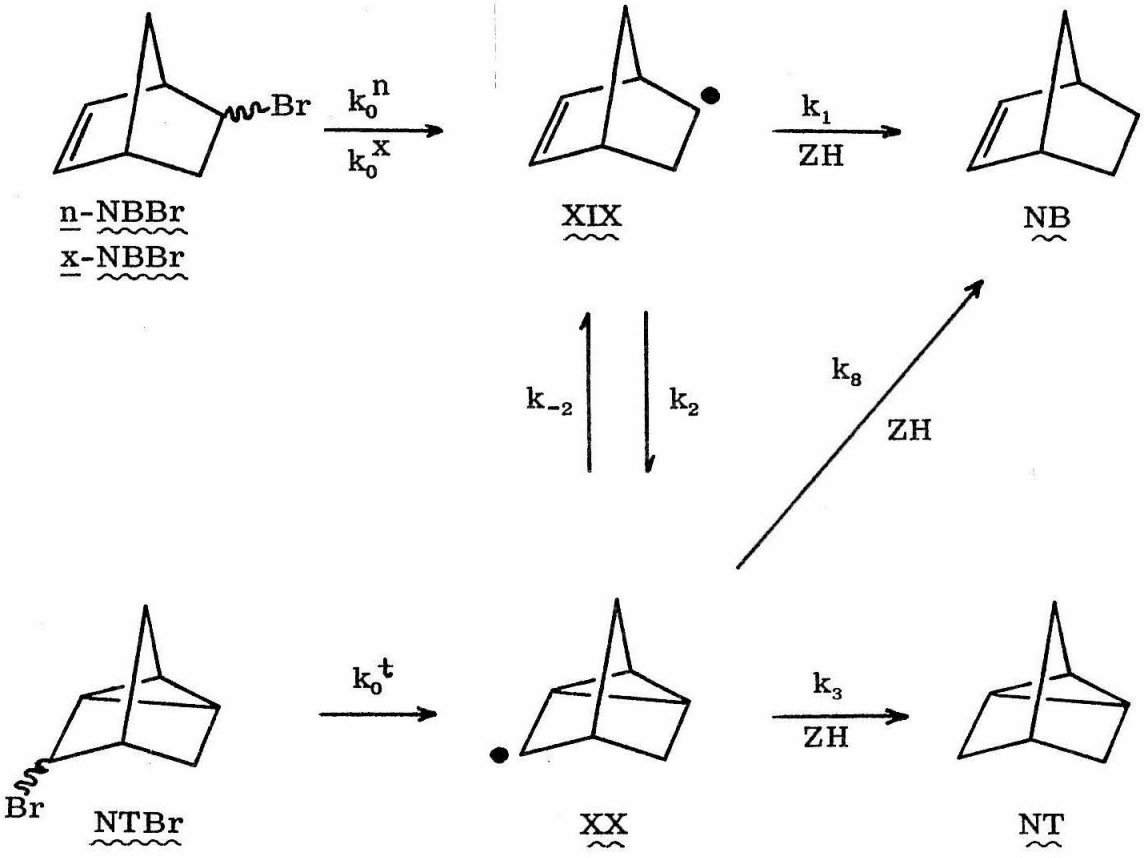
$$\frac{[\underset{\sim}{\sim}NB_u]+[\underset{\sim}{\sim}NB_r]}{[\underset{\sim}{\sim}NT-\underline{d}_3]} \simeq \left(\frac{1-\beta}{2\beta}\right)\left(\frac{k_1k_2}{\beta k_2k_3+k_1k_3[ZH]}\right)+\left(\frac{\beta+1}{2\beta}\right)\frac{k_1k_{-2}}{k_2k_3}+\frac{k_1}{k_2}[ZH]. \quad \text{(A.I.28)}$$

Substitution of A and B from (A.I.6) into (A.I.28) gives,

$$\frac{[\underset{\sim}{\sim}NB_u]+[\underset{\sim}{\sim}NB_r]}{[\underset{\sim}{\sim}NT-\underline{d}_3]} \simeq \left(\frac{1-\beta}{2\beta}\right)\left(\frac{A}{\beta+B[ZH]}\right)+\left(\frac{\beta+1}{2\beta}\right)A + B[ZH]. \quad \text{(A.I.29)}$$

Appendix II. Mechanism II – Complex Reversible Isomerization of the 5-Norbornenyl Radical (XIX) and the 2-Nortricyclyl Radical (XX), with Crossed Product Formation.

A. Where Norbornene Can Be Formed from the 2-Nortricyclyl Radical.



(a) The Ratio of Norbornene to Nortricyclene in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Hydride.

From n-NBBr or x-NBBr,

$$\frac{d[NB]}{dt} = k_1[XIX][ZH] + k_3[XX][ZH] \qquad \text{(A. II. 1)}$$

and,

$$\frac{d[NT]}{dt} = k_3[XX][ZH] \qquad \text{(A. II. 2)}$$

or,

$$\frac{\frac{d[NB]}{dt}}{\frac{d[NT]}{dt}} = \frac{k_1[XIV][ZH] + k_8[XX][ZH]}{k_3[XX][ZH]} \qquad \text{(A. II. 3)}$$

but,

$$\frac{d[XX]}{dt} = k_2[XIX] - k_{-2}[XX] - k_8[XX][ZH] - k_3[XX][ZH] \simeq 0 \qquad \text{(A. II. 4)}$$

therefore,

$$[XIX] \simeq \frac{(k_{-2} - k_8[ZH] + k_3[ZH])[XX]}{k_2} . \qquad \text{(A. II. 5)}$$

Substitution of (A. II. 5) into (A. II. 3) gives,

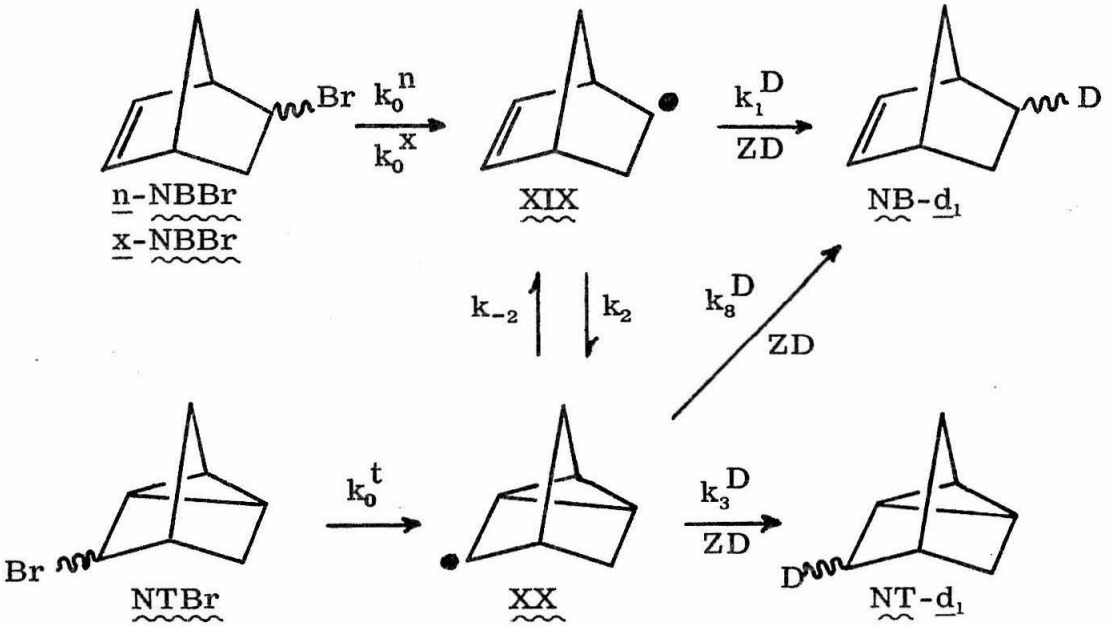
$$\frac{[\underset{\sim}{NB}]}{[\underset{\sim}{NT}]} \simeq \frac{k_1(k_{-2} + k_s[ZH] + k_3[ZH]) + k_2 k_s}{k_2 k_3}$$

$$\simeq \frac{k_1 k_{-2} + k_2 k_s}{k_2 k_3} + \frac{k_1(k_3 + k_s)[ZH]}{k_2 k_3} . \qquad \text{(A. II. 6)}$$

(b) The Ratio of Nortricyclene to Norbornene in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride.

$$\frac{[\underset{\sim}{NT}]}{[\underset{\sim}{NB}]} \simeq \frac{k_2 k_3 + k_1 k_3[ZH]}{k_1 k_{-2} + k_2 k_s + k_1 k_s[ZH]} . \qquad \text{(A. II. 7)}$$

(c) The Ratio of Norbornene-d_1 to Nortricyclene-d_1 in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Deuteride.



Assuming that,

$$k_1^D = \frac{k_1}{\epsilon_1} \quad \text{and} \quad k_3^D = \frac{k_3}{\epsilon_3} \quad \text{and} \quad k_8^D = \frac{k_8}{\epsilon_8}$$

then substitution of these constants into (A. II. 6) gives,

$$\frac{[\underset{\sim}{\sim}\underset{\sim}{\text{NB}}\text{-}\underline{d}_1]}{[\underset{\sim}{\sim}\underset{\sim}{\text{NT}}\text{-}\underline{d}_1]} \simeq \frac{\frac{k_1k_{-2}}{\epsilon_1} + \frac{k_2k_8}{\epsilon_8}}{\frac{k_2k_3}{\epsilon_3}} + \frac{\frac{k_1}{\epsilon_1}\left(\frac{k_3}{\epsilon_3} + \frac{k_8}{\epsilon_8}\right)[ZD]}{\frac{k_2k_3}{\epsilon_3}} . \qquad \text{(A. II. 8)}$$

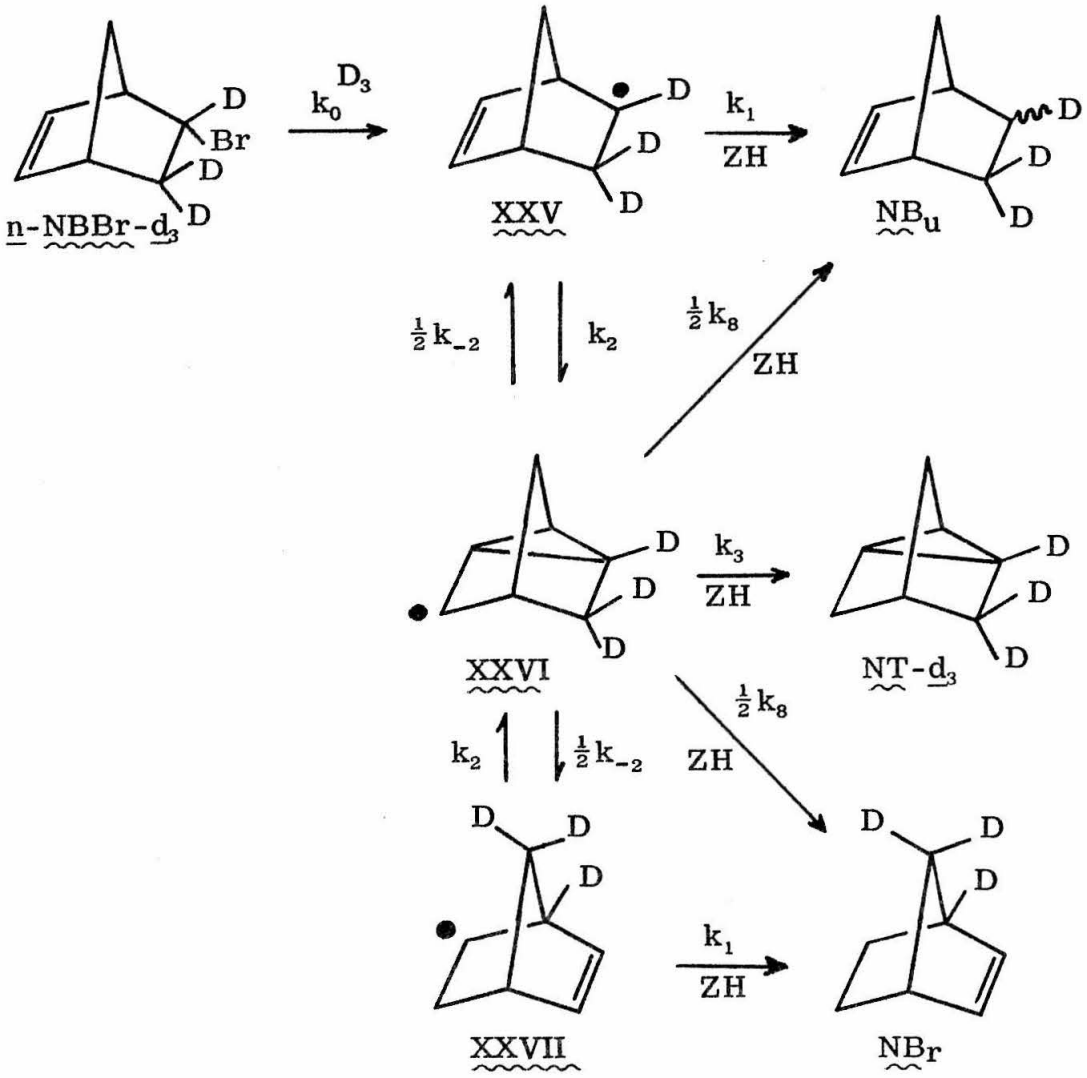
(d) The Ratio of Nortricyclene-$\underline{d}_1$ to Norbornene-$\underline{d}_1$ in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Deuteride.

Substitution of the rate constants used to derive (A. II. 8) into (A. II. 7) gives,

$$\frac{[\underset{\sim}{\sim}\underset{\sim}{\text{NT}}\text{-}\underline{d}_1]}{[\underset{\sim}{\sim}\underset{\sim}{\text{NB}}\text{-}\underline{d}_1]} \simeq \frac{\frac{k_2k_3}{\epsilon_3} + \frac{k_1k_3}{\epsilon_1\epsilon_3}[ZD]}{\frac{k_1k_{-2}}{\epsilon_1} + \frac{k_2k_8}{\epsilon_8} + \frac{k_1k_8}{\epsilon_1\epsilon_8}[ZD]} . \qquad \text{(A. II. 9)}$$

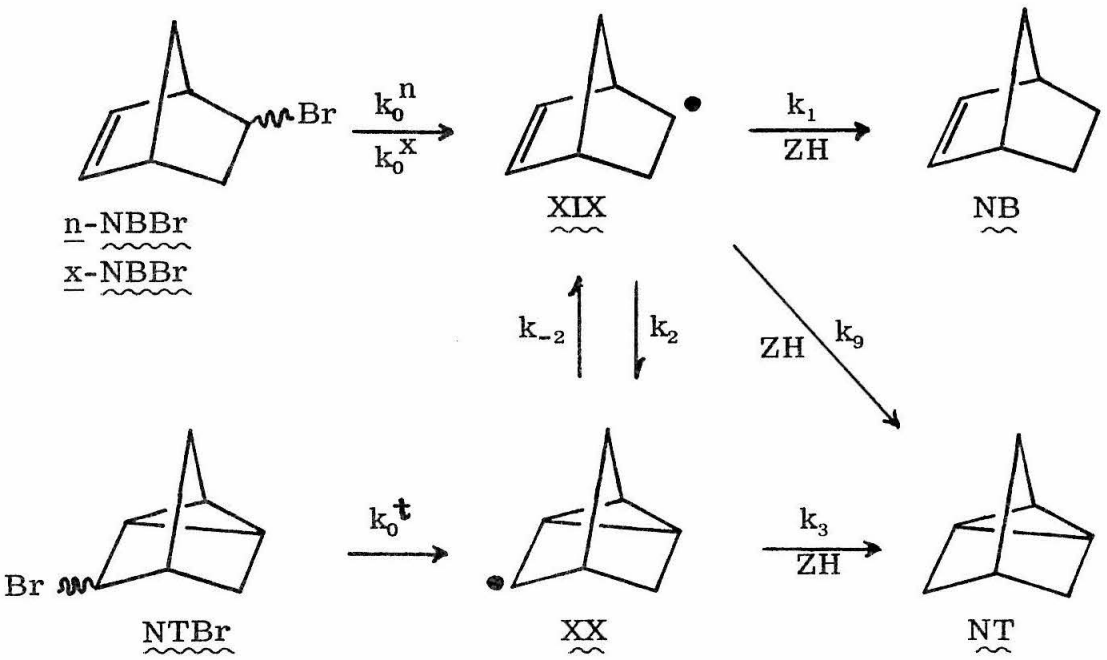
(e) Skeletal Rearrangement in the Reduction of endo-5-Bromonorbornene-5, 6, 6-$\underline{d}_3$ with Tri-n-butyltin Hydride.

(1) -- Assuming there are no significant secondary deuterium isotope effects present.



The equations for the ratio of [NBu]/[NBr] becomes too complex to be of much quantitative use. Qualitatively, however, it can be seen that this mechanism will be very similar to Mechanism I, in that it predicts that some "trapping" of (XXV) will occur, but as soon as the isomerization to (XXVI) occurs, [NBu] and [NBr] will be produced in a 1:1 ratio.

B. Where Nortricyclene Can Be Formed from the 5-Norbornenyl Radical.



(a) The Ratio of Norbornene to Nortricyclene in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Hydride

Steps analogous to (A. II. 1) through (A. II. 5) give,

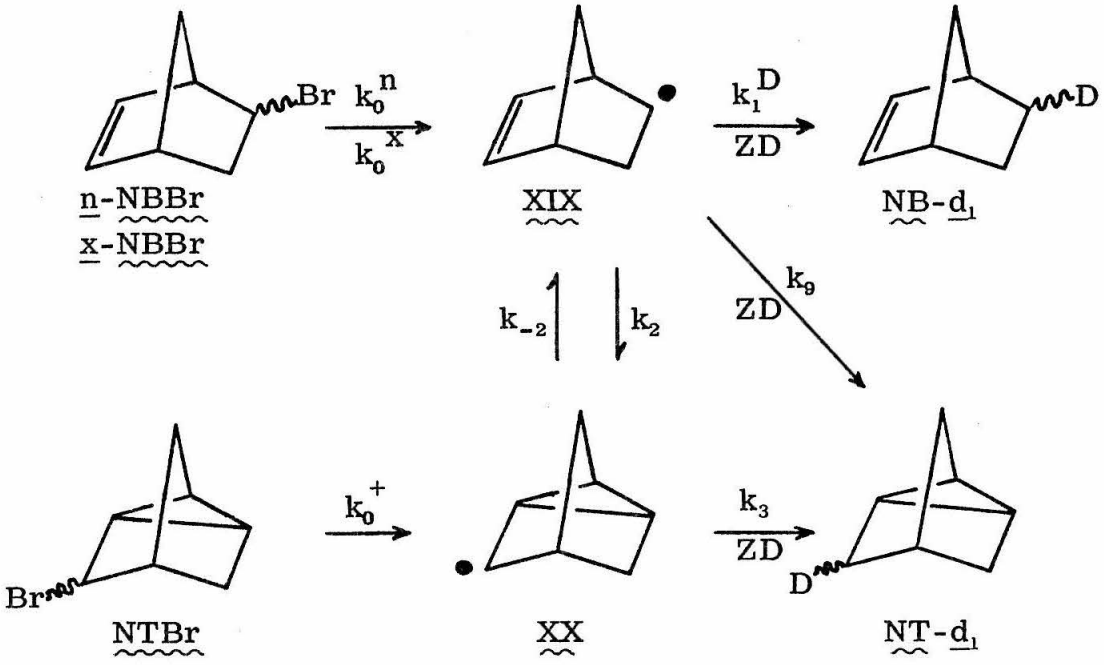
$$\frac{[\underset{\sim}{NB}]}{[\underset{\sim}{NT}]} \simeq \frac{k_1 k_{-2} + k_1 k_3 [ZH]}{k_{-2} k_9 + k_2 k_3 + k_3 k_9 [ZH]} . \qquad \text{(A. II. 10)}$$

(b) The Ratio of Nortricyclene to Norbornene in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride.

Steps analogous to (A. II. 1) through (A. II. 5) give,

$$\frac{[\underset{\sim}{NT}]}{[\underset{\sim}{NB}]} \simeq \frac{k_2 k_3 + k_{-2} k_9}{k_1 k_{-2}} + \frac{k_3(k_1 + k_9)[ZH]}{k_1 k_{-2}} \quad . \qquad \text{(A. II. 11)}$$

(c) The Ratio of Norbornene-$\underline{d}_1$ to Nortricyclene-$\underline{d}_1$ in the Reductions of endo- and exo-5-Bromonornene with Tri-n-butyltin Deuteride.



Assuming that,

$$k_1^D = \frac{k_1}{\epsilon_1} \quad \text{and} \quad k_3^D = \frac{k_3}{\epsilon_3} \quad \text{and} \quad k_8^D = \frac{k_8}{\epsilon_8}$$

then substitution of these constants into equation (A. II. 10) gives,

$$\frac{[\underset{\sim}{NB}\text{-}\underline{d}_1]}{[\underset{\sim}{NT}\text{-}\underline{d}_1]} \simeq \frac{\frac{k_1k_2}{\epsilon_1} + \frac{k_1k_3}{\epsilon_1\epsilon_3}[ZD]}{\frac{k_2k_9}{\epsilon_9} + \frac{k_2k_3}{\epsilon_3} + \frac{k_3k_9}{\epsilon_3\epsilon_9}[ZD]} . \qquad \text{(A. II. 12)}$$

(d) The Ratio of Nortricyclene-$\underline{d}_1$ to Norbornene-$\underline{d}_1$ in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Deuteride.

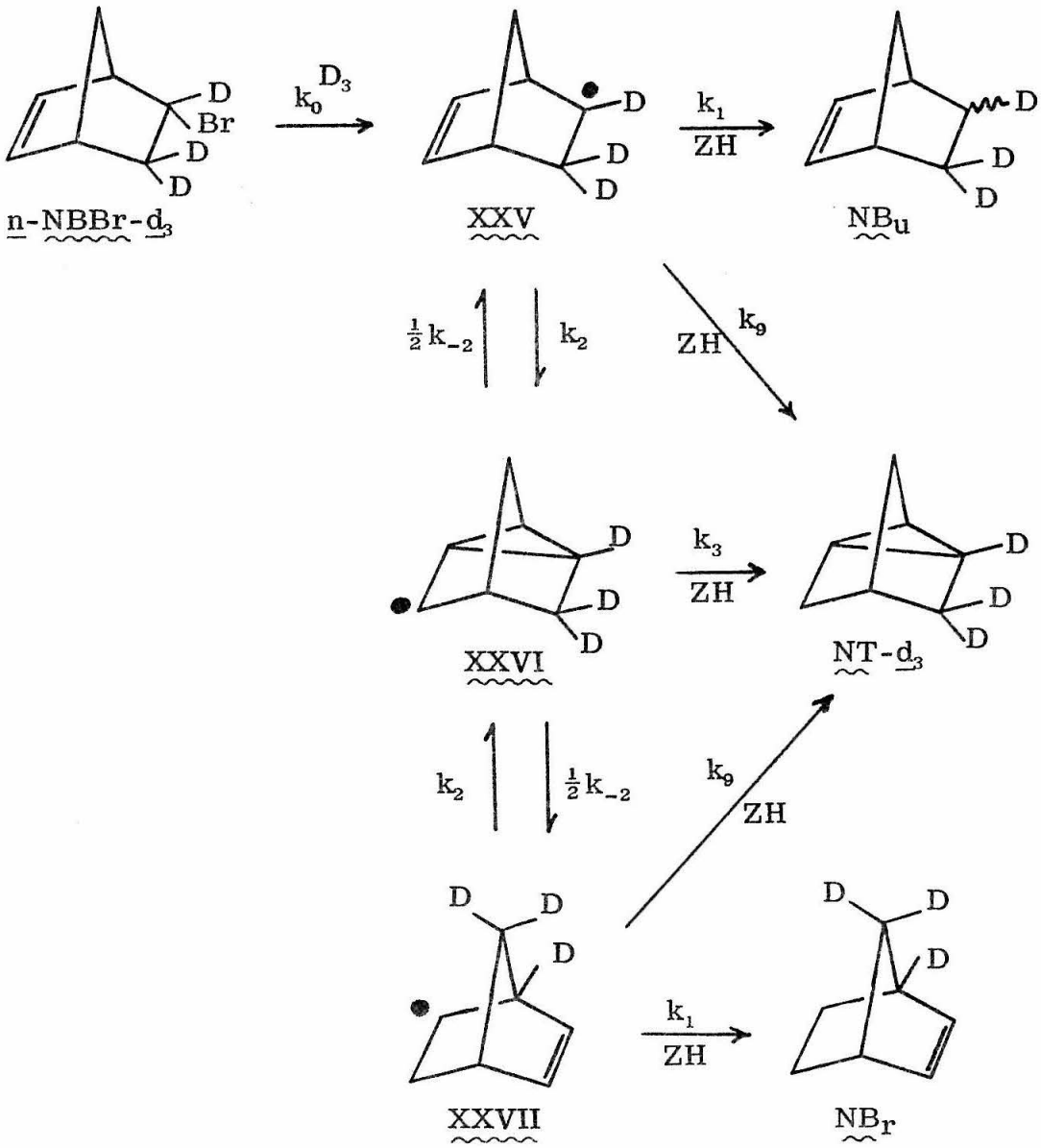
Substitution of the constants used to derive (A. II. 12) into (A. II. 11) gives,

$$\frac{[\underset{\sim}{NT}\text{-}\underline{d}_1]}{[\underset{\sim}{NB}\text{-}\underline{d}_1]} \simeq \frac{\frac{k_2k_3}{\epsilon_3} + \frac{k_{-2}k_9}{\epsilon_9}}{\frac{k_1k_{-2}}{\epsilon_1}} + \frac{\frac{k_3}{\epsilon_3}\frac{k_1}{\epsilon_1} + \frac{k_9}{\epsilon_9}[ZD]}{\frac{k_1k_{-2}}{\epsilon_1}} . \qquad \text{(A. II. 13)}$$

(e) Skeletal Rearrangement in the Reduction of endo-5-Bromonorbornene-5, 6, -$\underline{d}_3$ with Tri-n-butyltin Hydride.

(1) -- Assuming there are no significant secondary deuterium isotope effects present.

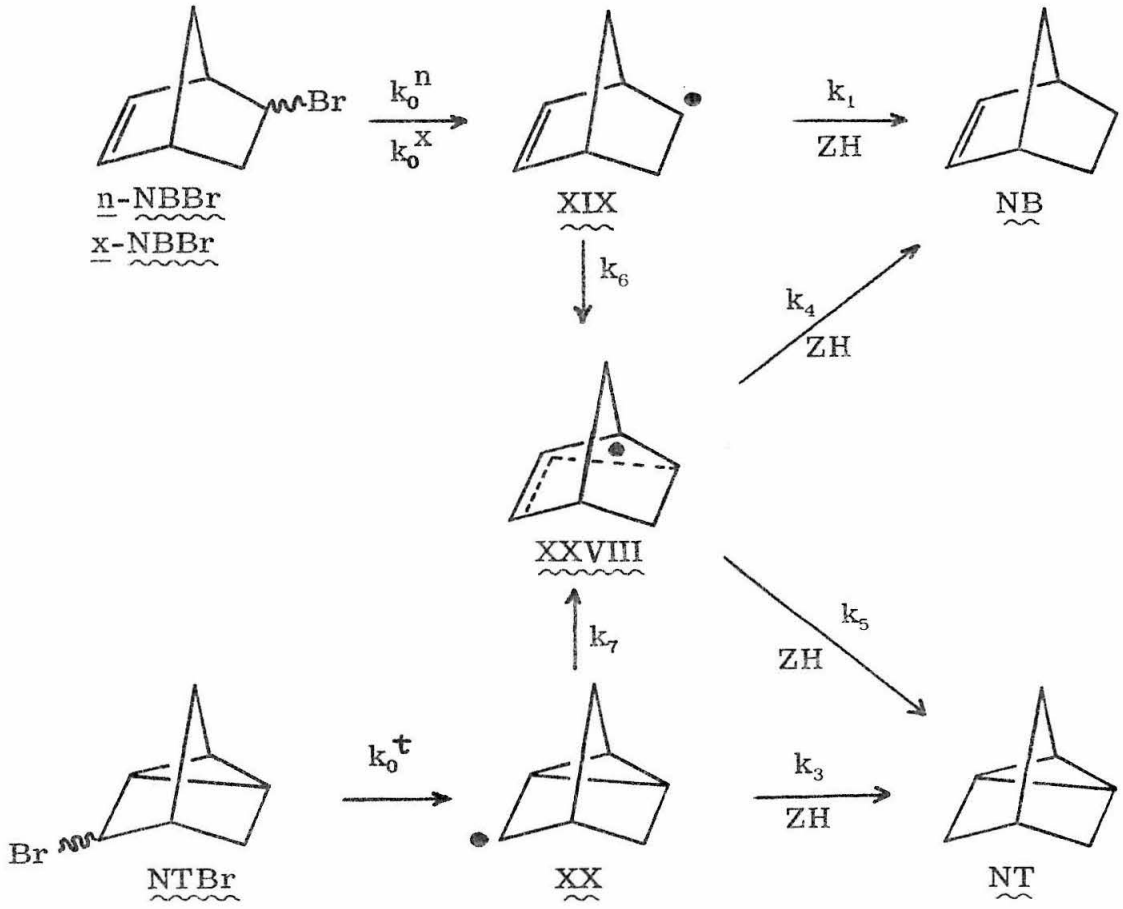
The equations for the ratio of $[\underset{\sim}{NB}_u]/[\underset{\sim}{NB}_r]$ become too complex to be of much quantitative value. Qualitatively, however, it can be seen that if there is a substantial contribution to the formation of ($\underset{\sim}{NT}$-$\underline{d}_3$) from ($\underset{\sim\sim}{XXV}$), via the crossed rate constant k_9, then the ratio of the rate constants k_1/k_2 is substantially higher than is predicted by Mechanism I. Therefore, the ratio of $[\underset{\sim}{NB}_u]/[\underset{\sim}{NB}_r]$ would be appreciably higher than predicted by Mechanism I, because it is the



ratio of k_1/k_2 which primarily governs the ratio of $[\underset{\sim}{NB_u}]/[\underset{\sim}{NB_r}]$ (assuming (XXVI) has identical C_3-C_4 and C_3-C_5 bonds).

Appendix III. Mechanism IIIA – Participation of a "Bridged" Radical which is Irreversibly Formed in the Isomerizations of the 5-Norbornenyl Radical (XIX) and the 2-Nortricyclyl Radical (XX).

The "bridged" radical (XXVIII) is an intermediate of undefined geometry and bond structure from which norbornene, nortricyclene, or both are presumed to be formed.



(a) The Ratio of Norbornene to Nortricyclene in the Free-Radical Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Hydride.

From either n-NBBr or x-NBBr,

$$\frac{d[NB]}{dt} = k_1[XIX][ZH] + k_4[XXVIII][ZH] \qquad \text{(A. III. 1)}$$

and,

$$\frac{d[NT]}{dt} = k_5[XXVIII][ZH] \qquad \text{(A. III. 2)}$$

or,

$$\frac{\frac{d[NB]}{dt}}{\frac{d[NT]}{dt}} = \frac{k_1[XIX][ZH] + k_4[XXVIII][ZH]}{k_5[XXVIII][ZH]} \simeq \frac{[NB]}{[NT]} . \qquad \text{(A. III. 3)}$$

But,

$$\frac{d[XXV]}{dt} = k_6[XIX] - k_4[XXVIII][ZH] - k_5[XXVIII][ZH] \simeq 0. \qquad \text{(A. III. 4)}$$

Therefore,

$$[XXVIII] = \frac{k_6[XIX]}{(k_4 + k_5)[ZH]} . \qquad \text{(A. III. 5)}$$

Substitution of (A. III. 5) into (A. III. 3) gives,

$$\frac{[\underset{\sim}{NB}]}{[\underset{\sim}{NT}]} \simeq \frac{k_1[\underset{\sim}{XIX}][ZH] + \dfrac{k_4k_6[\underset{\sim}{XIX}][ZH]}{(k_4+k_5)[ZH]}}{\dfrac{k_5k_6[\underset{\sim}{XIX}]}{(k_4+k_5)[ZH]}}$$

$$\simeq \frac{k_4}{k_5} + \frac{k_1(k_4+k_5)[ZH]}{k_5\,k_6} \qquad \text{(A. III. 6)}$$

$$\simeq C + D[ZH]$$

where,

$$C = \frac{k_4}{k_5} \qquad \text{and} \qquad D = \frac{k_1(k_4+k_5)}{k_5\,k_6}\,.$$

(b) <u>The Ratio of Nortricyclene to Norbornene in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride.</u>

Steps analogous to (A. III. 1) through (A. III. 6) give,

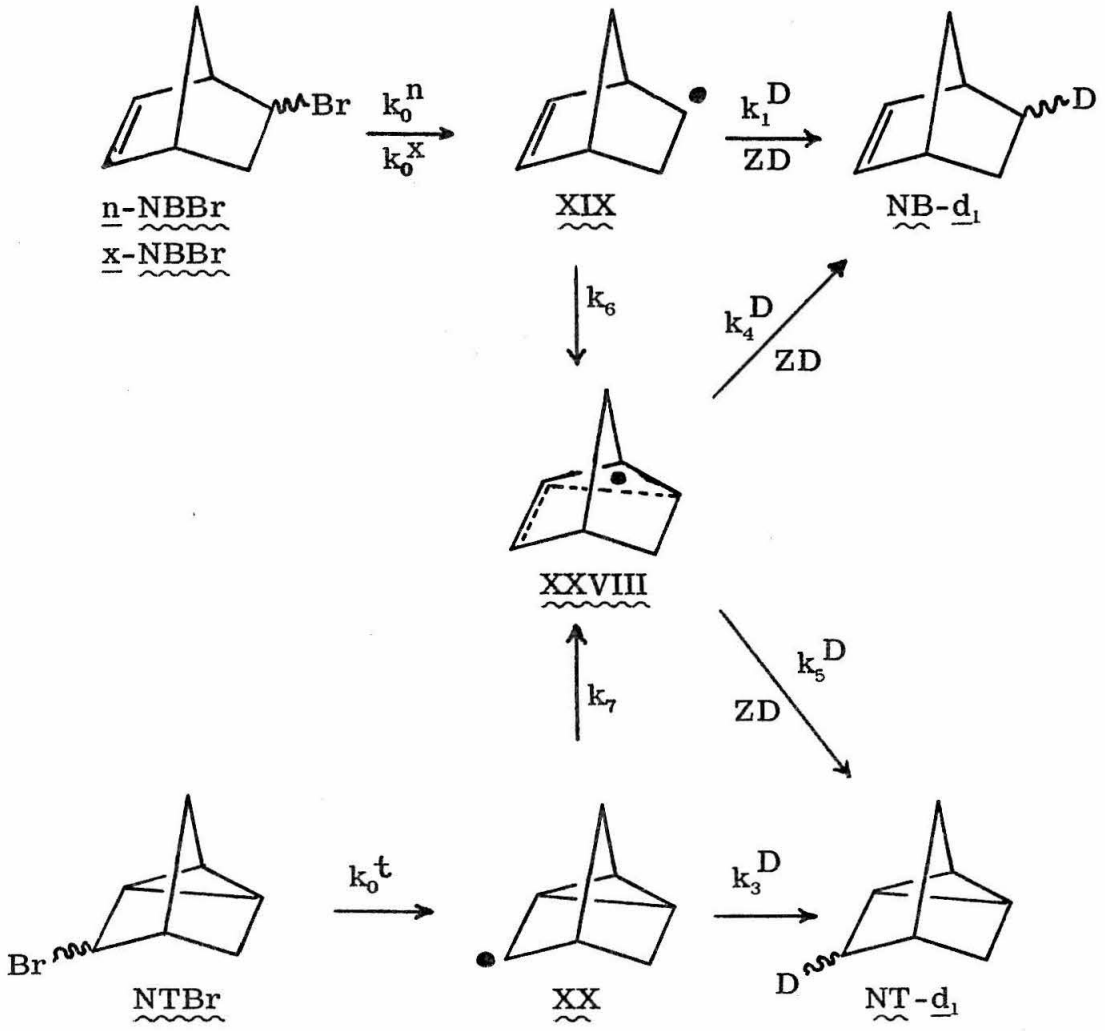
$$\frac{[\underset{\sim}{NT}]}{[\underset{\sim}{NB}]} \simeq \frac{k_5}{k_6} + \frac{k_3(k_4+k_5)}{k_4\,k_7}[ZH] \qquad \text{(A. III. 7)}$$

$$\simeq \frac{1}{C} + \frac{E}{C}[ZH]$$

where $E = \dfrac{k_3(k_4+k_5)}{k_5\,k_7}$

and $E = D$ only if $\dfrac{k_1}{k_3} = \dfrac{k_6}{k_7}$.

(c) The Ratio of Norbornene-$\underline{d}_1$ to Nortricyclene-$\underline{d}_1$ in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Deuteride.



Assuming that,

$k_1^D = \frac{k_1}{\epsilon_1}$, and $k_4^D = \frac{k_4}{\epsilon_4}$, and $k_5^D = \frac{k_5}{\epsilon_5}$,

substitution of these constants into (A. III. 6) gives,

$$\frac{[\underset{\sim\sim}{NB}\text{-}\underline{d}_1]}{[\underset{\sim\sim}{NT}\text{-}\underline{d}_1]} \simeq \frac{\epsilon_5 k_4}{\epsilon_4 k_5} + \frac{\epsilon_5 k_1 \left(\frac{k_4}{\epsilon_4} + \frac{k_5}{\epsilon_5}\right)[ZD]}{\epsilon_1 k_5 k_6} \qquad \text{(A. III. 8)}$$

or, if ϵ_4 is close to ϵ_5, then,

$$\frac{[\underset{\sim\sim}{NB}\text{-}\underline{d}_1]}{[\underset{\sim\sim}{NT}\text{-}\underline{d}_1]} \simeq \frac{\epsilon_5 C}{\epsilon_4} + \frac{D[ZH]}{\epsilon_1}.$$

(d) The Ratio of Nortricyclene-$\underline{d}_1$ to Norbornene-$\underline{d}_1$ in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Deuteride.

Assuming that,

$$k_3^D = \frac{k_3}{\epsilon_3}, \quad \text{and} \quad k_4^D = \frac{k_4}{\epsilon_4}, \quad \text{and} \quad k_5^D = \frac{k_5}{\epsilon_5},$$

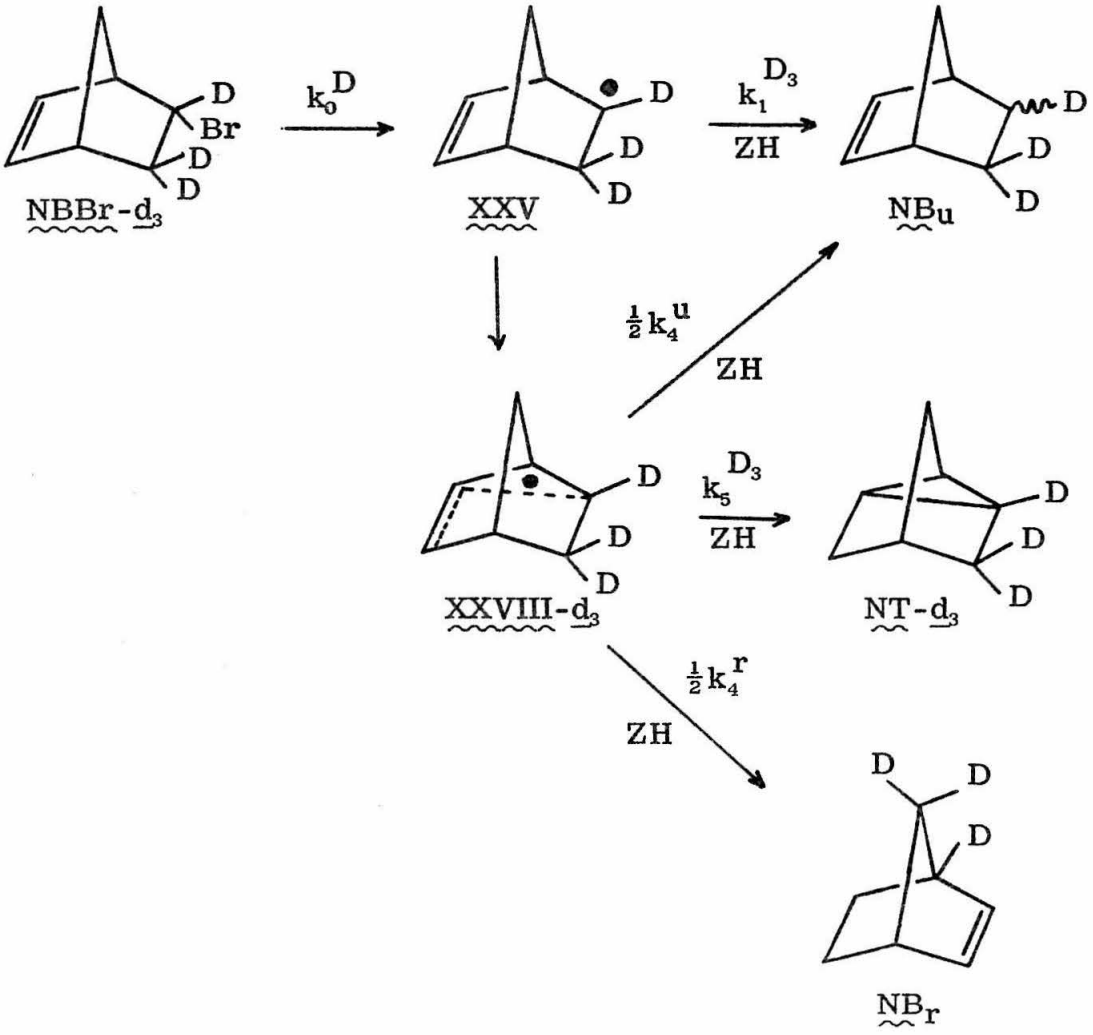
substitution of these constants into (A. III. 7) gives,

$$\frac{[\underset{\sim\sim}{NT}\text{-}\underline{d}_1]}{[\underset{\sim\sim}{NB}\text{-}\underline{d}_1]} \simeq \frac{\epsilon_4 k_5}{\epsilon_5 k_4} + \frac{\epsilon_4 k_3 \left(\frac{k_4}{\epsilon_4} + \frac{k_5}{\epsilon_5}\right)[ZH]}{\epsilon_3 k_4 k_7} \qquad \text{(A. III. 9)}$$

or, if ϵ_4 is close to ϵ_5, then,

$$\frac{[\underset{\sim\sim}{NT}\text{-}\underline{d}_1]}{[\underset{\sim\sim}{NB}\text{-}\underline{d}_1]} \simeq \frac{\epsilon_4}{\epsilon_5 C} \quad \frac{E[ZH]}{\epsilon_3 C}.$$

(e) Skeletal Rearrangement in the Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride. *



* It is important to note that if the C_3-C_4 and C_3-C_5 bonds in (XXVIII-d_3) do not become chemically equivalent, then little or no (NBr) will be formed.

(1) -- Assuming that there are no significant secondary deuterium isotope effects present.

Then,

$$\frac{\frac{d[\underset{\sim}{NB_u}]}{dt}}{\frac{d[\underset{\sim}{NB_r}]}{dt}} = \frac{k_1^{D_3}[\underset{\sim}{XXV}][ZH] + \frac{1}{2}k_4^{u}[\underset{\sim}{XXVIII\text{-}d_3}][ZH]}{\frac{1}{2}k_4^{r}[\underset{\sim}{XXVIII\text{-}d_3}][ZH]} \simeq \frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \qquad \text{(A. III. 10)}$$

or,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{k_1[\underset{\sim}{XXV}][ZH] + \frac{1}{2}k_4[\underset{\sim}{XXVIII\text{-}d_3}][ZH]}{\frac{1}{2}k_4[\underset{\sim}{XXVIII\text{-}d_3}][ZH]} . \qquad \text{(A. III. 11)}$$

But,

$$\frac{d[\underset{\sim}{XXVIII\text{-}d_3}]}{dt} = k_6[\underset{\sim}{XXV}] - \frac{1}{2}k_4^{u}[\underset{\sim}{XXVIII\text{-}d_3}][ZH]$$

$$- \frac{1}{2}k_4^{r}[\underset{\sim}{XXVIII\text{-}d_3}][ZH] - k_5[\underset{\sim}{XXVIII\text{-}d_3}][ZH] \simeq 0. \qquad \text{(A. III. 12)}$$

Therefore,

$$[\underset{\sim}{XXVIII\text{-}d_3}] \simeq \frac{k_6[\underset{\sim}{XXV}]}{(k_4 + k_5)[ZH]} . \qquad \text{(A. III. 13)}$$

Substitution of (A. III. 13) into (A. III. 11) gives,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq 1 + \frac{k_1[\underset{\sim}{XXV}][ZH]}{\frac{1}{2}k_4\left(\frac{k_6[\underset{\sim}{XXV}]}{(k_4 + k_5)[ZH]}\right)[ZH]}$$

$$\simeq 1 + \frac{2\,k_1(k_4+k_5)[ZH]}{k_4\,k_6} \qquad \text{(A. III. 14)}$$

$$\simeq 1 + \frac{2D}{C}[ZH] .$$

(2) -- Allowing for secondary deuterium isotope effects.

Assuming that,

$$k_1^{D_3} = \frac{k_1}{\epsilon_1} \qquad \text{and} \qquad \tfrac{1}{2}\,k_4^{u} = \tfrac{1}{2}\,\frac{k_4}{\epsilon_4}$$

then substitution of these constants into (A. III. 10) and (A. III. 12) gives,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{\frac{k_1}{\epsilon_1}[\underset{\sim}{XXV}][ZH] + \frac{k_4}{2\epsilon_4}[\underset{\sim}{XXVIII}\text{-}\underline{d_3}][ZH]}{\frac{1}{2}k_4[\underset{\sim}{XXVIII}\text{-}\underline{d_3}][ZH]} \qquad \text{(A. III. 15)}$$

and,

$$[\underset{\sim}{XXVIII}\text{-}\underline{d_3}] \simeq \frac{k_6[\underset{\sim}{XXV}]}{\left(\left(\frac{\epsilon_4+1}{2\,\epsilon_4}\right)k_4 + k_5\right)[ZH]} . \qquad \text{(A. III. 16)}$$

Substitution of (A. III. 16) into (A. III. 15) gives,

$$\frac{[\underset{\sim}{NB_u}]}{[\underset{\sim}{NB_r}]} \simeq \frac{1}{\epsilon_4} + \frac{2\,k_1\left(\left(\frac{\epsilon_4+1}{2\epsilon_4}\right)k_4 + k_5\right)[ZH]}{\epsilon_1\,k_4\,k_6} . \qquad \text{(A. III. 17)}$$

(f) The Ratio of Norbornene-$\underline{d}_3$ to Nortricyclene-$\underline{d}_3$ in the Reduction of endo-5-Bromonorbornene-5, 6, 6, -$\underline{d}_3$ with Tri-n-butyltin Hydride.

Assuming that,

$$k_1^{D_3} = \frac{k_1}{\epsilon_1} \quad \text{and} \quad \tfrac{1}{2} k_4^{u} = \frac{k_4}{2\epsilon_4}$$

then,

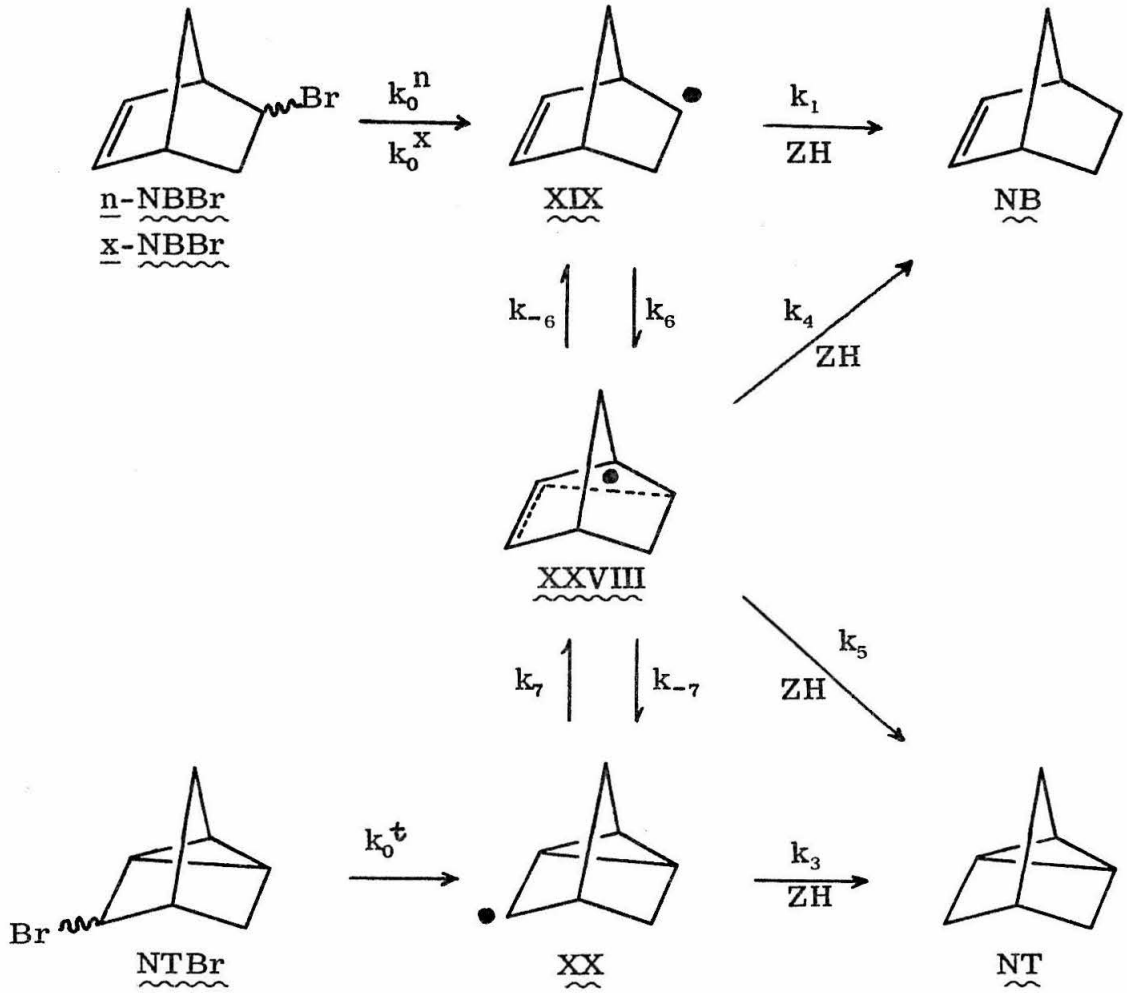
$$\frac{[\underset{\sim}{NB_u}]+[\underset{\sim}{NB_r}]}{[\underset{\sim}{NT}\text{-}\underline{d}_3]} =$$

$$\frac{\frac{k_1}{\epsilon_1}[\underset{\sim}{XXV}][ZH] + \frac{k_4}{2\epsilon_4}[\underset{\sim}{XXVIII}\text{-}\underline{d}_3][ZH] + \frac{k_4}{2}[\underset{\sim}{XXVIII}\text{-}\underline{d}_3][ZH]}{k_5[\underset{\sim}{XXVIII}\text{-}\underline{d}_3][ZH]} \qquad \text{(A. III. 18)}$$

$$\frac{[\underset{\sim}{NB_u}]+[\underset{\sim}{NB_r}]}{[\underset{\sim}{NT}\text{-}\underline{d}_3]} \simeq \left(\frac{\epsilon_4+1}{2\epsilon_4}\right)\frac{k_4}{k_5} + \frac{k_1\left(\left(\frac{\epsilon_4+1}{2\epsilon_4}\right)k_4 + k_5\right)[ZH]}{\epsilon_1 k_5 k_6} . \qquad \text{(A. III. 19)}$$

Mechanism IIIB – Participation of a "Bridged" Radical which is Formed Reversibly from Either the 5-Norbornenyl Radical or the 2-Nortricyclyl Radical.

The "bridged" radical (XXVIII) is an intermediate of undefined geometry and bond structure from which norbornene, nortricyclene, or both are presumed to be formed.



(a) The Ratio of Norbornene to Nortricyclene in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Hydride.

From either n-NBBr or x-NBBr,

$$\frac{\frac{d[NB]}{dt}}{\frac{d[NT]}{dt}} = \frac{k_1[XIX][ZH] + k_4[XXVIII][ZH]}{k_3[XX][ZH] + k_5[XXVIII][ZH]} \quad \frac{[NB]}{[NT]}. \qquad \text{(A. III. 20)}$$

But,

$$\frac{d[XX]}{dt} = k_{-7}[XXVIII] - k_7[XX] - k_3[XX][ZH] \simeq 0 \qquad \text{(A. III. 21)}$$

therefore,

$$[XX] \simeq \frac{k_{-7}[XXVIII]}{k_7 + k_3[ZH]} \qquad \text{(A. III. 22)}$$

and,

$$[XXVIII] \simeq \frac{(k_7 + k_3[ZH])[XX]}{k_{-7}}. \qquad \text{(A. III. 23)}$$

Also,

$$\frac{d[XXVIII]}{dt} = k_6[XIX] + k_7[XX] - k_{-6}[XXVIII] - k_{-7}[XXVIII]$$

$$- k_4[XXVIII][ZH] - k_5[XXVIII][ZH] \simeq 0. \qquad \text{(A. III. 24)}$$

Substitution of (A. III. 22) into (A. III. 24) gives,

$$[\underset{\sim}{\underset{\sim}{\text{XXVIII}}}] \simeq \frac{k_6[\underset{\sim}{\underset{\sim}{\text{XIX}}}]}{k_{-6}+k_{-7}+(k_4+k_5)[ZH] \quad \frac{k_7 k_{-7}}{k_7+k_3[ZH]}} \qquad \text{(A. III. 25)}$$

and substitution of (A. III. 23) into (A. III. 24) gives,

$$[\underset{\sim}{\underset{\sim}{\text{XX}}}] \simeq \frac{k_6[\underset{\sim}{\underset{\sim}{\text{XIX}}}]}{(k_{-6}+k_{-7}+(k_4+k_5)[ZH]) \quad \frac{k_7+k_3[ZH]}{k_{-7}} - k_7} . \qquad \text{(A. III. 26)}$$

Now substitution of (A. III. 25) and (A. III. 26) into (A. III. 21) gives,

$$\frac{[\underset{\sim}{\text{NB}}]}{[\underset{\sim}{\text{NT}}]} \simeq \frac{k_4 k_6 (k_3[ZH]+k_7)}{k_5 k_6 (k_7+k_3[ZH]) + k_3 k_6 k_{-7}}$$

$$+ \frac{k_1(k_{-6}k_3[ZH]+k_{-6}k_7+k_3k_{-7}[ZH]+k_7(k_4+k_5)[ZH]+k_3(k_4+k_5)[ZH]^2)}{k_5 k_6 (k_7+k_3[ZH]) + k_3 k_6 k_{-7}} .$$

(A. III. 27)

Equation (A. III. 27) cannot be constructively simplified further, but in the limiting case, as $[ZH] \rightarrow 0$,

$$\frac{[\underset{\sim}{\text{NB}}]}{[\underset{\sim}{\text{NT}}]_{\text{equilibrium}}} = \frac{k_4 k_6 k_7 + k_1 k_{-6} k_7}{k_5 k_6 k_7 + k_3 k_6 k_{-7}} . \qquad \text{(A. III. 28)}$$

(b) The Ratio of Nortricyclene to Norbornene in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Hydride.

From NTBr, equations analogous to (A. III. 21) through (A. III. 27) give,

$$\frac{[NT]}{[NB]} \simeq \frac{k_5 k_7 (k_6 + k_1[ZH])}{k_4 k_7 (k_{-6} + k_1[ZH]) + k_1 k_{-6} k_7}$$

$$+ \frac{k_3 (k_{-6} k_1 [ZH] + k_6 k_{-7} + k_1 k_{-7} [ZH] + k_6 (k_4 + k_5)[ZH] + k_1 (k_4 + k_5)[ZH]^2)}{k_4 k_7 (k_{-6} + k_1[ZH]) + k_1 k_{-6} k_7} . \quad \text{(A. III. 29)}$$

Equation (A. III. 29) cannot be constructively simplified further, but in the limiting case, as $[ZH] \rightarrow 0$,

$$\frac{[NT]}{[NB]}_{\text{equilibrium}} = \frac{k_5 k_6 k_7 + k_3 k_6 k_{-7}}{k_4 k_7 k_6 + k_1 k_{-6} k_7} . \quad \text{(A. III. 30)}$$

(c) The Ratio of Norbornene-d_1 to Nortricyclene-d_1 in the Reductions of endo- and exo-5-Bromonorbornene with Tri-n-butyltin Deuteride.

Equation (A. III. 27), upon substitution of constants allowing for primary deuterium isotope effects in the abstraction reaction of (XIX), (XX), and (XXVIII), become too complex to be of much practical value. It is apparent, however, that there are two

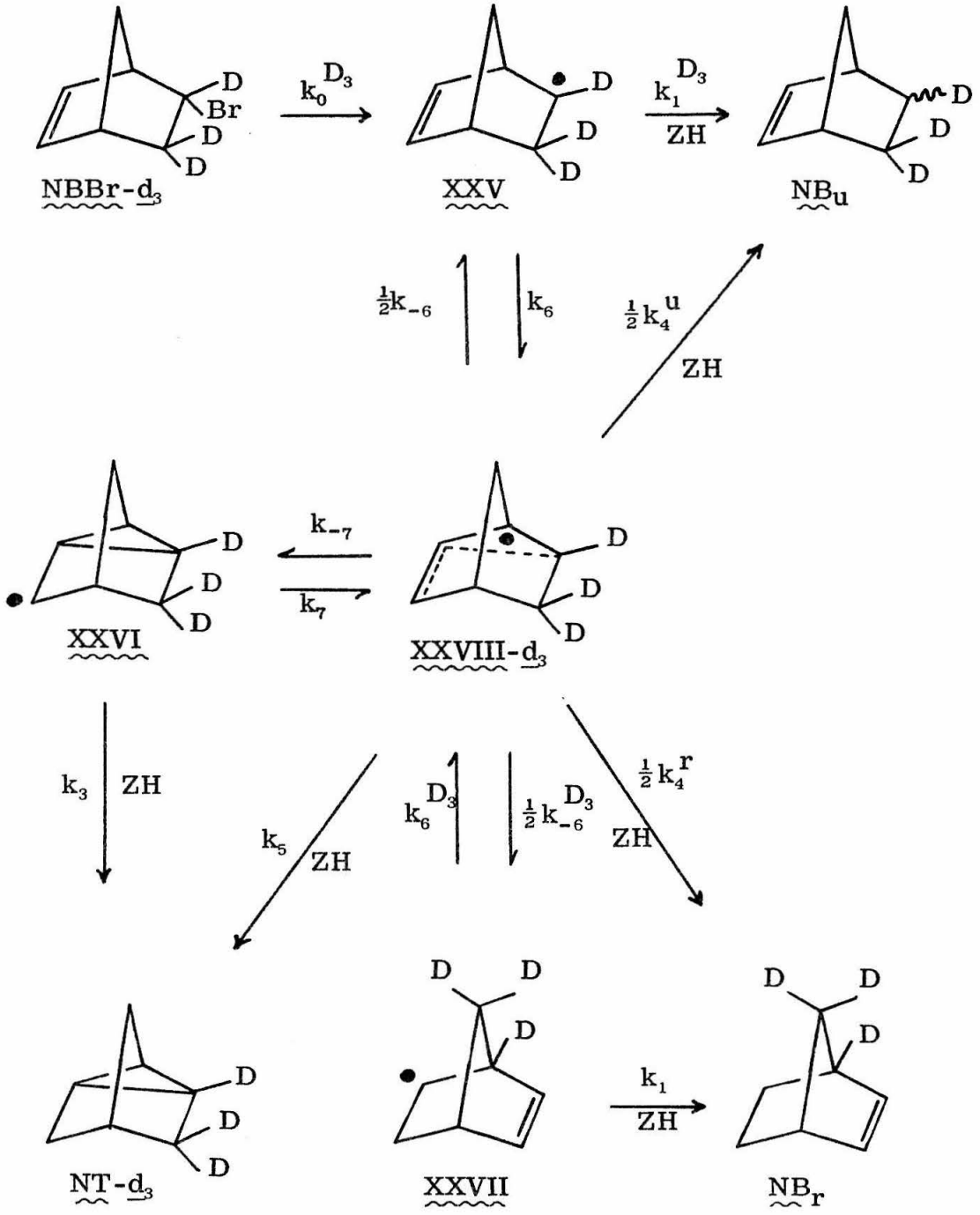
abstraction reactions leading to each product. The contribution of each of the two reactions leading to either of the products will be dependent upon the starting bromide and the concentration of tri-n-butyltin deuteride, so that differences in the isotope effects for the two reaction leading either product should be manifested by differences in the "average" isotope effect for formation of that product with differences in the concentration of tri-n-butyltin deuteride.

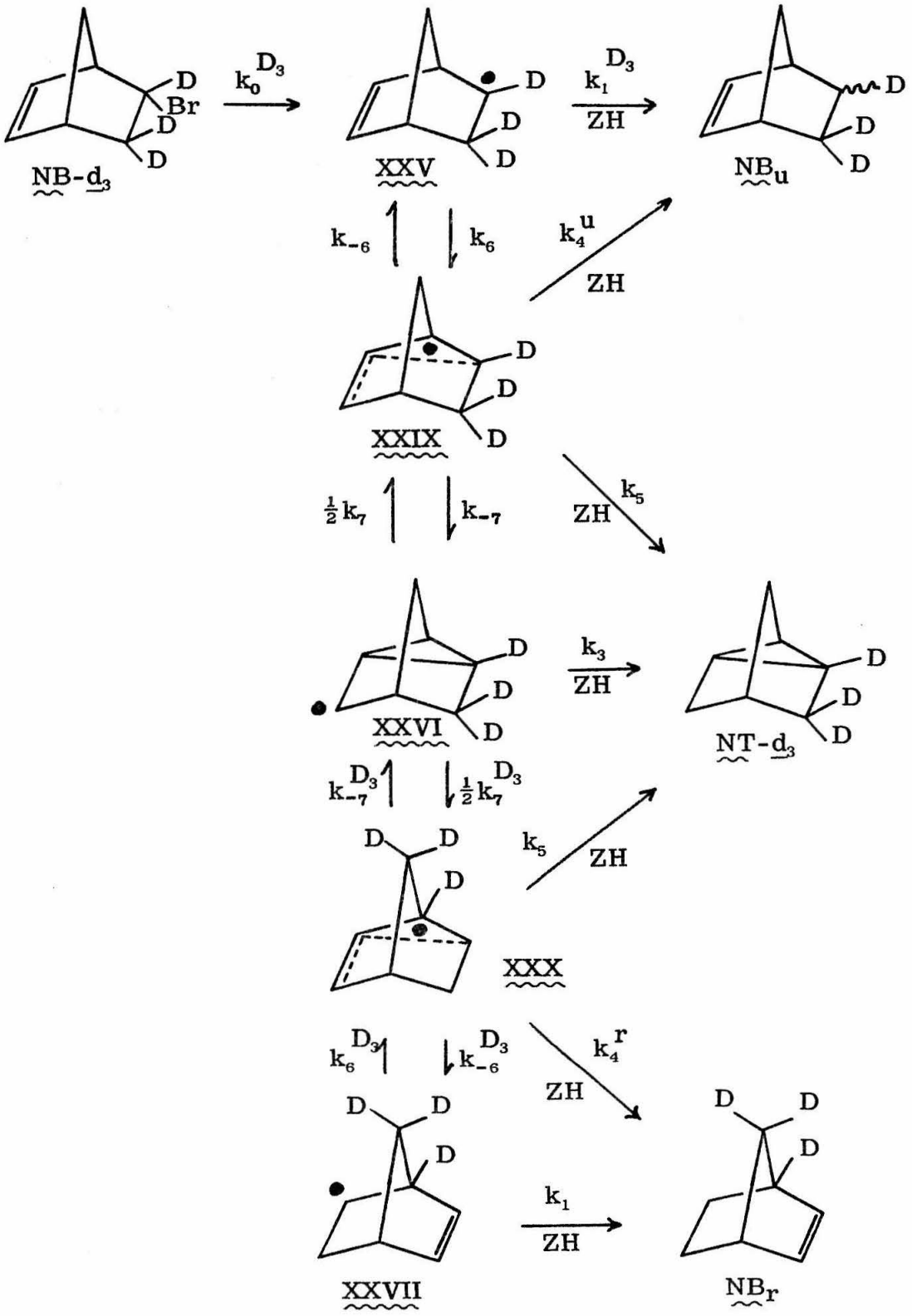
(d) The Ratio of Nortricyclene-d_1 to Norbornene-d_1 in the Reduction of 2-Bromonortricyclene with Tri-n-butyltin Deuteride.

Analogous comments to those in (c), above, pertaining to (A. III. 27), apply to (A. III. 29). Also the comments concerning the primary kinetic deuterium isotope effects in (c), above, apply here.

(e) Skeletal Rearrangement in the Reduction of endo-5-Bromonorbornene-5, 6, 6-d_3 with Tri-n-butyltin Hydride.

(1) -- Assuming that the "bridged" intermediate (XXVIII-d_3) has chemically equivalent C_3-C_4 and C_3-C_5 bonds, and will therefore form both NB_u and NB_r at rates differing only through secondary deuterium isotope effects.


NBBr-d3
k0 D3
XXV
k1 D3
ZH
NBu
½k-6
k6
½k4u
ZH
XXVI
k-7
k7
XXVIII-d3
k3 ZH
k5 ZH
k6 D3
½k-6 D3
½k4r
ZH
NT-d3
XXVII
k1
ZH
NBr


NB-d3
k0 D3
XXV
k1 D3
ZH
NBu
k-6
k6
k4 u
ZH
XXIX
½k7
k-7
ZH
k5
XXVI
k3
ZH
NT-d3
k-7 D3
½k7 D3
k5
ZH
XXX
k6 D3
k-6 D3
k4 r
ZH
XXVII
k1
ZH
NBr

The equations for the ratio of ($\underset{\sim}{NB_u}$) to ($\underset{\sim}{NB_r}$) become very complex, and of little practical value. Qualitatively, however, it can be seen that as soon as the initial isomerization of ($\underset{\sim}{XXV}$) to ($\underset{\sim}{XXVIII}$-$\underline{d_3}$) occurs, then except for secondary deuterium isotope effects, $\underset{\sim}{NB_u}$ and $\underset{\sim}{NB_r}$ will be produced in equal amounts.

(2) -- Assuming that the "bridged" radical does not have chemically equivalent C_3–C_4 and C_3–C_5 bonds, and must therefore isomerize through the nortricyclyl-$\underline{d_3}$ radical before these bonds become chemically equivalent, resulting in ($\underset{\sim}{XXX}$) being the first radical which can produce rearranged norbornene-1, 7, 7-$\underline{d_3}$ ($\underset{\sim}{NB_r}$).

The equations for the ratio of ($\underset{\sim}{NB_u}$) to ($\underset{\sim}{NB_r}$) are again too complex to be of much practical value. It can be seen, however, that because the first "bridged" radical ($\underset{\sim}{XXIX}$) can produce only the unrearranged norbornene-$\underline{d_3}$ ($\underset{\sim}{NB_u}$), then this mechanism would predict that the ratio of ($\underset{\sim}{NB_u}$) to ($\underset{\sim}{NB_r}$) would be greater than that predicted by Mechanism I (A. I. 25) or Mechanism IIIA (A. III. 17).

(f) <u>The Ratio of Norbornene-$\underline{d_3}$ to Nortricyclene-$\underline{d_3}$ in the Reduction of endo-5-Bromonorbornene-5, 6, 6-$\underline{d_3}$ with Tri-n-butyltin Hydride.</u>

The equations for the ratio of norbornene-$\underline{d_3}$ to nortricyclene-$\underline{d_3}$ as a function of the concentration of tri-n-butyltin hydride in the reduction of endo-5-bromonorbornene-5, 6, 6-$\underline{d_3}$ become too complex to be of much practical value. Isotope effects in either the isomerization or abstraction reactions of the intermediates will affect both

the slope and intercept of the plot of this ratio as a function of the concentration of tri-n-butyltin hydride.

Appendix IV. Calculation of the Tin-Hydrogen Bond-Dissociation Energy in Tri-n-butyltin Hydride.

From thermochemical experiments, the average bond-dissociation energy of stannane was found to be 60.4 kcal/mole (69), while from infra-red spectroscopy, or mass-spectral appearance potentials, the average bond-dissociation energy of stannane was calculated to be between 70 and 75 kcal/mole* (70). The difference is obviously very substantial.

More recently, Yergey and Lampe used mass-spectral appearance potentials to determine the individual bond-dissociation energies for the reaction:

$$R_3SnX \longrightarrow R_3Sn\cdot + X\cdot \qquad X = CH_3,\ C_2H_5,\ Br,\ I,\ C_6H_5CH_2$$

They found that these bond-dissociation energies can be given by a general empirical formula

$$\text{Bond-dissociation energy} = \text{Average bond-dissociation energy} + 20\text{-}21 \text{ kcal/mole}$$

---

*It is important to note the difference between the average bond-dissociation energy, which is the total energy required to break a group of bonds, divided by the number of bonds broken, and the bond-dissociation energy, which is the energy required to break a specific bond under consideration.

where the average bond-dissociation energy is obtained from thermochemical experiments (71). The 20-21 kcal/mole was attributed to the required reorganization of the three remaining bonds to the tin atom while the fourth is being broken in the dissociation reaction.

More recently, Lampe and Niehaus have determined the bond-dissociation energies as tetramethyltin successively loses methyl groups. By mass-spectral means, they obtained the appearance potential for the trimethylstannyl cation, and the ionization potential for the trimethylstannyl radical (72). Assuming that the ionization potential is a true Franck-Condon vertical ionization potential, the bond-dissociation energy for the reaction:

$$(CH_3)_4Sn \longrightarrow (CH_3)_3Sn\cdot + \cdot CH_3$$

should equal the difference in the energies for the reactions:

$$(CH_3)_4Sn \xrightarrow{e^{\ominus}} (CH_3)_3Sn^{\oplus} + \cdot CH_3 + 2\,e^{\ominus}$$

and: $$(CH_3)_3Sn\cdot \xrightarrow{e^{\ominus}} (CH_3)_3Sn^{\oplus} + 2\,e^{\ominus}$$

which is the difference between the appearance potential for the trimethylstannyl cation from tetramethyltin, and the ionization potential for the trimethylstannyl radical. Both of these values were experimentally determined. The same technique was applied to obtain the successive bond-dissociation energies as tetramethyltin loses methyl groups, yielding the following values (72):

$(CH_3)_4Sn \longrightarrow (CH_3)_3Sn\cdot + \cdot CH_3$ Bond D. E. = 60.5 kcal/mole

$(CH_3)_3Sn\cdot \longrightarrow (CH_3)_3Sn\cdot + \cdot CH_3$ Bond D. E. = 58.5 kcal/mole

$(CH_3)_2Sn\cdot \longrightarrow CH_3Sn\cdot + \cdot CH_3$ Bond D. E. = 85.5 kcal/mole

$CH_3Sn\cdot \longrightarrow Sn + \cdot CH_3$ Bond D. E. = 44 kcal/mole

Average bond-dissociation energy = 62 kcal/mole

These results are in interesting contrast to previous calculations which would predict the bond-dissociation energy for breaking the first tin-methyl bond of tetramethyltin to be 20-21 kcal/mole greater (71) than the thermochemically-determined average bond-dissociation of about 52 kcal/mole for tetramethyltin (73). The reasons for the substantial disagreements in the values obtained by different means is not known, and is outside the scope of this thesis. However, the average bond-dissociation energy for tetramethyltin, and the bond-dissociation energy for the first tin-methyl bond of tetramethyltin are required in a later calculation so it is important to note the values, and the apparent uncertainty in them.

The standard enthalpy of formation of tri-n-butyltin hydride in the liquid state is -48.6 kcal/mole (74). From the heats of vaporization of a series of organotin compounds (74) (75), a good estimate of the heat of vaporization of tri-n-butyltin hydride should be 16-17 kcal/mole. The standard enthalpy of formation of tri-n-butyltin bromide in the gas phase is -65.5 kcal/mole (74), plus an amount equal to the difference between the bond-dissociation energy of the first tin-methyl bond of tetramethyltin and the average

Compound	H°_{vap} kcal/mole
$(CH_3)_3Sn$-i-C_3H_7	9.7 (53)
$(CH_3)_3Sn$-t-C_4H_9	10.5 (53)
(i-$C_3H_7)_4Sn$	15.5 (53)
(n-$C_4H_9)_4Sn$	19.8 (52)
(n-$C_4H_9)_3SnBr$	20 (52)

tin-methyl bond-dissociation energy in tetramethyltin * (74). When some additional data are taken from standard thermochemical tables (76), a reasonable estimate of the tin-hydrogen bond-dissociation energy in tri-n-butyltin hydride can be calculated. The value of X is uncertain, and might be approximately 20-21 kcal/mole (71). However, it seems reasonable that the more recent value for the tin-methyl bond-dissociation energy (which is obtained directly from mass-spectral results, rather than from less accurate thermochemical calculations) of about 60.5 kcal/mole (72), is likely to be the more reliable. This leaves a value for X of about 8.5 kcal/mole. Obviously, with the usual errors of several per cent or more in the thermochemical parameters listed in the calculation in Table 18, the error in the calculated value for the bond-dissociation energy of the tin-hydrogen bond of tri-n-butyltin hydride could be substantial, even without the uncertainty in X. One value which should be reasonably

---

*Assuming the average bond-dissociation energy for tetramethyltin is 52 kcal/mole.

Table 18. Calculation of the Tin-Hydrogen Bond-Dissociation Energy of tri-n-Butyltin Hydride.

Reaction	ΔH kcal/mole
$(n\text{-}C_4H_9)_3SnBr\ (g) \longrightarrow (n\text{-}C_4H_9)_3Sn\cdot + Br\cdot$	$+70.5 + X$ [a]
$12\,C + 13.5\,H_2 + Sn + 0.5\,Br_2\ (l) \longrightarrow (n\text{-}C_4H_9)_3SnBr\ (g)$	-65.5
$0.5\,Br_2\ (g) \longrightarrow 0.5\,Br_2\ (l)$	- 3.7
$Br\cdot \longrightarrow 0.5\,Br_2\ (g)$	-23.05
$(n\text{-}C_4H_9)_3SnH\ (l) \longrightarrow 12\,C + 13.5\,H_2 + Sn + 0.5\,H_2$	+48.6
$(n\text{-}C_4H_9)_3SnH\ (g) \longrightarrow (n\text{-}C_4H_9)_3SnH\ (l)$	-16.5
$0.5\,H_2 \longrightarrow H\cdot$	+52.1
Net Reaction:	
$(n\text{-}C_4H_9)_3SnH\ (g) \longrightarrow (n\text{-}C_4H_9)_3Sn\cdot + H\cdot$	$+62.4 + X$

[a] X equals the difference between the first tin-methyl bond-dissociation energy and the average tin-methyl bond-dissociation energy of tetramethyltin, assuming the latter is approximately 52 kcal/mole.

reliable is the difference between the tin-bromine and tin-hydrogen bond-dissociation energies of tri-n-butyltin bromide and tri-n-butyltin hydride, respectively, because any error in X will cancel out in this comparison. This leaves approximately 8 kcal/mole difference between the bond-dissociation energies of the tin-hydrogen bond of tri-n-butyltin hydride, and the tin-bromine bond of tri-n-butyltin bromide. If the value of X is taken to be 8.5 kcal/mole, the bond-dissociation energy of the tin-hydrogen bond of tri-n-butyltin hydride is calculated to be 71 kcal/mole, and the bond-dissociation energy of the tin-bromine bond of tri-n-butyltin bromide is calculated to be 79 kcal/mole.

The bond-dissociation energies for the carbon-bromine bonds of endo- and exo-5-bromonorbornene and 2-bromonortricyclene and for the carbon-hydrogen bonds of the endo- and exo-5-positions of norbornene and the 2-position of nortricyclene may be easily estimated. Bond-dissociation energies for a large number of organic bonds have been tabulated (76), and a series of rates of decomposition for t-butyl peresters is listed by Halgren (77). The decompositions of t-butyl alkylperformates are concerted, and the rates in order of the stability of the alkyl radical produced, when the alkyl group is secondary or teriary (8). Increasing radical stability should reflect a decreasing bond-dissociation energy for the carbon-carbon bond broken as the alkyl radical is formed. Then the bond-dissociation energies for the carbon-bromine bonds and carbon-hydrogen bonds which are broken in forming identical radicals from hydrocarbons or

Table 19. Perester Decomposition Rates and Carbon-Bromine and Carbon-Hydrogen Bond-Dissociation Energies.

Decomposition Half-Life[a]		Bond-Dissociation Energy				
$R-CO_2-O-\underline{t}-C_4H_9$	min at 110° in C_6H_5Cl	R-X		kcal/mole		
R		X	Cl	Br	I	H
CH_3	230[c]		83.5[b]	70[b]	56[b]	104[b]
$(C_6H_5)_2C{=}CHCH_2CH_2$	150					
$\underline{n}$-C_9H_{19}	139		81[e]	67[e]	53[e]	97[e]
<u>endo</u>-norbornyl	26					
<u>exo</u>-norbornyl	20					
<u>endo</u>-norbornenyl	36[d]					
<u>exo</u>-norbornenyl	30[d]					
$\underline{c}$-C_6H_{11}	14				49-52[c]	
$\underline{i}$-C_3H_7	135		81[b]	68[b]	53[b]	94.5[b]
$C_6H_5CH_2$	5.9		60.4[c]	50.5[c]	40[b]	85[b]
$\underline{t}$-C_4H_9	0.9		78.5[b]	63[b]	49[b]	91[b]

[a] From Ref. 6, p. 51 except as noted below.

[b] From Ref. 54a.

[c] From Ref. 54b.

[d] Approximate value from comparison of rate data for saturated and unsaturated systems in Ref. 14.

[e] Approximation 0.5 kcal less than <u>n</u>-propyl from Ref. 54a.

alkyl halides should be approximately proportional to the perester decomposition rates. From Table 19, it is reasonable to estimate bond-dissociation energies of 65 kcal/mole for the carbon-bromine bonds of endo- and exo-5-bromonorbornene and 93 kcal/mole for the carbon-hydrogen bonds in the endo- and exo-5-positions of norbornene. These values are unlikely to be in error by more than 2 kcal/mole. (From this thesis, a posteriori, it is likely that no substantial error would be involved if the same values of 65 kcal/mole for the bond-dissociation energy of the carbon-bromine bond of 2-bromonortricyclene and 93 kcal/mole for the bond-dissociation energy of the carbon-hydrogen bond in the 2-position of nortricyclene are assumed.)

Now some approximate energies can be determined for the chain-transfer steps for the free radical reductions of endo- and exo-5-bromonorbornene (and 2-bromonortricyclene) with tri-n-butyltin hydride, assuming the generally accepted free-radical chain process for the reactions (37).

Initiation

$$? \longrightarrow R\cdot$$

Propagation

(a) $R\cdot + (n\text{-}C_4H_9)_3SnH \longrightarrow RH + (n\text{-}C_4H_9)_3Sn\cdot$

$\Delta H_{(a)} = +71$ kcal/mole -93 kcal/mole $= -22$ kcal/mole

(b) $(n\text{-}C_4H_9)_3Sn\cdot + RBr \longrightarrow (n\text{-}C_4H_9)_3SnBr + R\cdot$

R = endo-5-norbornenyl
exo-5-norbornenyl
(2-nortricyclyl)

$\Delta H_{(b)}$ = +65 kcal/mole -79 kcal/mole = -14 kcal/mole

Heat of Reaction = $\Delta H_{(a)} + \Delta H_{(b)}$ = -36 kcal/mole.

The conclusion from the above calculation, even with generous error limits, is that the reductions of endo- and exo-5-bromonorbornene (and 2-bromonortricyclene) with tri-n-butyltin hydride involve two very exothermic chain-transfer steps, which explains the ease with which the reductions go. Recently, Carlsson and Ingold have determined the experimental heats of reaction for a number of organotin hydride reductions of alkyl halides. These heats of reaction were almost constant, ranging between about -35 and -42 kcal/mole, regardless of whether the halogen was chlorine or bromine, and regardless of which of several organotin hydrides was used (46). Our calculated value of -36 kcal/mole for the reductions of endo- and exo-5-bromonorbornene and 2-bromonortricyclene with tri-n-butyltin hydride appears to be in satisfactory agreement with these experimentally determined heats of reaction.

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