Formation of Carbon —Carbon and Carbon — Heteroatom Bonds via Organoboranes and Organoborates

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1. Introduction

Until recently the use of organometallics as discrete reagents and intermediates in organic synthesis had been largely restricted to a relatively few classes or compounds, such as those containing lithium and magnesium. Mainly within the last two decades, organocopper compounds (1) and organoboron compounds (2) have emerged as versatile and useful reagents and intermediates in organic synthesis. This review describes some of the key features common to various organoboron reactions used for the formation of carbon — carbon and carbon — heteroatom bonds and summarizes the available information on these reactions according to the product types. Hydration of olefins and acetylenes via hydroboration–oxidation was reviewed earlier, (3) and this chapter does not update this reaction. Also excluded is a detailed discussion of the synthesis of olefins and acetylenes via organoboron compounds.

1.1. Fundamental Properties of Organoboron Compounds

Except for carboranes, (4) organoboron compounds generally exist either as tricoordinate or as tetracoordinate species. The trisubstituted derivatives of boron are called *boranes*, which may exist either as essentially trigonal planar monomeric species or as aggregates in which the boron atoms occupy the central position of an essentially tetrahedral configuration. In fact, essentially all monoorganoboranes (RBH_2) and diorganoboranes (R_2BH) as well as the parent borane (BH_3) exist as the dimers, (5) whereas triorganoboranes (R_3B) are usually monomeric. For the sake of simplicity, however, all of these compounds are treated as monomers in this review, except when such a simplification is unacceptable.

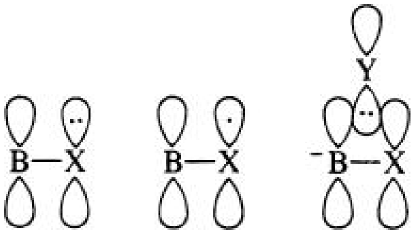
1.1.1.1. Electronegativity and Size

The electronegativity of boron has been estimated at 2.0, (6) which is relatively close to the corresponding value of 2.5 for carbon and is higher than those of the alkali and alkaline–earth metals, such as lithium and magnesium, as well as of essentially all transition metals, which range from 0.86 to 1.75. 6a With the use of an empirical equation, the boron — carbon bond is estimated to be about 90% covalent and 10% ionic. 6b It is, therefore, not suprising that organoboranes generally do not react like Grignard reagents or organolithium compounds with typical organic and inorganic electrophiles, such as (a) organic halides and sulfonates, (b) carbonyl compounds, (c) epoxides, and (d) water and other “active” hydrogen compounds, under the usual ionic reaction conditions. The relatively short carbon —boron bond length, e.g. 1.57 Å for $(CH_3)_3B$, must also be responsible for the high degree of inaccessibility of the bonding electrons of the carbon — boron bond in these and other reactions of organoboranes. However, this very property of organoboranes renders them highly tolerant of the presence of a variety of electrophilic functional groups.

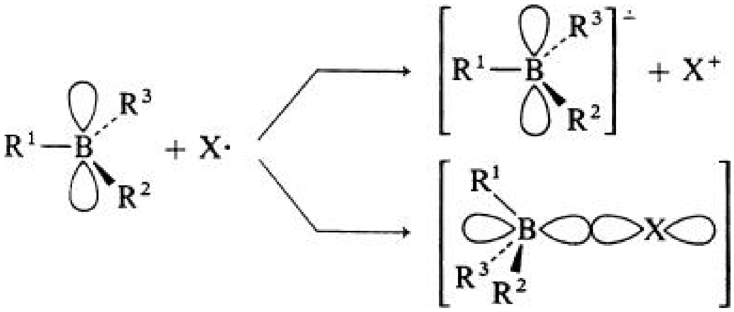
1.1.1.2. Empty p Orbital

The presence and/or ready availability of the empty *p* orbital makes organoboranes electrophilic or Lewis acidic. Thus organoboranes react readily with a variety of neutral or negatively charged bases to form the corresponding complexes. For example, organoboranes readily form 1:1 complexes with various amines and even with some ethers, such as tetrahydrofuran (THF). Similarly, their reaction with a negatively charged species forms the corresponding *organoborate*, for which the monomeric ion pair with the essentially tetrahedral borate anion appears to be a reasonable representation. (7) This complexation reaction seems to be one of the crucial steps in essentially all the ionic reactions of organoboranes. (7)

The Lewis acidic property mentioned above is shared by many other organometallics including organoalanes, and thus is not unique to organoboranes. Far more striking, however, is the ability of the boron *p* orbital to effectively participate in $p_\pi - p_\pi$ bonding with the adjacent *p* or sp^n (*n* = 1, 2, or 3) orbitals of other second-row elements, such as C, N, O, and F. This appears to be responsible, at least in part, for the unique 1,2-migration reactions and other reactions of organoboron compounds discussed later. Three types of $p_\pi - p_\pi$ interactions pertinent to the present discussion are shown below.



The low-lying empty *p* orbital can also readily accommodate either one electron or a free radical, thereby making organoboranes highly reactive in many free-radical reactions.



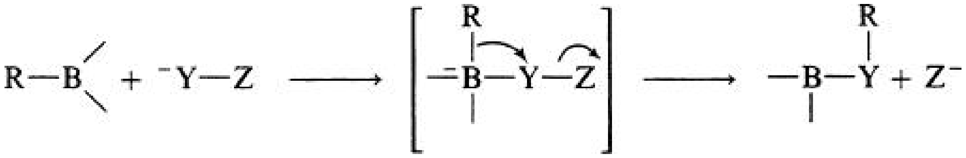
Although quantitative interpretations of the reactions of organoboron compounds remain difficult, chemists can rationalize and, in many reactions, even predict the results on a qualitative basis through consideration of a relatively few parameters such as those discussed above.

1.2. General Reaction Patterns

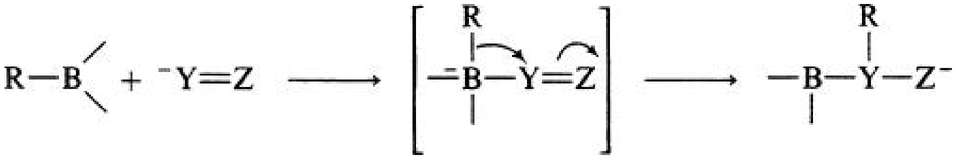
Although the mechanisms of organoboron reactions have seldom been fully established, it is useful to attempt to summarize and classify various organoboron reactions on the basis of the available data, including the reactant–product relations.

1.2.1.1. Ionic Reactions

The highly electrophilic but weakly nucleophilic nature of organoboranes has already been mentioned. The organoborates formed by the reaction of organoboranes with basic or nucleophilic species are often thermally stable and do not undergo any further spontaneous reactions. When the nucleophile is appropriately substituted, however, the 1,2-migration reactions represented by Eqs. 1–3 take place.



(1)



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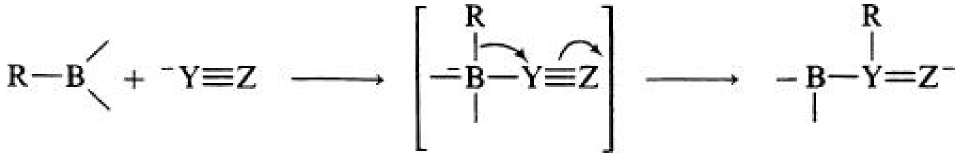
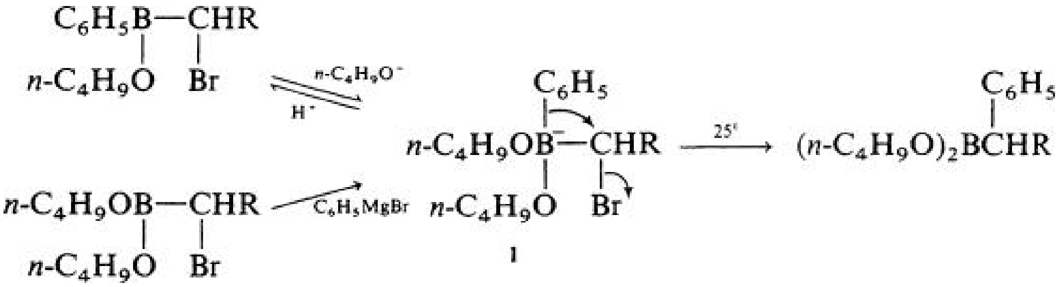

(3)

The key features common to all of these reactions are the formation of the borate anion as a transient species and its intramolecular 1,2-migration. Minor variations of these mechanistic pathways, such as stepwise analogs and vinylogs, are also conceivable. It is significant that the great majority of ionic reactions of organoboranes can be rationalized in terms of these mechanistic pathways. Although there is little doubt about the intermediacy of heterosubstituted organoborates, this point has seldom been established. However, the intermediacy of an α -bromoorganoborate (**1**) has been clearly established in one reaction. (8)



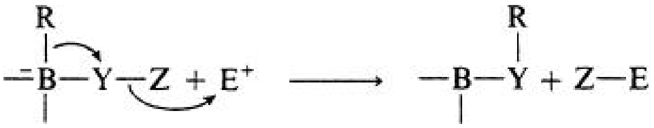
1.2.1.2. Ionic Reactions of Stable Organoborates

It has recently been recognized that thermally stable organoborate anions, which are negatively charged and coordinatively saturated, act as unique nucleophiles. (7) They react with a variety of organic and inorganic electrophiles via either intermolecular or intramolecular transfer.

Intermolecular transfer:

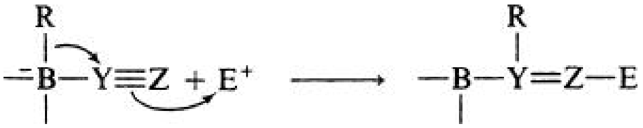

(4)

Intramolecular transfer:



(5)

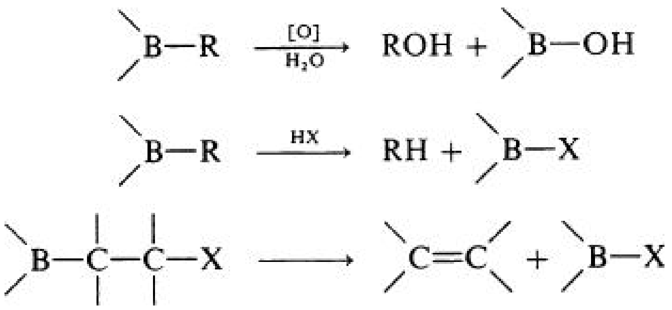
(6)



(7)

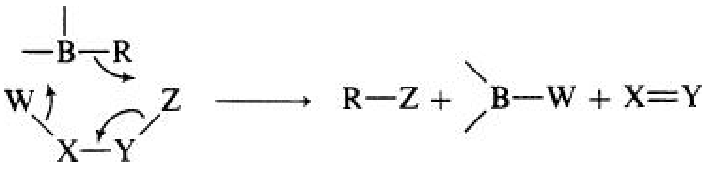
In the intermolecular transfer reaction the organoborate acts as the boron analog of a Grignard reagent with very mild reactivity. On the other hand, the intramolecular transfer reactions are closely related to those of organoboranes. The only difference is that the organoborate reactions require activation by electrophiles, whereas the organoborane reactions generally occur spontaneously. These intramolecular transfer reactions are not only highly unusual as organometallic reactions, but also tend to take place much more readily than the intermolecular reactions where both can occur. These reactions may be best interpreted within the framework of the well-known anionotropic 1,2-migration reactions, such as the Wagner–Meerwein rearrangement. Significantly, the intramolecular transfer reactions of both organoboranes and organoborates have proceeded with retention of configuration of the migrating group. Mechanistic considerations also predict inversion of configuration at the migration terminus, which has often been borne out. (9, 10)

The products of 1,2-migration reactions are new organoboranes that must be further converted into the desired organic compounds. This is achieved by one of three methods: (a) oxidation, (b) protonolysis, or (c) β elimination. These reactions are discussed later in more detail.

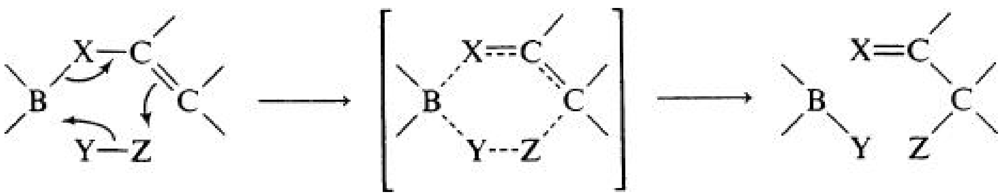


1.2.1.3. Concerted Reactions

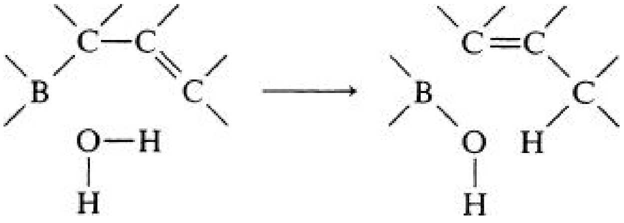
Considering the relatively covalent nature of the B—C bond and the size of the boron atom and its valence shell orbitals, which are comparable to those of the carbon atom, organoborons might be expected to participate readily in some concerted pericyclic reactions. The information available strongly indicates that the protonolysis of organoboranes with carboxylic acids is best viewed as a concerted $[2_s + 4_s]$ reaction in which the boranes act as two-electron components.



Within the last decade or two a considerable number of organoborane reactions have been observed that appear to be best represented by the concerted $[4_s + 2_s]$ reaction in which the boranes act as four-electron components.



Although the examples observed to date have been essentially restricted to reactions of allylic boranes and alkenyloxyboranes, the scope of this type of $[4_s + 2_s]$ reaction is likely to be broad.



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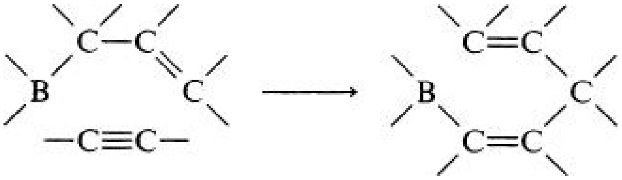

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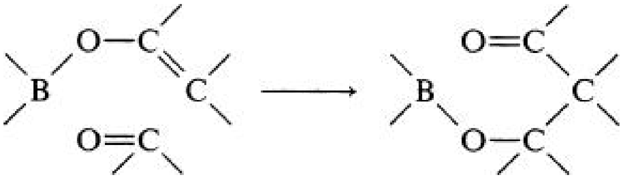
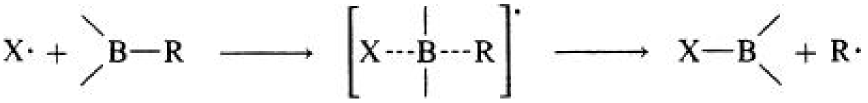


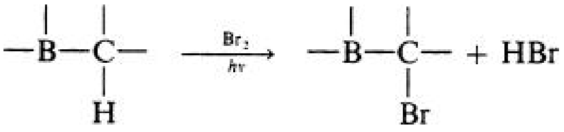
(10)

1.2.1.4. Free-Radical Reactions

Organoboranes participate readily in at least two distinctly different free-radical reactions. Although there has been essentially no firmly established example of the bimolecular homolytic substitution (S_H2) taking place at a simple saturated carbon center, organoboranes undergo this reaction. (11)



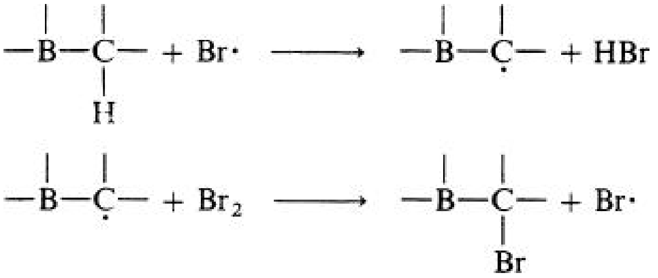
Another type of free-radical reaction of organoboranes is the α -abstraction reaction exemplified by bromination of organoboranes. (12)



$$-\overset{|}{B}-\underset{\underset{H}{|}}{\overset{|}{C}}- \xrightarrow[h\nu]{Br_2} -\overset{|}{B}-\underset{\underset{Br}{|}}{\overset{|}{C}}- + HBr$$

(11)

The available data support a free-radical chain mechanism.



(12)

The $p_{\pi} - p_{\pi}$ interaction discussed earlier must be responsible for promoting this reaction.

In general, nitrogen and oxygen free radicals participate in the S_H2 reaction, whereas the bromine free radical undergoes an α -abstraction. On the basis of these observations, we may tentatively conclude that those free radicals that can form thermodynamically highly stable bonds to boron, such as the B — O and B — N bonds, favor the S_H2 reaction. With others α -abstraction can be the dominant course of the reaction.

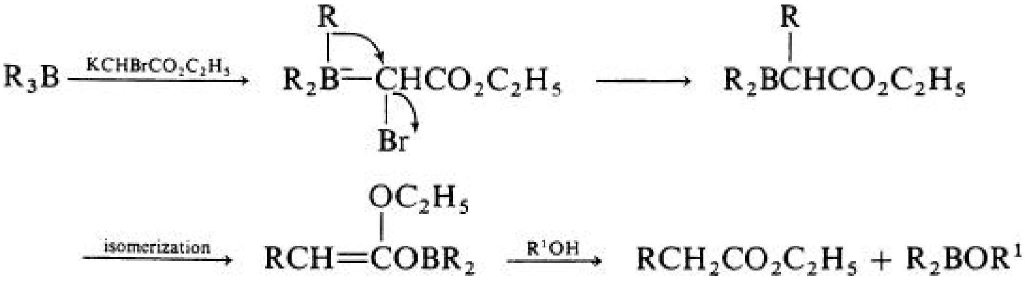
2. Brief Survey of Reactions of Organoboranes and Organoborates

In this section various types of reactions of organoboranes and organoborates are discussed and illustrated by representative examples.

2.1. Formation of Carbon — Carbon Bonds via Reactions of Organoboranes with Nucleophilic Reagents

2.1.1.1. Reactions with α -Hetero-Substitutedα-Carbonyl Carbon Nucleophiles

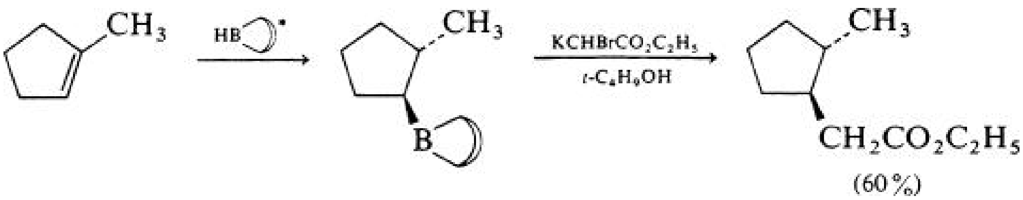
The reaction of organoboranes withα-halo enolate anions provides a useful method forαalkylation andαarylation of carbonyl compounds. (13)



$$R_3B \xrightarrow{KCHBrCO_2C_2H_5} R_2\overset{R}{\overset{|}{B^-}}-\underset{Br}{CHCO_2C_2H_5} \longrightarrow R_2B\overset{R}{CHCO_2C_2H_5}$$
$$\xrightarrow{\text{isomerization}} RCH{=}\overset{OC_2H_5}{C}OBR_2 \xrightarrow{R^1OH} RCH_2CO_2C_2H_5 + R_2BOR^1$$

(13)

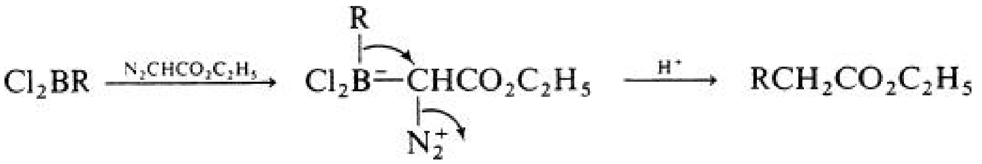
The unusually facile protonolysis involves the reaction of enolboranes formed via isomerization. (14) A wide variety ofα-halo enolate anions and related species undergo this alkylation reaction. Several observations are worth noting: (a) introduction of hindered and/or stereo-defined alkyl groups and aryl groups in theα position of carbonyl compounds can now be achieved, (15) and (b)



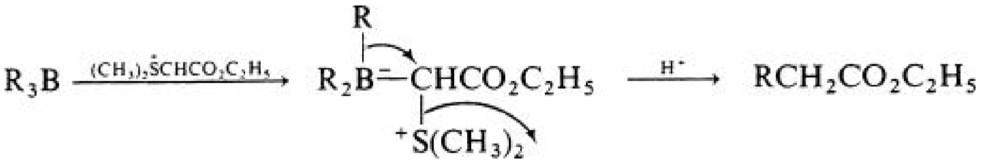
α, α-dihalo enolate anions can be converted into eitherα-halo-α-alkyl orα, α-dialkyl derivatives (Eq. 14). (16)

$$(n\text{-}C_6H_{13})_3B \xrightarrow[t\text{-}C_4H_9OK,\ t\text{-}C_4H_9OH]{Br_2CHCO_2C_2H_5} \underset{(98\%)}{n\text{-}C_6H_{13}CHBrCO_2C_2H_5}$$
$$\xrightarrow[t\text{-}C_4H_9OK,\ t\text{-}C_4H_9OH]{(C_2H_5)_3B} \underset{(72\%)}{n\text{-}C_6H_{13}CH(C_2H_5)CO_2C_2H_5} \quad (14)$$

Related to these alkylation reactions are the reactions of organoboranes with α -diazo carbonyl compounds (Eq. 15) (17, 18) and the corresponding sulfur ylides (Eq. 16). (19)



$$\mathrm{Cl_2BR} \xrightarrow{\mathrm{N_2CHCO_2C_2H_5}} \mathrm{Cl_2}\overset{\mathrm{R}}{\bar{\mathrm{B}}}\mathrm{-}\underset{\mathrm{N_2^+}}{\mathrm{C}}\mathrm{HCO_2C_2H_5} \xrightarrow{\mathrm{H^+}} \mathrm{RCH_2CO_2C_2H_5} \quad (15)$$

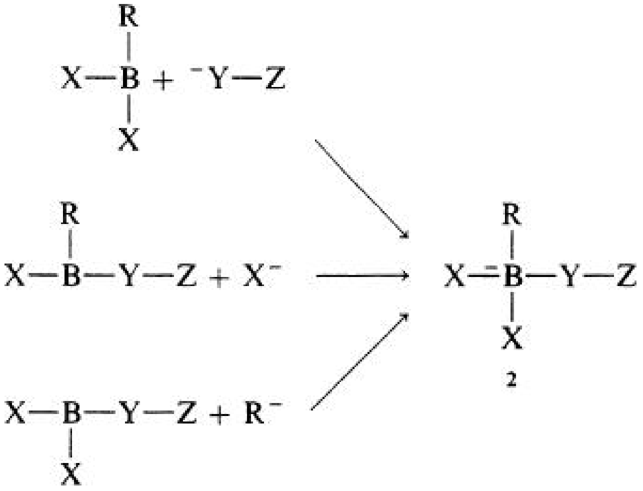


$$\mathrm{R_3B} \xrightarrow{\mathrm{(CH_3)_2\dot{S}CHCO_2C_2H_5}} \mathrm{R_2}\overset{\mathrm{R}}{\bar{\mathrm{B}}}\mathrm{-}\underset{\mathrm{^+S(CH_3)_2}}{\mathrm{C}}\mathrm{HCO_2C_2H_5} \xrightarrow{\mathrm{H^+}} \mathrm{RCH_2CO_2C_2H_5} \quad (16)$$

Various otherα-hetero-substituted carbon nucleophiles, such as those derived from aldimines (20, 21) vinyl ethers (22) and furan, (23) have been shown to undergo related migration reactions.

2.1.1.2. Reactions of α*-Hetero-Substituted Organoboranes with Nucleophiles*

Inspection of the structure of the presumed key intermediate **2** in the intramolecular transfer reaction of organoboranes discussed above suggests that, in addition to this route, there are at least two other routes to **2**.

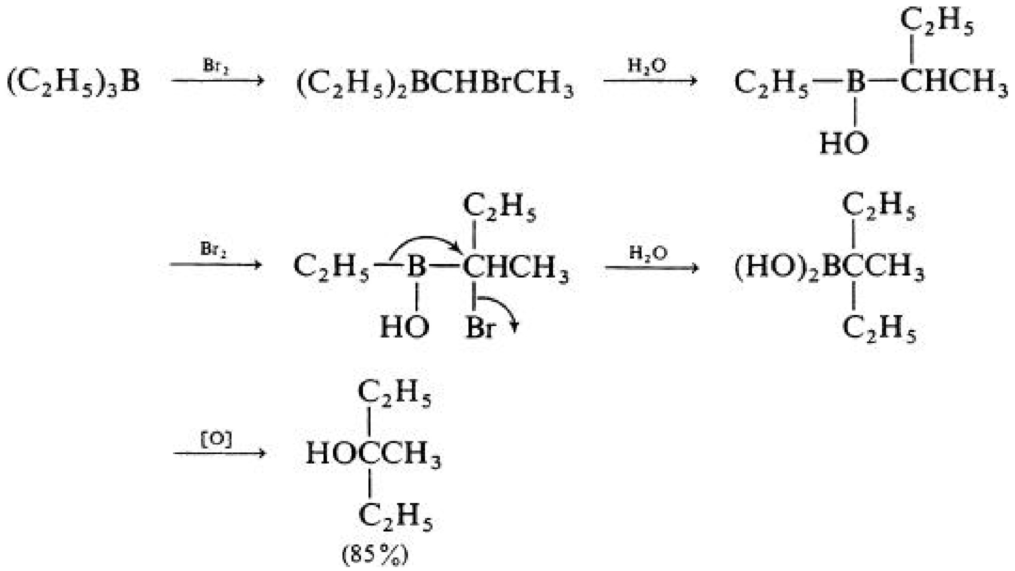


(X, Y, Z = carbon or a heteroatom group)

The required α-hetero-substituted organoboranes can be prepared by various methods, of which the free-radical bromination of organoboranes and the hydroboration of haloalkenes and haloalkynes have been most widely used.

2.1.1.3.1. Reaction of α-Bromoboranes Obtained via Bromination of Organoboranes

The reaction of triethylborane with bromine in the presence of water has been shown to proceed by the mechanism described in Eq. 17, in which the free-radical bromination and the intramolecular 1,2 migration alternate. (24) The reaction sequence represents a unique method for coupling two boron-bound carbon groups, (25-28)



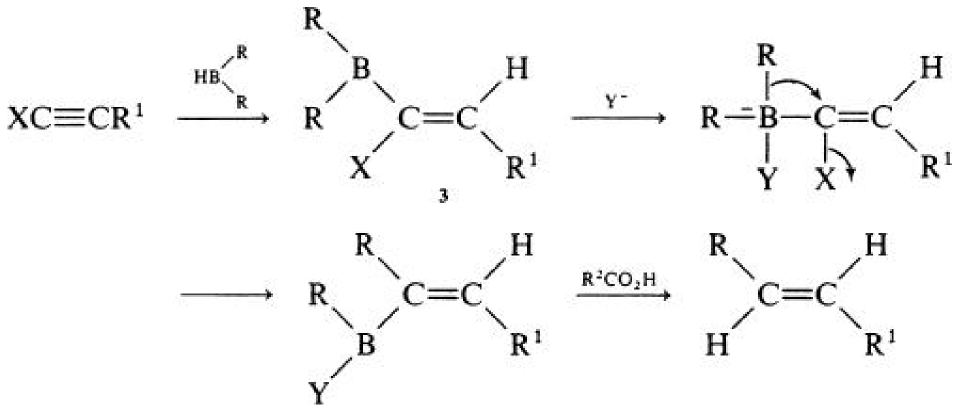
$$(C_2H_5)_3B \xrightarrow{Br_2} (C_2H_5)_2BCHBrCH_3 \xrightarrow{H_2O} C_2H_5-\underset{HO}{B}-\overset{C_2H_5}{C}HCH_3$$

$$\xrightarrow{Br_2} C_2H_5-\underset{HO}{B}-\underset{Br}{\overset{C_2H_5}{C}}HCH_3 \xrightarrow{H_2O} (HO)_2B\underset{C_2H_5}{\overset{C_2H_5}{C}}CH_3 \qquad (17)$$

$$\xrightarrow{[O]} HO\underset{C_2H_5}{\overset{C_2H_5}{C}}CH_3 \quad (85\%)$$

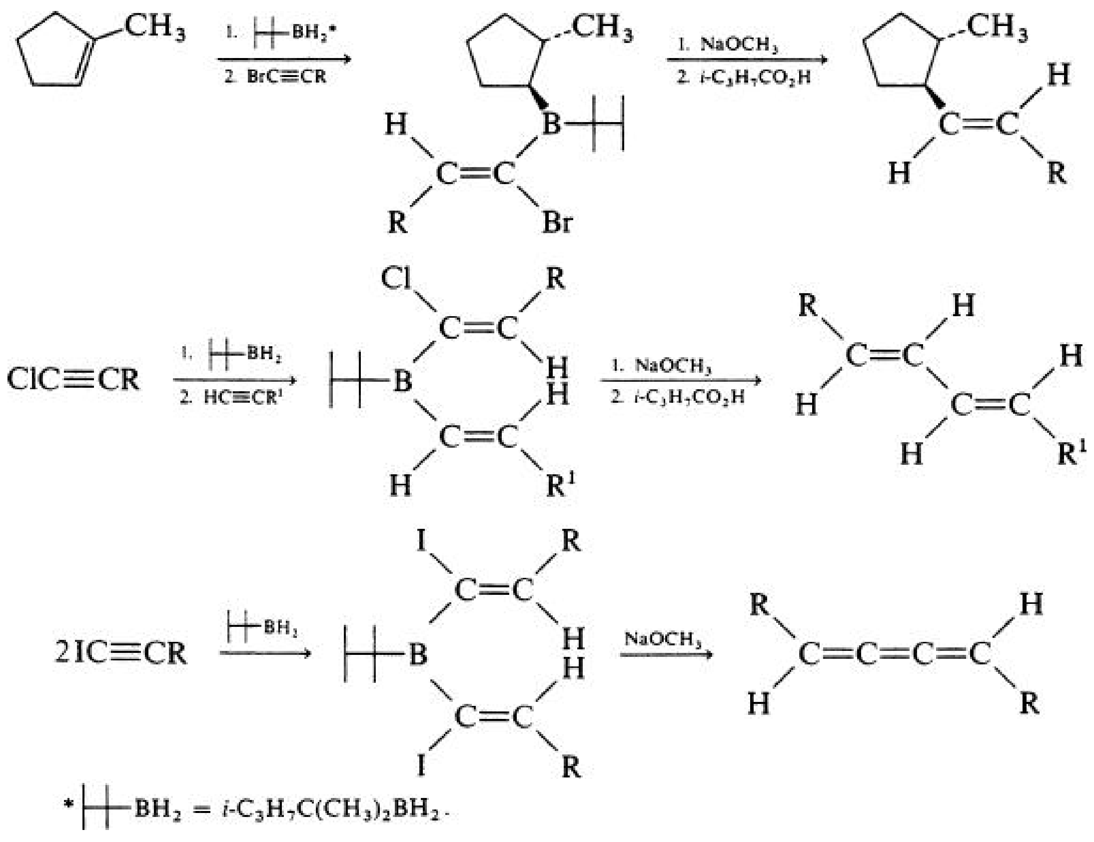
2.1.1.3.2. Reaction ofα-Haloboranes Obtained via Hydroboration

Hydroboration of alkenyl and alkynyl halides producesα-haloboranes. Especially noteworthy is the nearly exclusive formation of 1-halo-1-alkenylboranes **3** in a regio- and stereoselective manner. Even more interesting is the reaction of **3** with nucleophiles, which induces intramolecular 1,2 migration. The reaction proceeds with complete inversion of configuration at the migration terminus. (29)



(18)

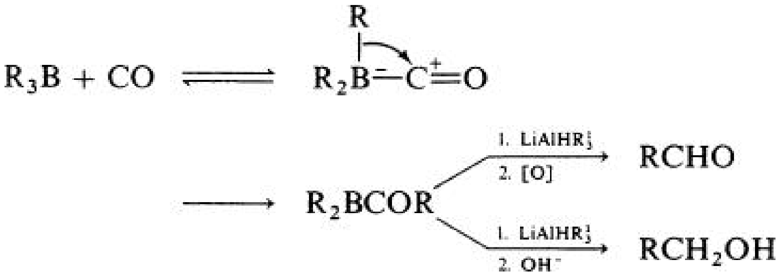
The configuration of the migrating group is completely retained. Protonolysis of the alkenylboranes thus formed also proceeds with complete retention. Various highly stereoselective procedures for the synthesis of monoolefins, (30, 31) conjugated (*E,E*)-dienes, (32) and even (*E*)-1,2,3-butatrienes (33) have been developed on the basis of the sequence shown in Eq. 18.



2.1.1.4. *Carbonylation and Related Reactions of Organoboranes*

The organoboranes also undergo double and triple 1,2 migrations, such as carbonylation (34) and reactions withα-polyhalogenated carbon nucleophiles. (35-40)

Closely related to these reactions is the multiple migration reaction of cyanoborates induced by Lewis acids. (41) These reactions provide a novel method (“stitching and riveting”) for synthesizing tertiary alcohols, ketones, and aldehydes, as discussed later in detail. In the carbonylation of organoboranes carbon monoxide acts as a Lewis base carbene equivalent. The overall scope and a proposed mechanism are indicated in Eqs. 19–21.



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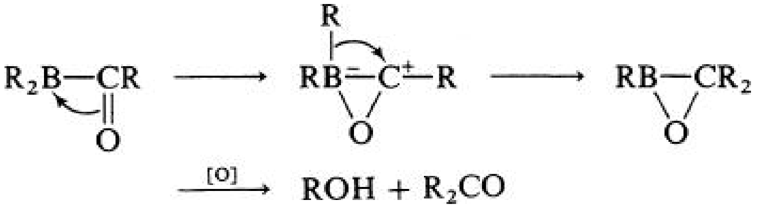

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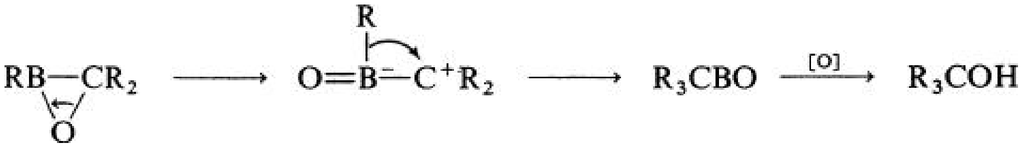


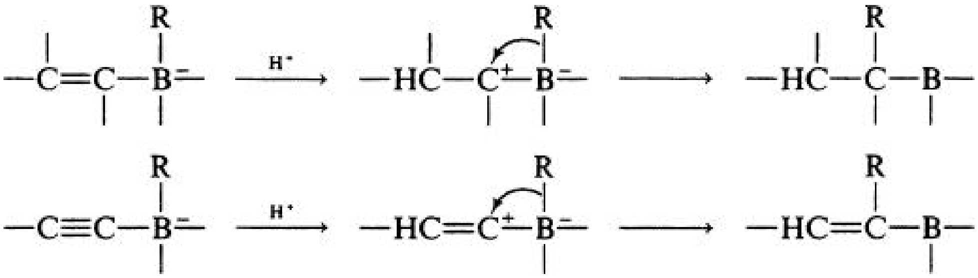
(21)

2.2. Formation of Carbon — Carbon Bonds by Reactions of Organoborons with Electrophilic Reagents

Although organoboranes do not react readily with electrophilic reagents, the corresponding organoborates can either act as Grignard-like reagents or undergo intramolecular transfer reactions (Eqs. 4–7) in their interaction with electrophiles. Under appropriate conditions, however, even organoboranes can react with electrophilic reagents via free-radical or concerted mechanisms. Some typical carbon — carbon bond-forming reactions of organoboranes and organoborates with electrophilic reagents are discussed in this section.

2.2.1.1. Reaction with Proton Donors

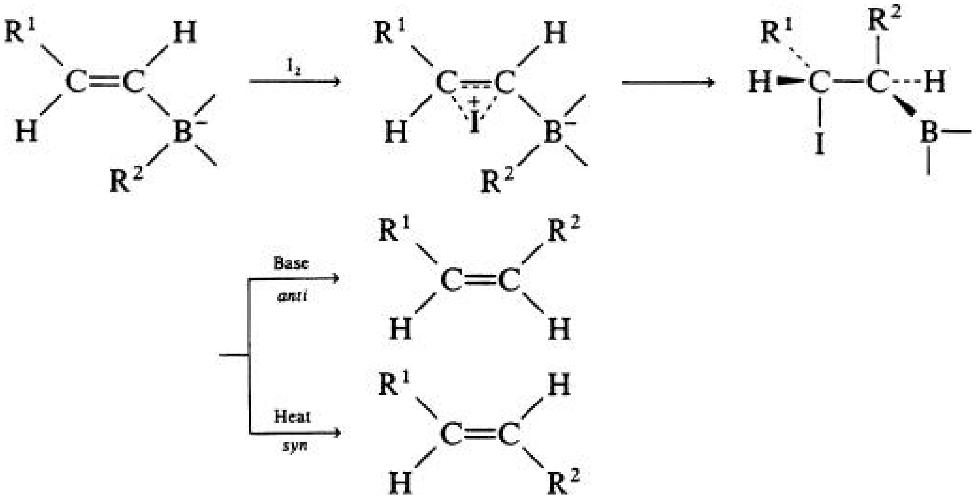
Whereas alkyl-, aryl-, allyl-, and benzylboron derivatives undergo cleavage of the B — C bond with certain Brønsted acids, the corresponding reactions of alkenyl- and alkynylborates generally lead to the formation of a carbon — carbon bond between two boron-bound organic groups via 1,2 migration.



The reaction provides a route to certain Markovnikov organoboranes that cannot be readily prepared by hydroboration. (42) The organoborane intermediates have been converted into alcohols, aldehydes, or ketones via oxidation (42, 43) or into olefins via protonolysis (44) or dehydroboration. (45)

2.2.1.2. Reaction with Iodine or Bromine

The reaction of alkenyl- or alkynylborates with iodine or bromine can provide an efficient and selective method of coupling two unlike boron-bound groups. Di- and trisubstituted olefins (Eqs. 22–25), (46-50) acetylenes (Eq. 26), (51), conjugated enynes (Eq. 27), (52, 53) and conjugated diynes (Eq. 28) (54) have been prepared in high yields.



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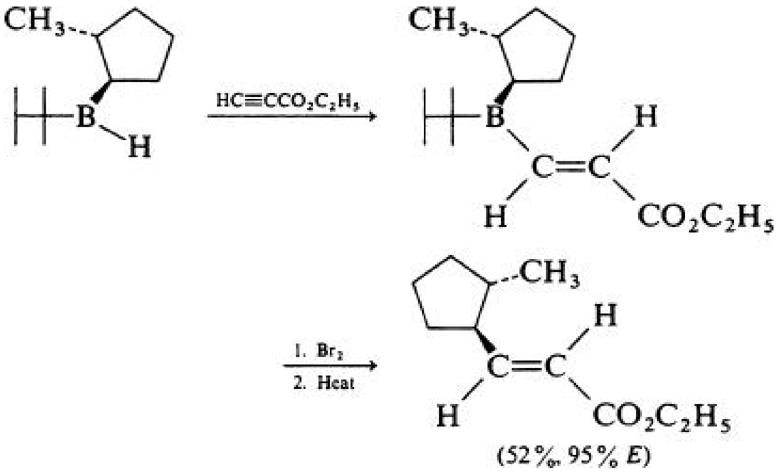

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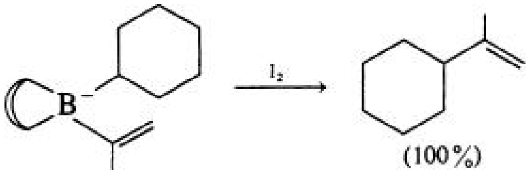

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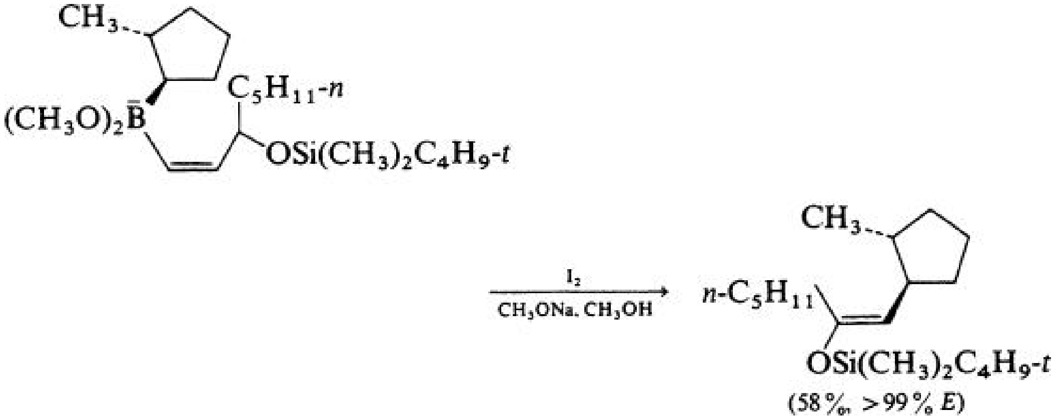

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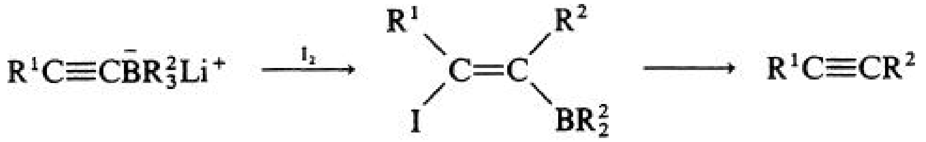
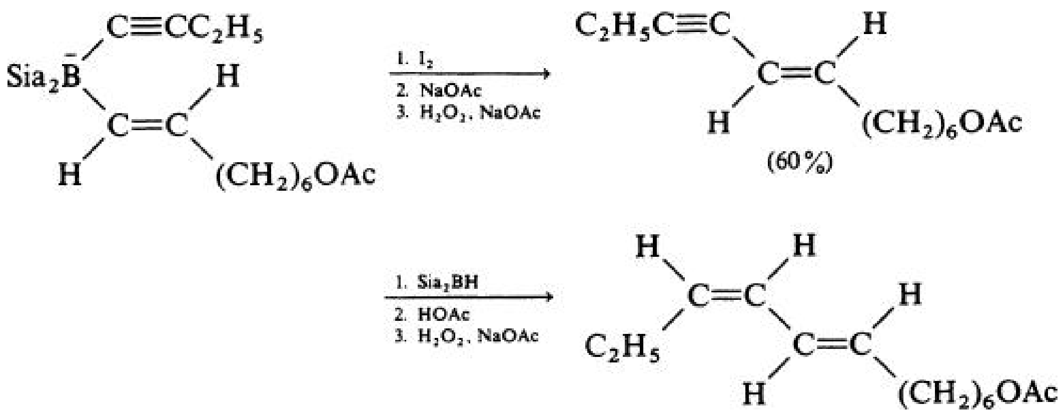


(26)

(R^1 = H or an organic group, R^2 = alkyl or aryl)



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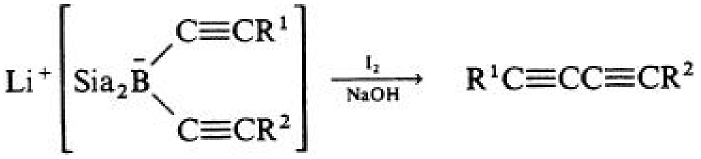


(28)

* Sia = $i\text{-}C_3H_7CH(CH_3)—$.

A few related reactions of tetraarylborates are known (Eq. 29). (55) Currently available procedures, however, do not appear suitable for the selective coupling of two dissimilar aryl groups.

$$KB(C_6H_5)_4 \xrightarrow{Br_2} C_6H_5C_6H_5 + C_6H_5Br \qquad (29)$$

2.2.2. Reactions with Alkyl Halides, Acyl Halides, and Epoxides

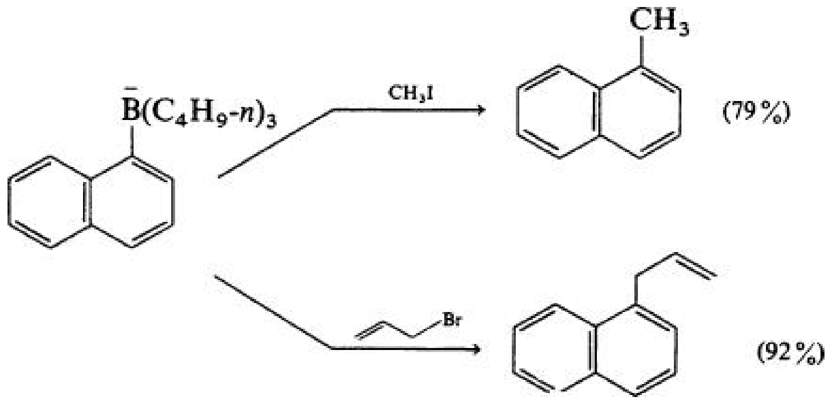
2.2.2.1.1. Intermolecular Transfer Reactions

The Grignard-like reaction, that is, intermolecular transfer reaction, of organoborates is relatively rare. Acyl halides represent about the only class of carbon electrophiles that can participate readily in the intermolecular transfer reaction (Eq. 30). (56, 57) This ketone synthesis is highly chemoselective.

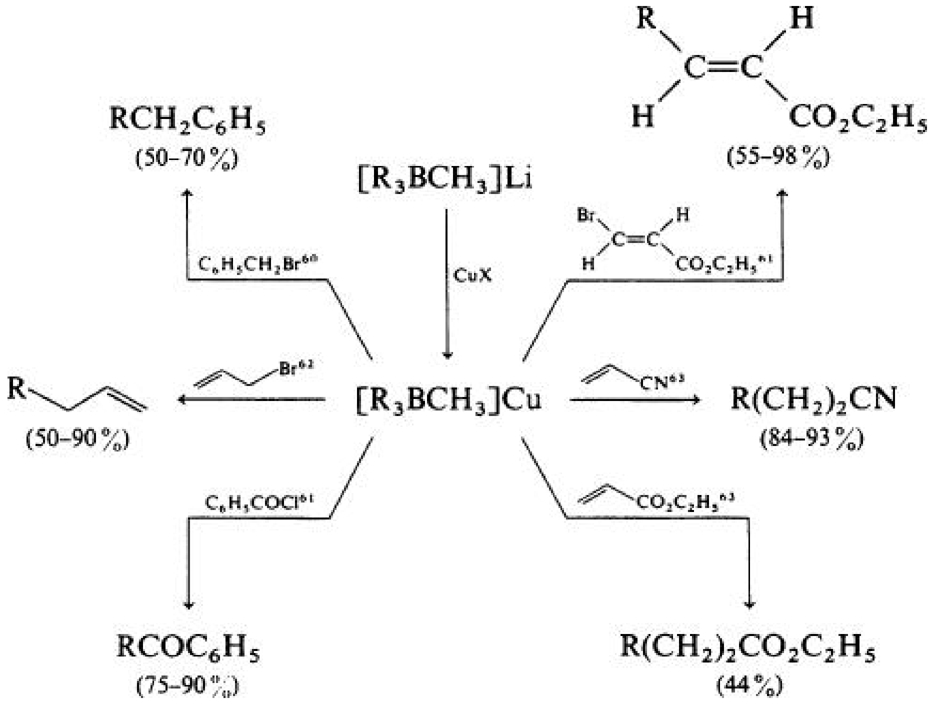
$$Li^+(R^1\bar{B}R_3) + R^2COX \xrightarrow{25^\circ} R^1COR^2 + BR_3 \qquad (30)$$
$$(R^1 = \text{Alkyl, benzyl, aryl, } CH_3COCH_2)$$

Even acyl halides, however, preferentially undergo the intramolecular transfer reaction with cyanoborates, (41) alkenyl- and alkynylborates, (58) and thioalkoxymethylborates. (59)

Alkyl halides and epoxides are generally quite reluctant to participate in the intermolecular transfer reaction. Only highly reactive alkyl halides, such as CH_3I and allyl bromides, react with lithium arylborates and sulfinyl- and sulfonyl-substituted lithium borates to form cross-coupled products. (7)



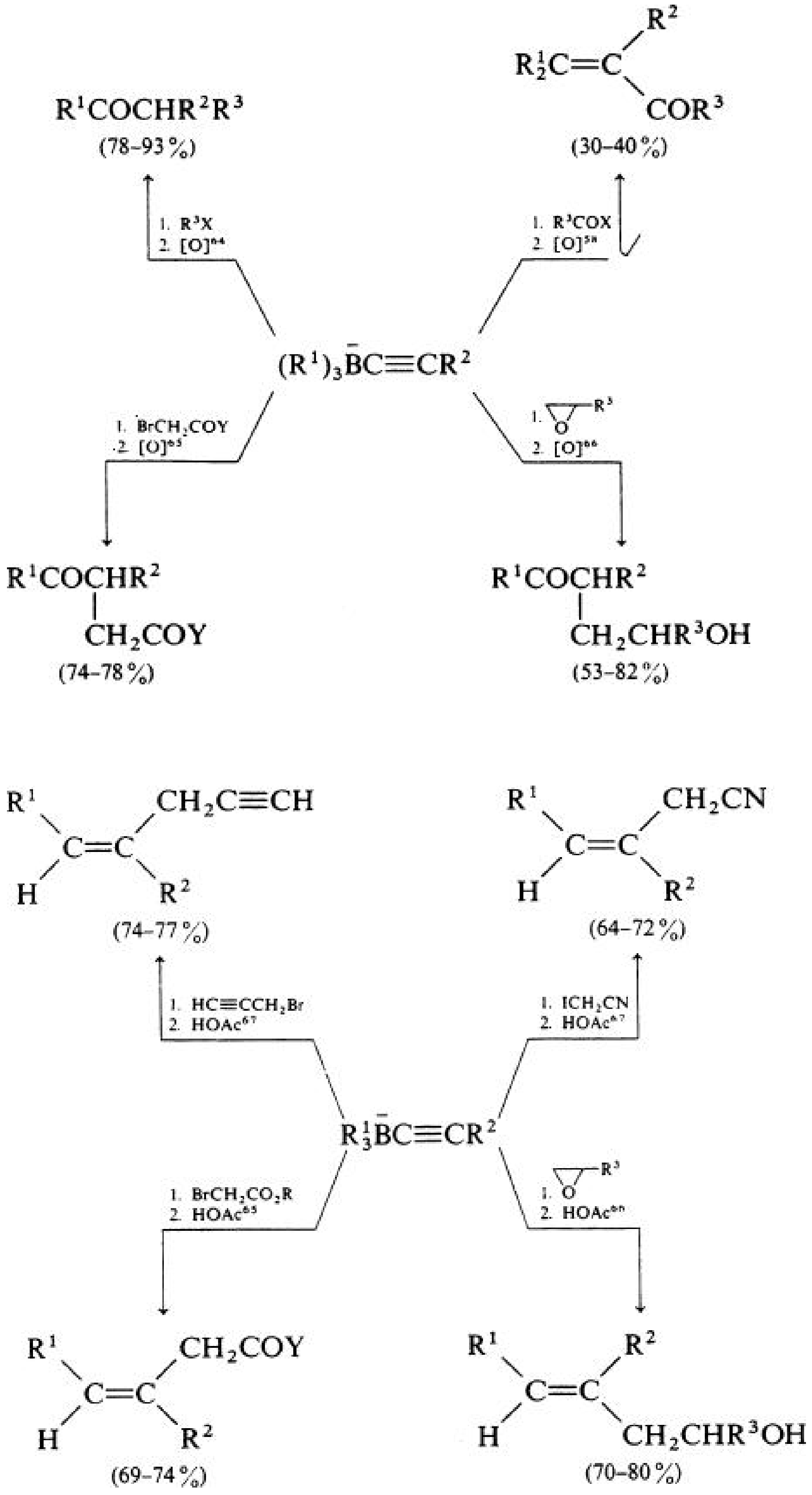
More recently, however, it has been found that the intermolecular transferability of organoborates can be enhanced by forming copper(I) borates. Despite these promising new developments, it may be said that the intermolecular transferability of organoborates is generally low, whereas organoboranes are quite nonnucleophilic.



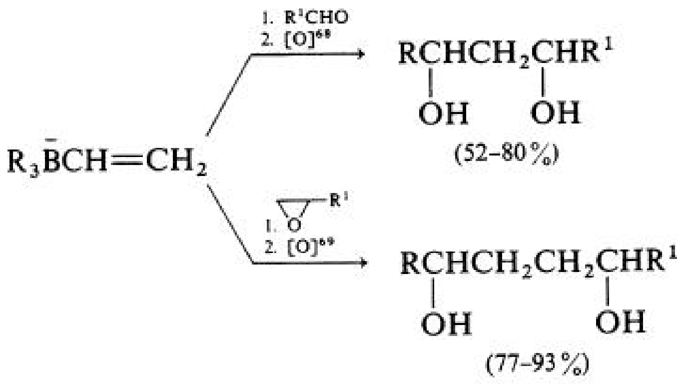
(30a)

2.2.2.1.2. Intramolecular Transfer Reactions

α, β -Unsaturated organoborates, such as alkynyl-, alkenyl-, and cyanoborates, have a strong tendency to undergo the intramolecular transfer reaction. The organoborane products thus formed can be either oxidized or subjected to protonolysis to obtain organic products.


R¹COCHR²R³
(78–93%)
1. R³X
2. [O]⁶⁴
R¹₂C=C(R²)COR³
(30–40%)
1. R³COX
2. [O]⁵⁸
(R¹)₃B̄C≡CR²
1. BrCH₂COY
2. [O]⁶⁵
1. epoxide R³
2. [O]⁶⁶
R¹COCHR² CH₂COY
(74–78%)
R¹COCHR² CH₂CHR³OH
(53–82%)
R¹(H)C=C(R²)CH₂C≡CH
(74–77%)
1. HC≡CCH₂Br
2. HOAc⁶⁷
R¹(H)C=C(R²)CH₂CN
(64–72%)
1. ICH₂CN
2. HOAc⁶⁷
R¹₃B̄C≡CR²
1. BrCH₂CO₂R
2. HOAc⁶⁵
1. epoxide R³
2. HOAc⁶⁶
R¹(H)C=C(R²)CH₂COY
(69–74%)
R¹(H)C=C(R²)CH₂CHR³OH
(70–80%)

(31)

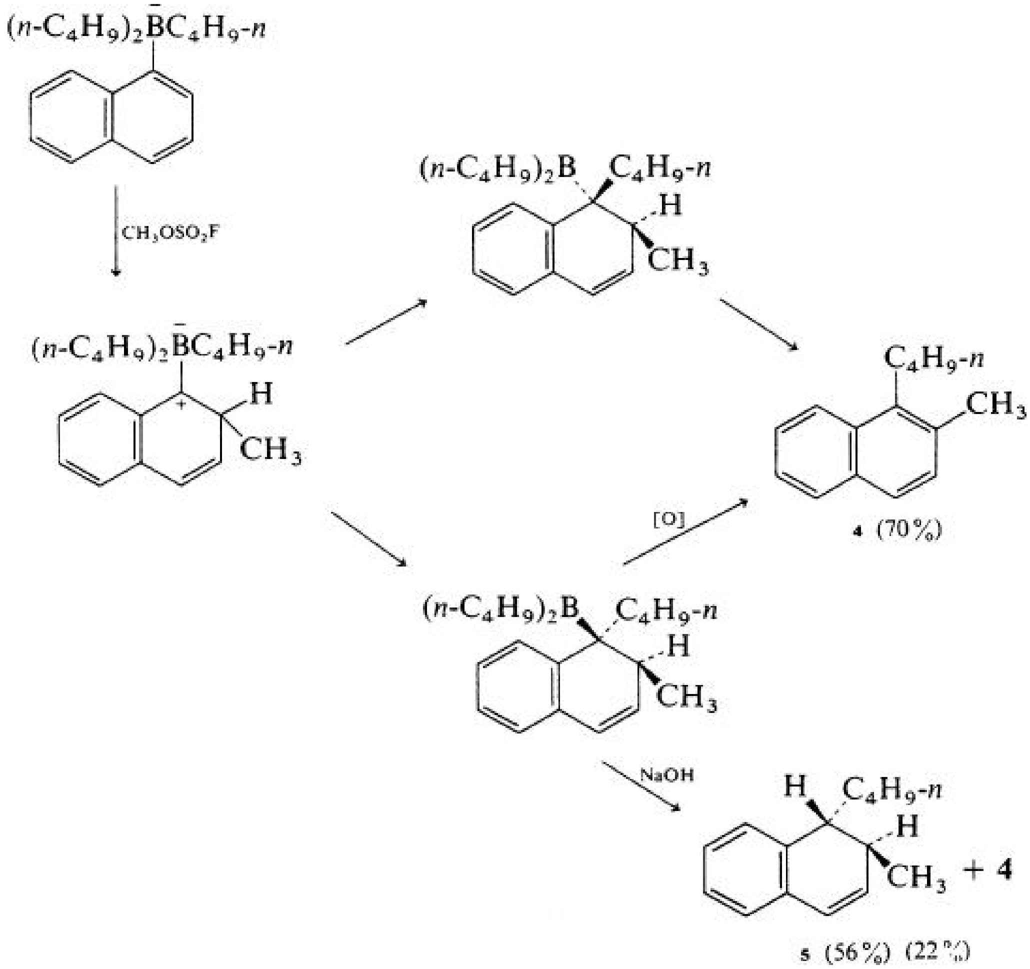


(X = halogen, Y = alkoxy)

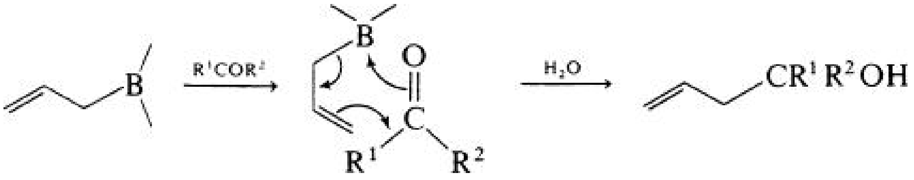
Alkylation of arylborates can proceed by either intermolecular or intramolecular transfer. The reaction of lithium 1-naphthyl-tri-*n*-butylborate with methyl fluorosulfonate produces a double alkylation product **4** after oxidation or a dihydroaromatic derivative **5** along with **4** after hydrolysis. (70)

2.2.2.2. Reactions with Aldehydes, Ketones, and α, β -Unsaturated Carbonyl Compounds

Ketones are generally quite inert to organoborons, although allylboranes, (71) enolboranes, (72-74) and enolborates (75) react with ketones.



(32)



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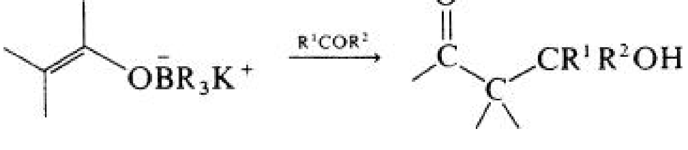
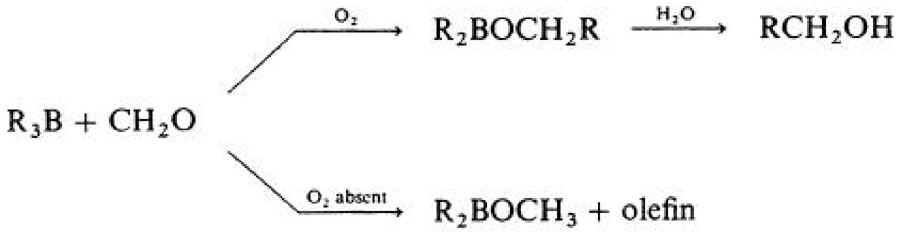
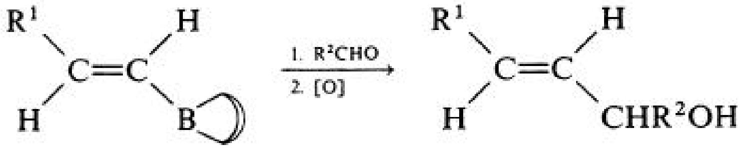


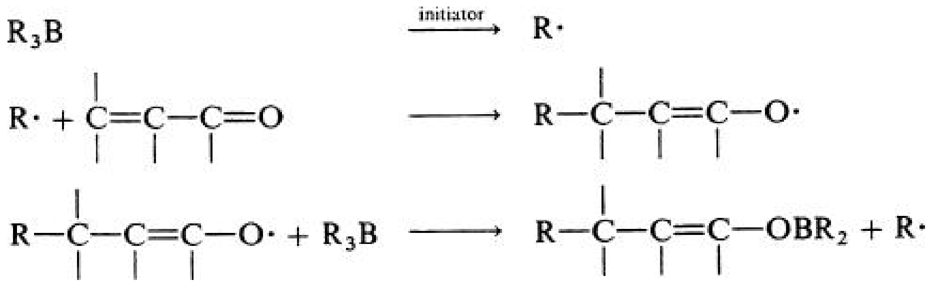
(34)

The reactions of allylboranes and enolboranes can be best viewed as $[2_s + 4_s]$ pericyclic processes. Aldehydes can participate in yet another reaction with organoborons. Monomeric formaldehyde reacts with organoboranes in the presence of air to give one-carbon homologated alcohols. (76) More recently it has been shown that alkenyl-9-borabicyclo[3.3.1]nonanes (alkenyl-9-BBN's) undergo a Grignard-like addition reaction with aldehydes at 65°. The yields, however, are generally modest. (77)

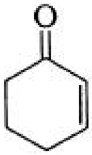


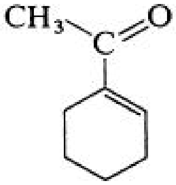


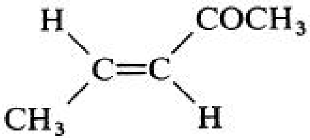
Unlike simple aldehydes and ketones, their α, β -unsaturated derivatives are quite reactive toward organoboranes. Most of the earlier results have been reviewed. (78) Many of these reactions have been shown to proceed by a free-radical chain mechanism (Eq. 35). The reactions of β -unsubstituted enones are very facile and quite useful in that most of the other conjugate addition reactions, such as those involving copper, 1a tend to give poor results with these unhindered enones. Methyl vinyl ketone, acrolein, α-methyl-, andα-bromoacroleins react satisfactorily. (79-81) On the other hand, the conjugate addition reaction of β -monosubstituted enones generally requires some external free-radical source, such as oxygen, peroxides, or light. Under these conditions, the following enones react with organoboranes to give 1,4 adducts. (82-84)

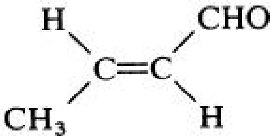


$$\begin{aligned} &R_3B \xrightarrow{\text{initiator}} R\cdot \\ &R\cdot + C{=}C{-}C{=}O \longrightarrow R{-}C{-}C{=}C{-}O\cdot \\ &R{-}C{-}C{=}C{-}O\cdot + R_3B \longrightarrow R{-}C{-}C{=}C{-}OBR_2 + R\cdot \end{aligned} \tag{35}$$

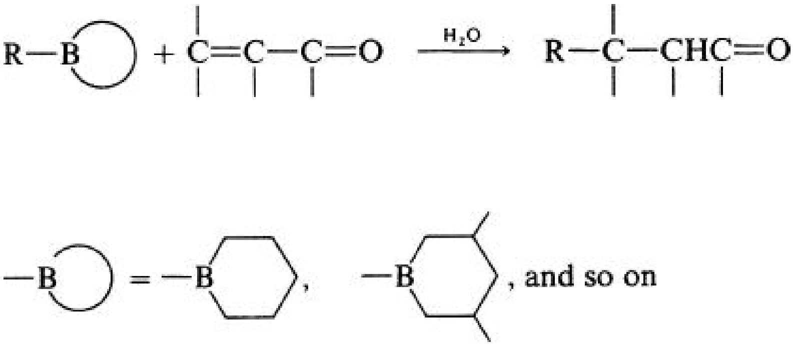






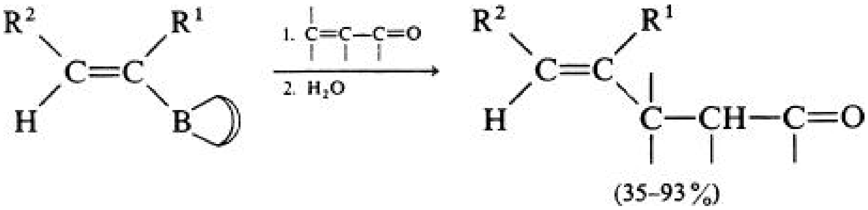


One serious limitation of the 1,4-addition reactions of organoboranes is that only one of the three organic groups is utilized. This problem has been partially overcome by using *B*-alkyl-boracyclanes. (85)

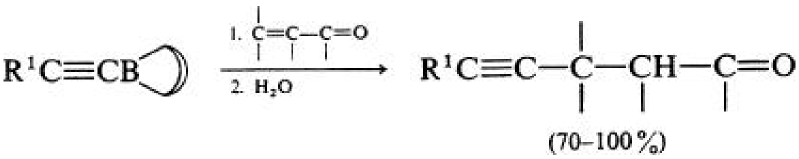


(36)

It has recently been reported that alkenyl- and alkynyl-9-BBN's react with enones to produce 1,4 adducts. (86-88) Even some β, β -disubstituted enones react, albeit slowly. Enones capable of assuming a cisoid conformation react, whereas transoid enones do not. These results are not consistent with the free-radical mechanism presented in Eq. 35. The six-centered pericyclic mechanism shown in Eq. 39 has been suggested as a plausible path.



(37)



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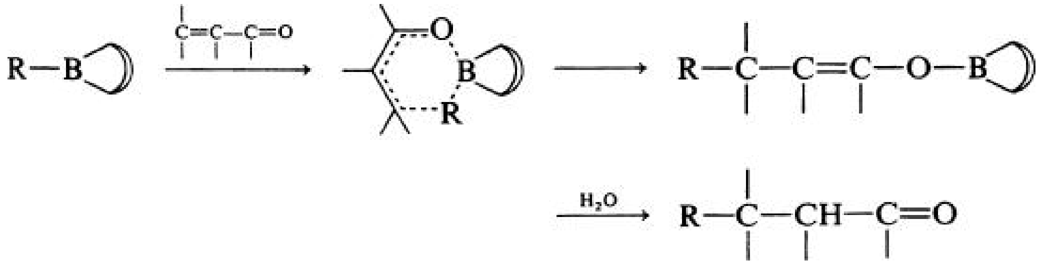
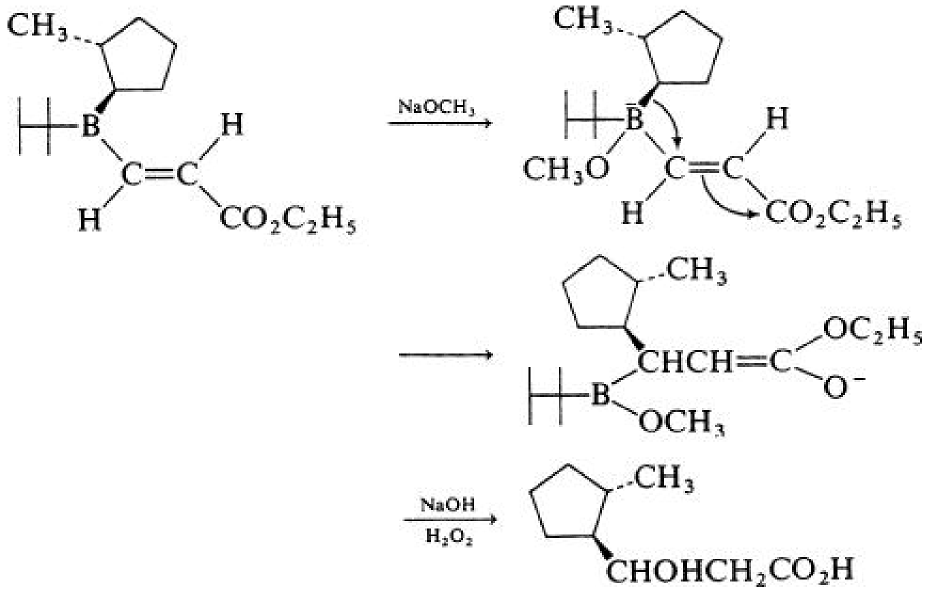


(39)

Organoborates should be capable of undergoing conjugate addition reactions. Until recently, however, only the intramolecular version of such reactions was known (Eq. 40). (89)



(40)

A few intermolecular conjugate addition reactions of organoborates involving copper borates (63) and alkynylborates (90) have been reported recently. The full scope of such reactions, however, remains to be explored further.

2.3. Other Carbon － Carbon Bond-Forming and Bond-Cleaving Reactions of Organoborons

2.3.1. Miscellaneous Elimination Reactions

2.3.1.1.1. Cyclopropane Synthesis via γ Elimination

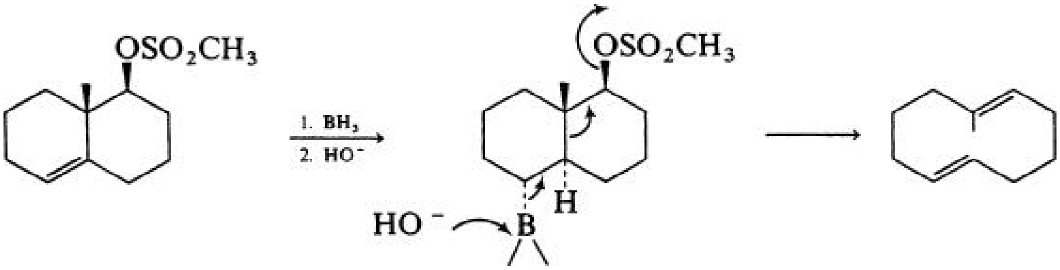
Organoborons carrying a good leaving group in the γ position undergo a facile γ elimination to form cyclopropane derivatives. (91-95)

(41)

(X = halogen or OSO_2R)

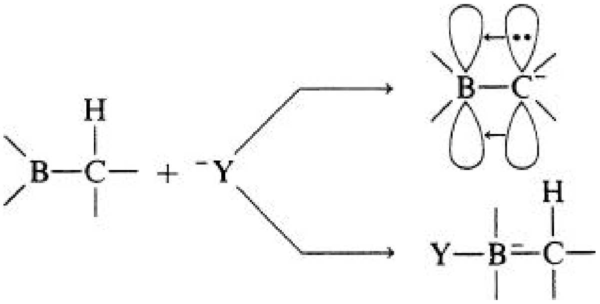
2.3.1.1.2. Fragmentation Reactions of δ -Hetero-Substituted Organoborons

δ -Hetero-substituted organoborons can undergo either formation of cyclobutanes (94) or a Grob-type fragmentation reaction. (96) The latter appears to require rigid and favorable conformational arrangements.



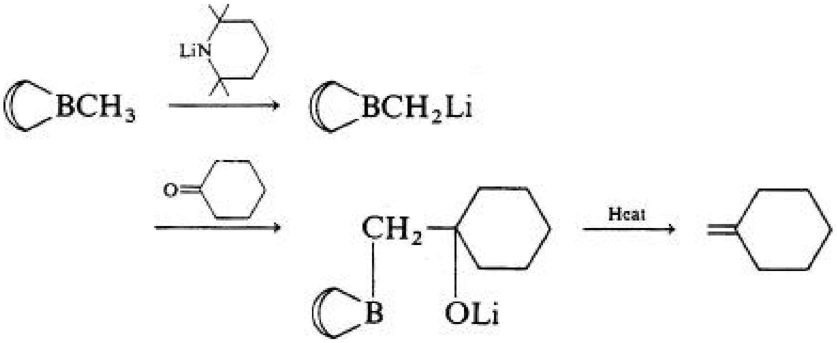
2.3.1.2. Generation and Reactions of Boron-Stabilized Carbanions

Just as the carbonyl group stabilizes an adjacent carbanionic center, the empty *p* orbital of the boron atom of organoboranes should also exhibit a similar effect. The intrinsic difficulty lies in the generation of such species without forming undesirable organoborate complexes.



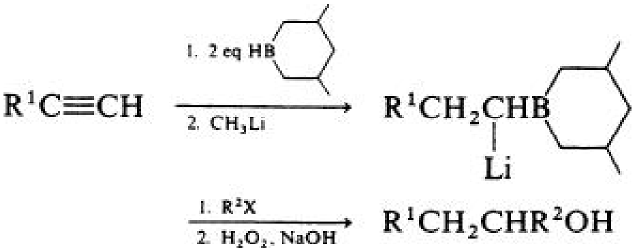
(42)

One successful approach involves the use of highly basic but nonnucleophilic bases. (97) The boron-stabilized carbanions thus generated can react with carbonyl compounds to undergo a Wittig-like reaction.

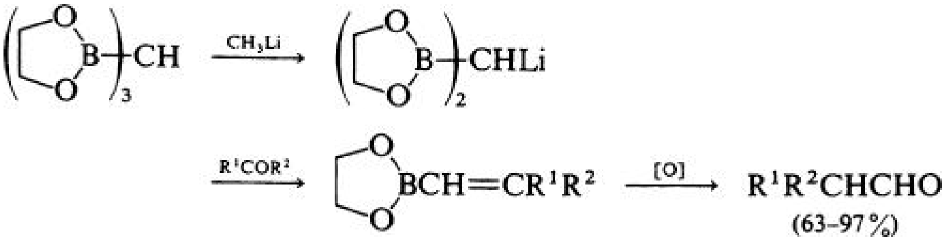


(43)

An alternative approach involves generation of *gem*-dibora and *gem*-tribora compounds followed by treatment with a base. (98-101)



(44)



(45)

2.3.1.3. Miscellaneous One-Electron Transfer Reactions

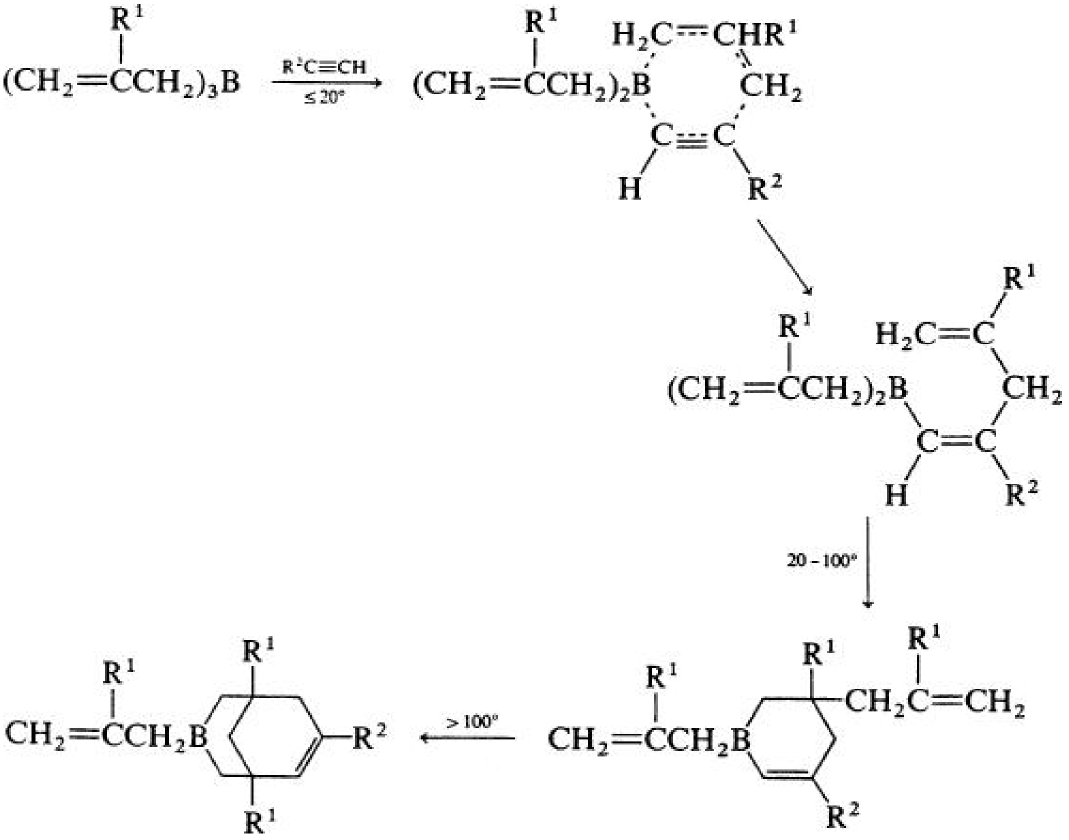
It has been amply demonstrated that organoborons are good sources of carbon free radicals. It now appears that, under electrolytic conditions, even carbocations can be generated from organoboranes via free radicals. The anodic oxidation of organoboranes using graphite as the anode produces alkyl methyl ethers when carried out in the presence of sodium perchlorate, sodium methoxide, and methanol and alkyl acetates when carried out in the presence of sodium acetate and acetic acid. (102) The formation of alkyl methyl ethers has been rationalized as shown in Eq. 46.

$$R_3B \xrightarrow{^{-}OCH_3} R_3\overset{-}{B}OCH_3 \xrightarrow{-e} R_3\dot{B}OCH_3 \longrightarrow R\cdot + R_2BOCH_3$$
$$R\cdot \longrightarrow R^+ \xrightarrow{CH_3OH} ROCH_3 \qquad (46)$$

Electrolysis of organoboranes in acetonitrile (103) and nitromethane (104) has produced homologated nitriles and nitro compounds, respectively.

2.3.1.4. Carboboration Reactions

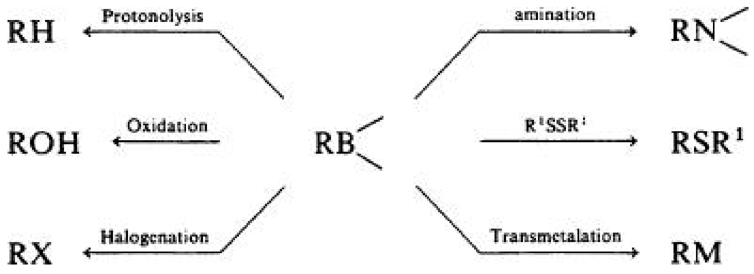
Unlike organoalanes, ordinary organoboranes do not readily undergo carbometallation with olefins and acetylenes. Allylboranes, however, are exceptional and react with acetylenes and olefins to form the corresponding addition products. (71) The results have been interpreted in terms of a $[2_s + 4_s]$ process.



The formation of the monocyclic intermediate involves an allylboration reaction of the terminal olefin group, whereas that of the bicyclic product must be a rare example of the addition of an alkenyl–boron bond to an olefin.

2.4. Formation of Carbon — Heteroatom Bonds via Organoborons

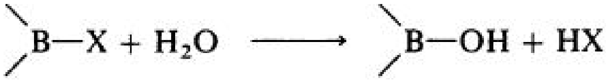
Organoboron compounds can be converted into various organic compounds containing C — H, C — O, C —X (X = halogen), C — N, and C — S bonds as well as organometallic compounds containing mercury (105) and other transition metals via transmetalation.



Formation of C — X, C — N, and C — S bonds via organoborons is discussed in sections describing the syntheses of compounds containing these bonds. Transmetalation reactions of organoborons are outside the scope of this review and are not discussed here. As mentioned earlier, protonolysis and oxidation are the two most commonly used reactions for converting organoborons into organic products. These reactions are often used in conjunction with various carbon — carbon bond-forming reactions described earlier.

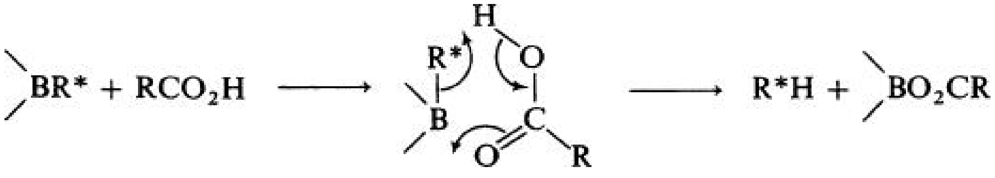
2.4.1.1. Protonolysis

Although B —N, B — O, and B — S bonds are thermodynamically highly stable, they are solvolytically quite labile. Thus hydrolysis of borane derivatives containing these bonds readily produces the corresponding amines, alcohols, and thiols, respectively.



(X = NR^1R^2, OR, or SR, where R = an organic group)

Although the B — C bond of organoboranes is usually quite resistant to hydrolysis, it can generally be cleaved by a carboxylic acid. (2) Stronger acids, such as hydrochloric acid, are less effective. The effectiveness of carboxylic acids has been interpreted in terms of the mechanism shown in Eq. 47.



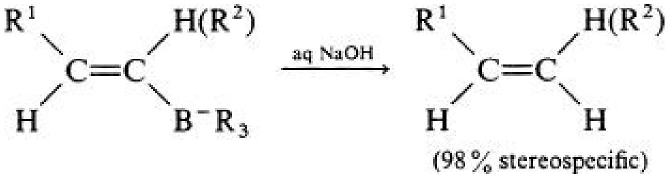
(47)

This reaction may be viewed as a concerted $[2_s + 4_s]$ reaction that proceeds with retention of configuration of the R group. The order of the ease of protonolysis is: alkynyl > alkenyl or aryl > alkyl.

Unlike organoboranes, certain tetraorganoborates undergo a very facile cleavage of one of the four B — C bonds when treated with various proton donors.

$$R^*\overset{-}{B}R_3 \xrightarrow{HX} R^*H + BR_3 + X^-$$
$$(R^* = \text{alkyl or aryl})$$

Under acidic conditions, alkenyl- and alkynylborates undergo an entirely different reaction, which involves the formation of carbon — carbon bonds, as discussed on p. 16. These organoborates, however, can be cleaved stereo-specifically with aqueous bases (Eq. 48). (106) Under the same conditions, alkenylboranes are unaffected. This basic hydrolysis nicely complements the conventional acidic protonolysis and should prove useful with organoborons that contain acid-sensitive groups.



(48)

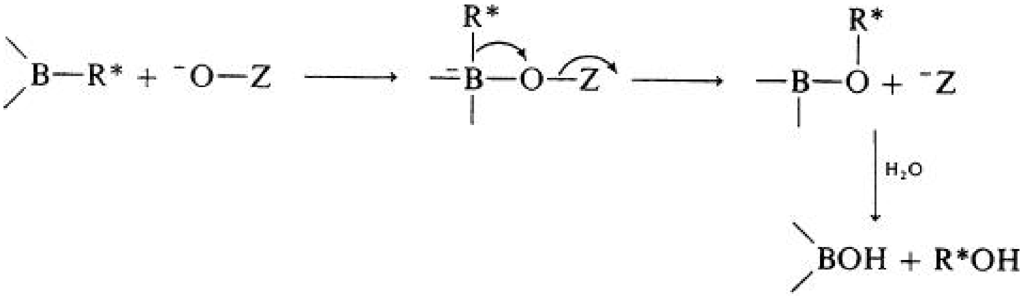
The basic hydrolysis of the alkynyl–boron bond of either organoboranes or organoborates is very facile. The allyl–boron bond can be cleaved readily even with water. It is also worth noting that the B — C bond is quite stable to hydrogenolysis. Although hydrogenolysis can be effected at elevated temperatures, it is not clear whether the reaction involves direct cleavage of the B — C bond with hydrogen or dehydroboration–hydrogenation. (107)

2.4.1.2. Oxidation

Organoboranes are readily oxidized by a variety of reagents. The presence of an empty *p* orbital and the high thermodynamic stability of the B — O bond (115–135 kcal/mol) must be responsible for the ease of oxidation.

2.4.1.2.1. Oxidation with Alkaline Hydrogen Peroxide and Tertiary Amine N-Oxides

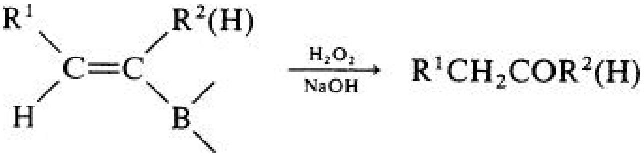
The oxidation of organoboranes with 30% hydrogen peroxide and a suitable base, such as NaOH, NaOAc, or NaH_2PO_4- K_2HPO_4 buffer solution, is by far the most dependable and convenient laboratory method. (2) This reaction, as well as the reaction with amine *N*-oxides, is believed to proceed as shown in Eq. 49.



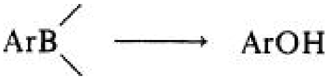
$(Z = -OH \text{ or } -N^+R_3)$

(49)

Essentially all types of organoboranes can be converted into the corresponding alcohols with retention of configuration. Alkenylboranes are converted into ketones and aldehydes (Eq. 50) and arylboranes into phenols (Eq. 51). (108) Under aqueous conditions, however, the alkynyl–boron bond undergoes protonolysis preferentially.



(50)



(51)

As might be expected from the mechanism shown in Eq. 49, the coordinatively saturated organoborates are not oxidized until they are converted into organoboranes via protonolysis or some other reaction. Thus, for example, only three of the four alkyl groups of a tetraalkylborate can be converted into alcohols.

2.4.1.2.2. Other Oxidation Reactions

Organoboranes can be directly converted into ketones by oxidation with chromic acid. (109) The reaction of organoboranes with oxygen involves an S_H2 reaction. (110) The initial product is a peroxide (Eq. 52), (111) which reacts with a second mole of oxygen to form a diperoxide (Eq. 53).

$$R_3B + O_2 \longrightarrow R_2BO_2R \qquad (52)$$

$$R_2BO_2R + O_2 \longrightarrow RB(O_2R)_2 \qquad (53)$$

Addition of 30% hydrogen peroxide liberates the alkyl hydroperoxide. (112, 113)

$$RB(O_2R)_2 + H_2O_2 + 2H_2O \longrightarrow 2RO_2H + ROH + B(OH)_3$$

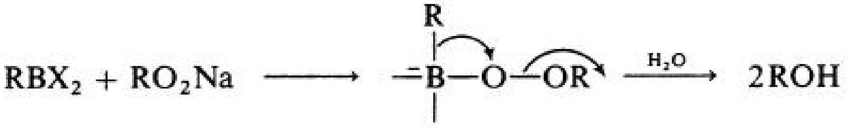
A free-radical chain mechanism involving an S_H2 reaction is consistent with the results. (110)

$$R_3B + O_2 \longrightarrow R\cdot + R_2BO_2\cdot$$
$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + R_3B \longrightarrow R_2BO_2R + R\cdot$$

When a trialkylborane is reacted with 1.5 molar equivalents of oxygen and then with aqueous sodium hydroxide, all three alkyl groups are converted into the corresponding alcohol in >90% yield. The course of the reaction may be depicted as shown in Eq. 54.

$$2R_3B + 3O_2 \longrightarrow R_2BO_2R + RB(O_2R)_2$$

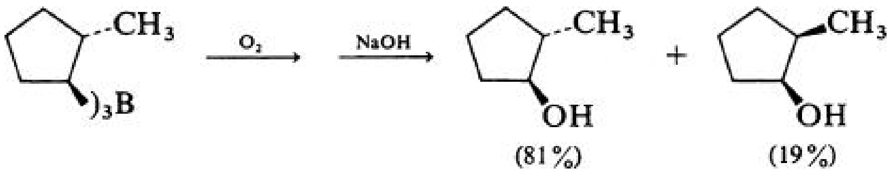
$$R_2BO_2R + RB(O_2R)_2 \xrightarrow[H_2O]{NaOH} R_2BOH + RB(OH)_2 + 3RO_2Na$$



$$RBX_2 + RO_2Na \longrightarrow \overset{R}{\overset{|}{\underset{|}{\bar{-}B}}}-O-OR \xrightarrow{H_2O} 2ROH \qquad (54)$$

$$R_2BX + 2RO_2Na \xrightarrow{H_2O} 4ROH$$

One drawback of the free-radical oxidation is that it is not stereospecific; see, for example, Eq. 55.



(55)

3. Preparation of Organic Compounds via Organoboranes and Organoborates

Various methods of preparation of organic compounds using organoboron derivatives are discussed in this section according to the functional groups of the organic products as well as the number of carbon atoms inserted between the organic group on boron and the functional group.

3.1. Alcohols

The preparation of alcohols by direct hydroxylation of organoboranes is not discussed in this review.

3.1.1.1. Alcohols via One-Carbon Homologation

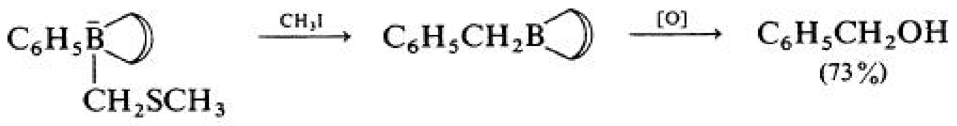
The preparation of alcohols by one-carbon homologation can be achieved by either single, double, or triple transfer of organic groups from boron to carbon.

3.1.1.1.1. Primary Alcohols

An organic group on boron can be converted into its methylol derivative by several one-carbon homologation reactions. The oxygen-induced reaction of trialkylboranes (R_3B) with monomeric formaldehyde, which presumably proceeds by a free-radical mechanism, gives one-carbon homologated alcohols (RCH_2OH) in low to modest yields. (76) The corresponding reaction of *B*-alkenyl-9-BBN's produces allylic alcohols in modest yields. (77) This reaction is slow but does not require oxygen. It is thus unlikely that it proceeds by a free-radical mechanism. In contrast to these relatively low-yield reactions, allylboranes react readily with formaldehyde to produce homoallylic alcohols. (71, 114) The reaction is, in fact, quite general with respect to the carbonyl compounds, and essentially all types of aldehydes and ketones can be used to produce primary, secondary, tertiary, or homoallylic alcohols (Eq. 33).

Carbonylation of organoboranes in the presence of a metal hydride, such as lithium borohydride, followed by alkaline hydrolysis (Eq. 56), (115, 116) and the reaction of thiomethoxymethyltriorganoborates, such as **6**, with an appropriate electrophile, such as methyl iodide, followed by oxidation (59) (Eq. 57), probably represent the two most generally applicable methods for hydroxymethylation of organoboranes.

$$R_3B \xrightarrow[\text{2. KOH}]{\text{1. CO, MBH}_4} RCH_2OH + R_2BOH \qquad (56)$$



6

(57)

An aryl group is preferentially homologated in the latter reaction (Eq. 57). Sulfonium and sulfoxonium ylides react with organoboranes to induce reactions (117, 118) that are closely related to that shown in Eq. 57. Unfortunately, the intrinsic instability of these ylide reagents limits the synthetic applicability of these reactions.

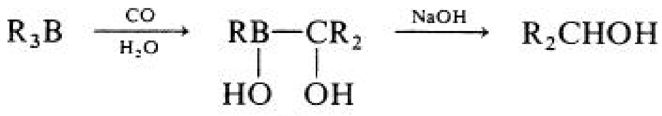
3.1.1.1.2. Secondary Alcohols

The reaction of allylboranes with aldehydes produces secondary homoallylic alcohols (Eq. 33). In addition, there are several single-and double-migration reactions that can be used to prepare secondary alcohols. Protonation of alkenyltrialkylboranes induces a single-migration reaction. Oxidation of the organoborane intermediates gives secondary alcohols in excellent yields. (42)

$$R_3\bar{B}CH{=}CH_2 \xrightarrow{H^+} R_2BCHRCH_3 \xrightarrow{[O]} CH_3CH(R)OH$$

The corresponding alkylation of alkenyltrialkylborates should also produce secondary alcohols in a similar manner; however, this does not appear to have been investigated.

There are at least three double-migration reactions applicable to the synthesis of secondary alcohols. Carbonylation of organoboranes at 50° in the presence of water induces migration of two carbon groups from boron to carbon to produce alcohol **7**, which presumably arises from the boraepoxide intermediate shown in Eq. 20. Alkaline hydrolysis of alcohol **7** gives secondary alcohols in high yields (Eq. 58). (119)

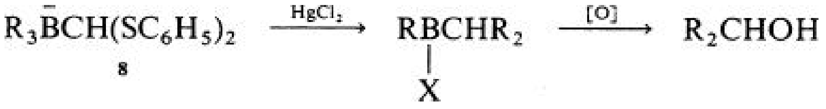


$$R_3B \xrightarrow[H_2O]{CO} \underset{HO}{RB}-\underset{OH}{CR_2} \xrightarrow{NaOH} R_2CHOH \qquad (58)$$

7

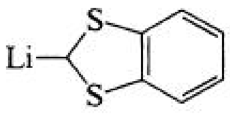
Acid treatment of the single-migration product obtained by carbonylation of organoboranes in the presence of a metal hydride, such as lithium trimethoxy-aluminum hydride, can also be used to effect migration of the second carbon group. (116) Dichloromethyl methyl ether can be substituted for carbon monoxide. (120)

Treatment of **8** with mercuric chloride followed by oxidation provides an organoborate route to secondary alcohols (Eq. 59). (121, 122)

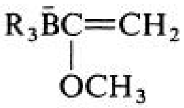


$$\underset{\mathbf{8}}{R_3\bar{B}CH(SC_6H_5)_2} \xrightarrow{HgCl_2} R\underset{\substack{|\\X}}{B}CHR_2 \xrightarrow{[O]} R_2CHOH \qquad (59)$$

A more recent study indicates that bicyclic organolithium **9** is superior to bis(phenylthio)methyllithium. (123)



9



$$R_3\bar{B}\underset{\substack{|\\OCH_3}}{C}{=}CH_2$$

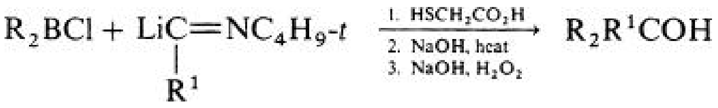
10

3.1.1.1.3. Tertiary Alcohols

Protonation of alkynyltrialkylborates produces alkenyl-dialkylboranes, which on heating undergo migration of the second alkyl group. Oxidation of the organoborane intermediates gives tertiary alcohols in good yields. (124)

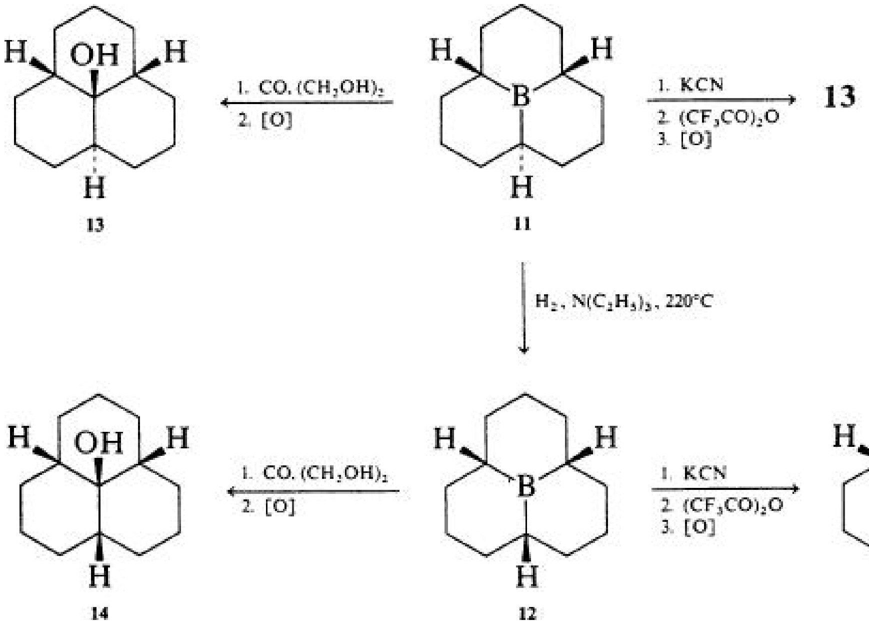
$$R_3\bar{B}C{\equiv}CR^1 \xrightarrow[\text{2. Heat}]{\text{1. HCl}} \xrightarrow{[O]} R^1CH_2CR_2OH$$

Closely related to this reaction is that of α -methoxyethenylborates (**10**). (22, 125) After one migration both of these reactions presumably produce the same alkenyldialkylboranes. The reaction of dialkylchloroboranes with lithioaldimines, which can be generated by treating isonitriles with organolithiums, also involves a double migration producing tertiary alcohols according to Eq. 60. (21)

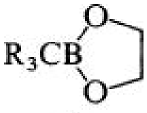


$$R_2BCl + Li\underset{\substack{|\\R^1}}{C}{=}NC_4H_9\text{-}t \xrightarrow[\substack{\text{2. NaOH, heat}\\ \text{3. NaOH, } H_2O_2}]{\text{1. } HSCH_2CO_2H} R_2R^1COH \qquad (60)$$

More general and useful are the triple-migration reactions of organoboron compounds (“stitching and riveting”). There are at least three different such triple-migration reactions: (1) carbonylation, (34) (2) reaction with dichloromethyl methyl ether (the DCME reaction), (35-40) and (3) the Lewis-acid-induced triple-migration reaction of cyanoborates. (41) All these reactions can convert trialkylboranes into the corresponding trialkylcarbinols with complete retention of all essential structural features of the starting organoboranes including regio- and stereochemistry. There are, however, some significant differences among them. First, the carbonylation reaction is carried out in essentially neutral conditions, whereas the DCME reaction and the cyanoborate reaction are carried out under basic and acidic conditions, respectively. Thus difficulties can arise when acid- or base-sensitive compounds are involved. On the other hand, many carbonylation reactions require a moderately high pressure (50–100 atm) of carbon monoxide, which often represents an inconvenience. Second, these triple-migration reactions generally provide the same products if the same organoboranes are used as starting compounds. When the two sides of an organoborane are different, however, these reactions may provide different ratios of stereoisomeric products. An example is the conversion of perhydro-9b-boraphenalenes into perhydro-9b-phenalenols. Whereas carbonylation of the *cis,cis* isomer **12** produces only the *cis,cis,cis* product **14**, (126) the cyanoborate reaction of **12** gives the *trans,trans,trans* isomer **15**. (127) The exclusive formation of **14**, which is at least 10 kcal/mol less stable than **15**, may seem puzzling but can be rationalized in terms of the highly strained and hence highly reactive *cis,cis,cis* intermediates.

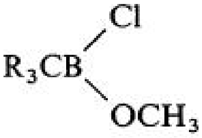


A proposed mechanism of the carbonylation reaction is shown in Eqs. 19–21. When tertiary alcohols are desired, the reaction is carried out at 150° in the presence of ethylene glycol. Under these conditions, the triple-migration products are 1,3,2-dioxaboroles **16**, which are relatively stable to air and moisture, but can be oxidized to tertiary alcohols.



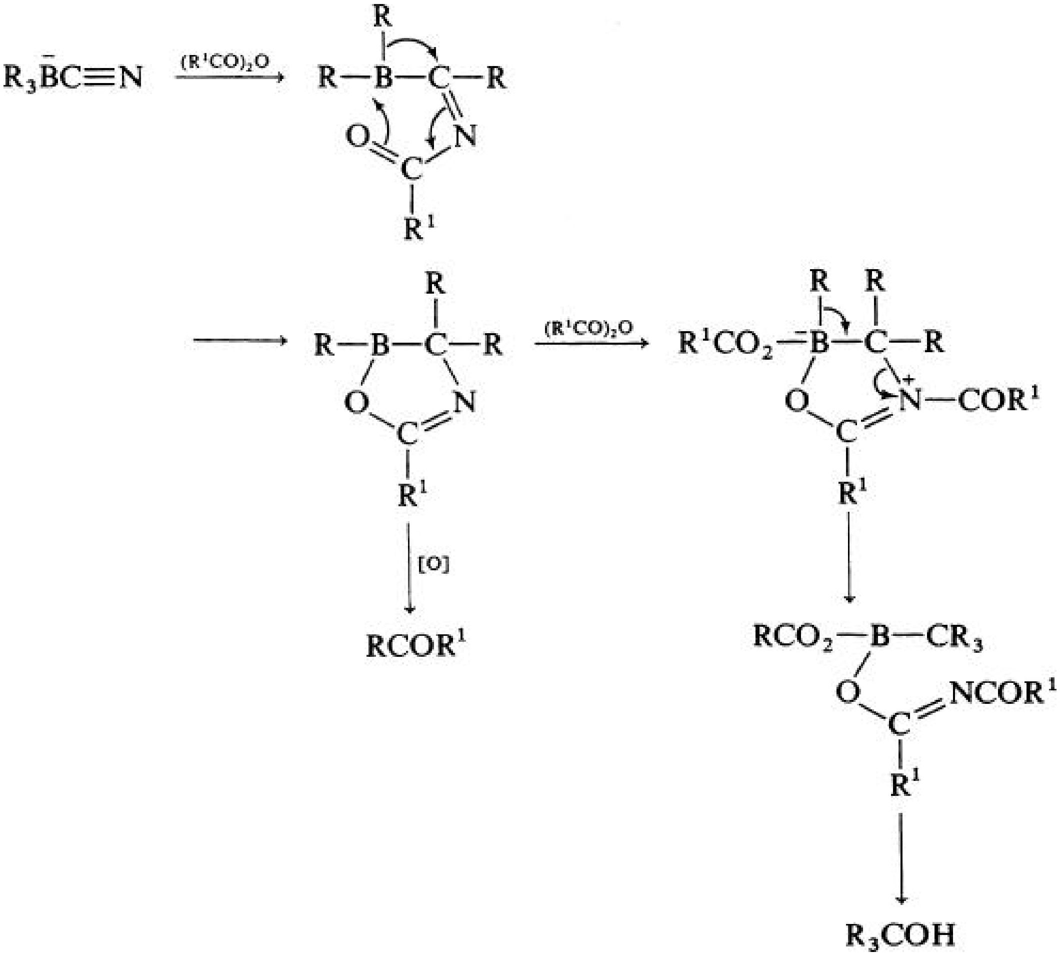
16

The precise mechanism of the DCME reaction, especially the order of participation of the leaving groups on carbon, is not clear, although the triple-migration products have been shown to have the structure **17**.



17

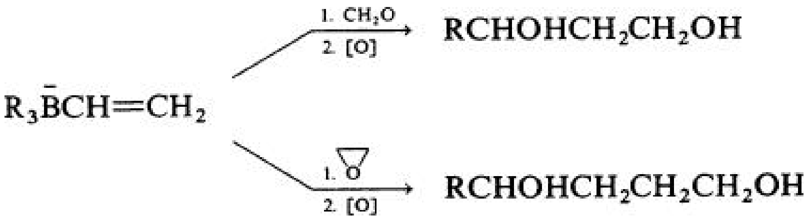
The cyanoborate reaction is thought to proceed according to Eq. 61. (41)



(61)

3.1.1.1.4. Glycols

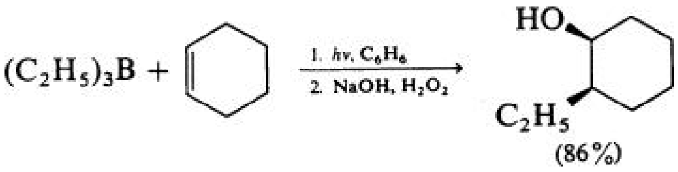
The reactions of vinyltrialkylborates with formaldehyde (68) and ethylene oxide (69) produce, after oxidation, 1,3- and 1,4-glycols, (128) respectively (Eq. 62).



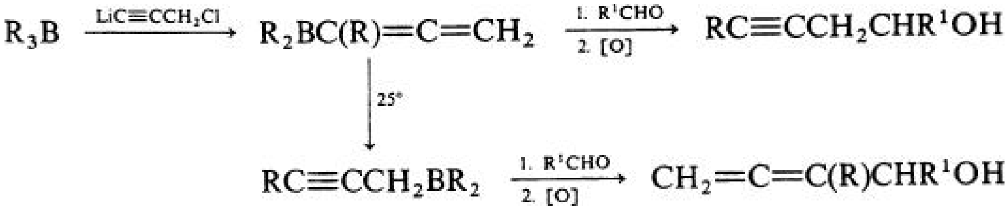
(62)

3.1.1.2. *Alcohols via Two-Carbon Homologation*

Organoboron reactions that permit the synthesis of alcohols by two-carbon homologation are rare. Organoboranes do not readily undergo the addition of the carbon — boron bond across carbon — carbon double or triple bonds. Under photochemical conditions, however, cycloalkenes can be converted into the highly strained *trans* isomers, which presumably are reactive enough to induce this addition reaction. (129, 130) Oxidation of the addition products gives the corresponding two-carbon homologated alcohols.



A related reaction of allylic boranes with cyclopropenes must proceed through a six-centered transition state in a manner similar to that shown in Eq. 9. (131-133) The reaction of organoboranes with 3-chloro-1-propynyllithium involves a single migration to form allenyldialkylboranes, which isomerize to propargylboranes at 25°. If the organoborane intermediate is treated with an aldehyde before isomerization, the corresponding homopropargyl alcohol is obtained. On the other hand, treatment with the aldehyde after isomerization produces an allenic alcohol. (134)



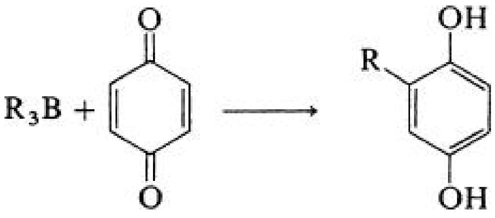
(63)

Enoxyboranes, obtainable by the reaction of organoboranes with diazoacetic esters, react readily with carbonyl compounds (Eq. 10) to give β -hydroxyesters. (72, 73, 135)

$$R_3B \xrightarrow{N_2CHCO_2C_2H_5} R_2BO\overset{OC_2H_5}{\overset{|}{C}}{=}CHR \xrightarrow{R^1COR^2} R^1R^2COHCHRCO_2C_2H_5$$

3.1.1.3. *Alcohols via Three-Carbon Homologation*

In addition to the reaction of alkenyltrialkylborates with aldehydes (Eq. 62), there are two other three-carbon homologation reactions, both of which involve conjugate addition. One is the reaction of organoboranes with benzoquinone and its derivatives to form the corresponding hydroquinones. (136-141)

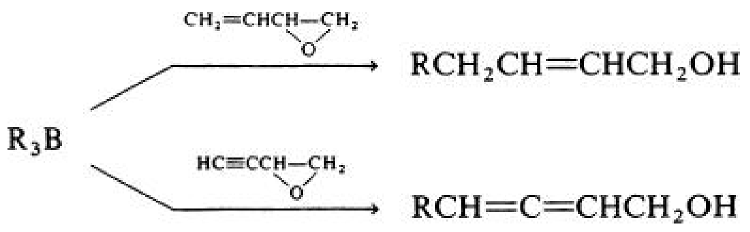


The other involves conjugate addition of organoboranes to enones. The enoxyborane products can undergo an aldol-type reaction with aldehydes to form β -hydroxy carbonyl compounds (Eq. 64). (135) Ketones also undergo this reaction, but with very low yields.

$$\begin{aligned} R_3B &\xrightarrow{CH_2{=}CHCOCH_3} RCH_2CH{=}C(CH_3)OBR_2 \\ &\xrightarrow{R^1CHO} R^1CHOHCH(CH_2R)COCH_3 \end{aligned} \qquad (64)$$

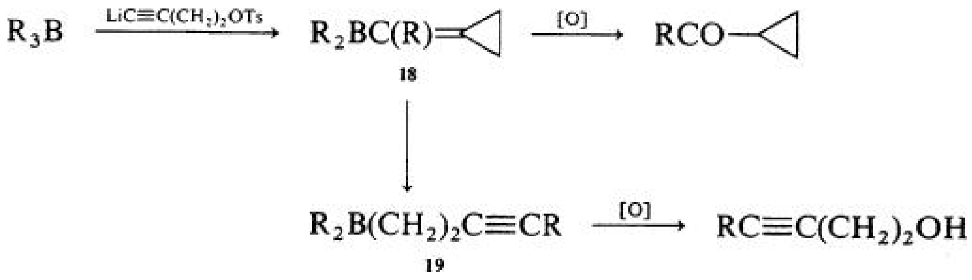
3.1.1.4. *Alcohols via Four- or More-Carbon Homologation*

The reaction of vinyl-trialkylborates with epoxides followed by oxidation to produce 1,4-glycols is illustrated in Eq. 62. Moreover, the reaction shown in Eq. 63 can be directed to either a two- or a four-carbon homologation. Organoboranes undergo addition reactions with 1,3-butadiene monoxide and 1,3-butenyne monoxide to produce allylic (142) and allenic alcohols, (143) respectively.



These reactions appear to proceed by free-radical mechanisms and must therefore be closely related to the free-radical conjugate addition reaction of organoboranes (Eq. 35). The product yields are only modest.

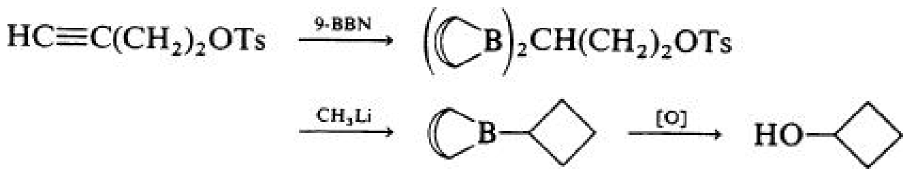
The reaction of organoboranes with 1-lithio-4-tosyloxy-1-butyne produces cyclopropane **18**, which on standing isomerizes to homopropargylborane **19**. The latter product can be converted into a homopropargyl alcohol by oxidation. (95)



The reaction of organoboranes with 2-lithiofuran followed by treatment with acetic acid and then with alkaline hydrogen peroxide gives 1,1-dialkyl-2-buten-1,4-diols. (23)

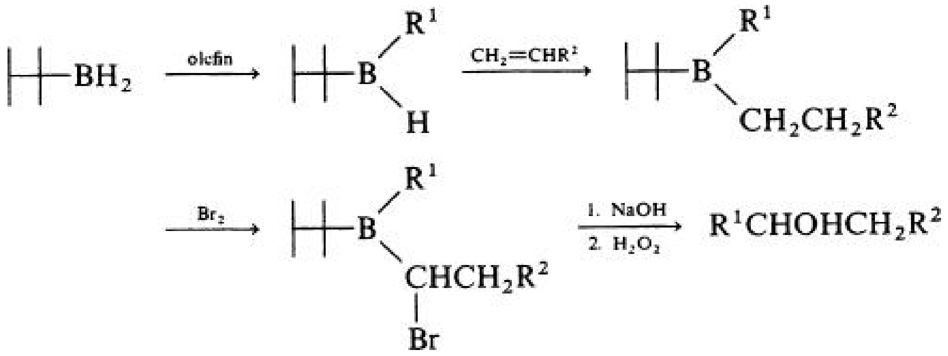
3.1.1.5. Miscellaneous Preparations of Alcohols

There are at least two other reactions of organoborons that can be used to prepare alcohols. One involves the α-boracarbanions shown in Eqs. 42–45. A direct approach to these carbanions is to treat an organoborane with a highly hindered base such as lithium 2,2,6,6-tetramethylpiperidide (Eq. 43). The resulting α-boracarbanion can react with an alkyl halide, and oxidation of the resulting organoborane gives the corresponding alcohol. (97) Unfortunately, the scope of this method is rather limited. An indirect but more generally applicable method involves generation of *gem*-dibora species by double hydroboration of acetylenes followed by treatment with organolithium compounds (Eq. 44). The reaction of α-boracarbanions with alkylating agents can also take place intramolecularly (Eq. 65). (94)



(65)

Another reaction for synthesis of alcohols involves bromination of organoboranes to generate α-bromoorganoboranes (Eq. 12), which can induce a single migration that couples two boron-bound carbon groups. (24-28, 144-147) Use of thexylborane* provides an attractive feature in that two different carbon groups can be attached to a boron atom and coupled without wasting the carbon groups of interest.



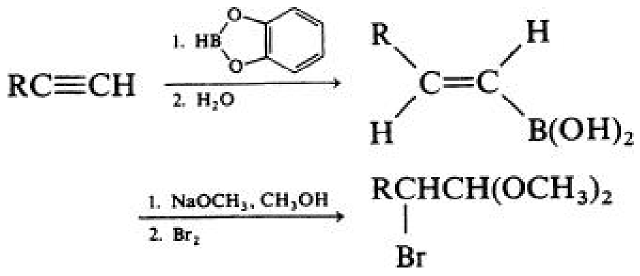
The reaction appears to have wide applicability.

3.2. Ethers

Only a few organoboron reactions generate the ether linkage. Electrolysis of organoboranes in the presence of sodium methoxide, sodium perchlorate, and methanol produces methyl ethers by direct functionalization. (102)

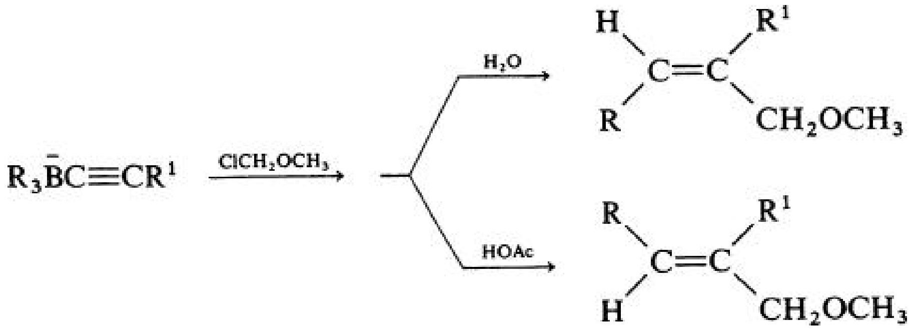
$$R_3B \xrightarrow[\substack{\text{2. electrolysis} \\ \text{3. NaOH, } H_2O_2}]{\text{1. } NaOCH_3\text{, } NaClO_4\text{, } CH_3OH} ROCH_3$$

Because only one of the three carbon groups is utilized, the synthetic value of this reaction is limited. A combination of hydrogen peroxide oxidation and the Williamson ether synthesis appears to be more attractive. Potentially more useful is the conversion of terminal acetylenes into α-bromoacetals shown in Eq. 66. (148)



(66)

The reaction of alkynyltrialkylborates with chloromethyl methyl ether followed by treatment with water or acetic acid gives (*Z*)- or (*E*)-allyl methyl ethers, respectively (Eq. 67). (149) The stereochemical results cannot be readily rationalized.



(67)

3.3. Peroxides

The low-temperature autoxidation of organoboranes provides a rapid and convenient synthesis of alkyl hydroperoxides. (112)

$$R_3B + 2O_2 \xrightarrow[-70\text{ to }0^\circ]{\text{THF}} RB(O_2R)_2 \xrightarrow[H_2O]{H_2O_2} 2RO_2H + ROH$$

Two of the three alkyl groups are utilized. It is convenient to oxidize the third alkyl group with hydrogen peroxide and then separate the alkyl hydroperoxide from the alcohol as its water-soluble potassium salt. Alternatively, use of monoalkyldichloroboranes circumvents the stoichiometry problem. (150)

3.4. Ketones

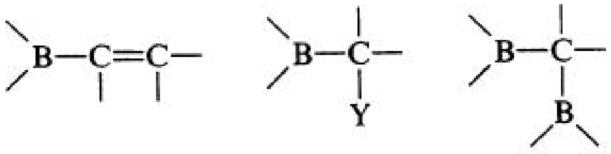
3.4.1.1. Ketones via One-Carbon Homologation

The synthesis of ketones using conventional organometallics, such as those containing lithium or magnesium, typically involves the use of carboxyl derivatives, such as acyl halides, as reagents. Although organoboranes are relatively inert to acyl halides and other carbonyl compounds, organoborates react smoothly with acyl halides to produce ketones by intermolecular transfer of one of the four carbon groups (Eq. 68). (56, 57)

$$R_3\overset{-}{B}R^1 + R^2COX \longrightarrow R^1COR^2 \qquad (68)$$

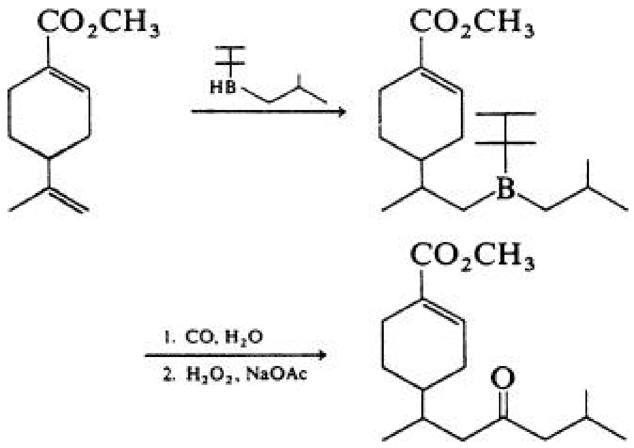
Aryl-and alkylsulfinylmethyl groups can be transferred in preference to primary alkyl groups, which in turn can be transferred in preference to secondary alkyl groups. Thus tricyclopentylborane or trinorbornylborane can provide convenient “dummy” groups. Treatment of lithium trialkylmethylborates with cuprous halides has been reported to produce reagents, presumably cuprous tetraalkylborates, that react readily with acyl halides to produce ketones. (151) It is not clear whether the cuprous halides are essential. The organoborate route is a very chemoselective method for the conversion of acyl halides into ketones.

In addition to these intermolecular transfer reactions there are various intramolecular transfer reactions that can be used to prepare ketones. These reactions generate the following types of organoborane intermediates, which can be oxidized to the corresponding ketones.

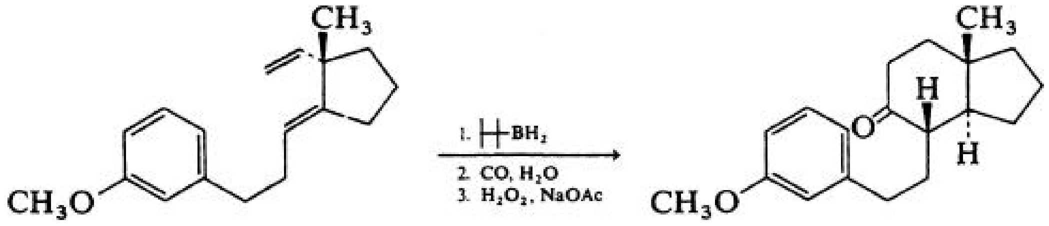


(Y = a group linked through N, O, or S)

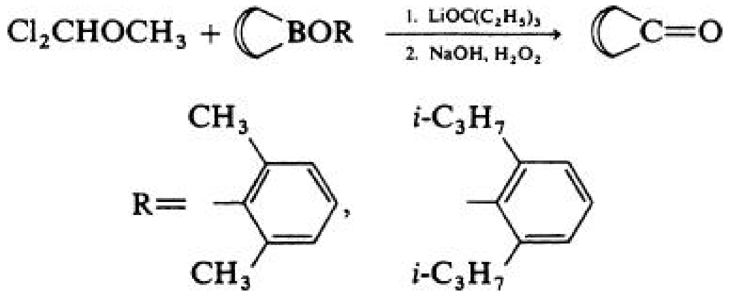
The three multiple-migration reactions applicable to the synthesis of secondary and tertiary alcohols are also applicable to the preparation of ketones. Perhaps the most widely investigated is the carbonylation of organoboranes. (34) The conditions required for ketone synthesis are identical with those required for secondary alcohol synthesis. Thus organoboranes are carbonylated at approximately 50° in the presence of water to produce α-hydroxyboranes (Eq. 58) that are then oxidized to ketones. (152, 153) The thexyl group, which has a very low migratory aptitude, serves as a useful “dummy” group. (154-156)



Dienes can be converted into cyclic (157) and bicyclic ketones. (158, 159)



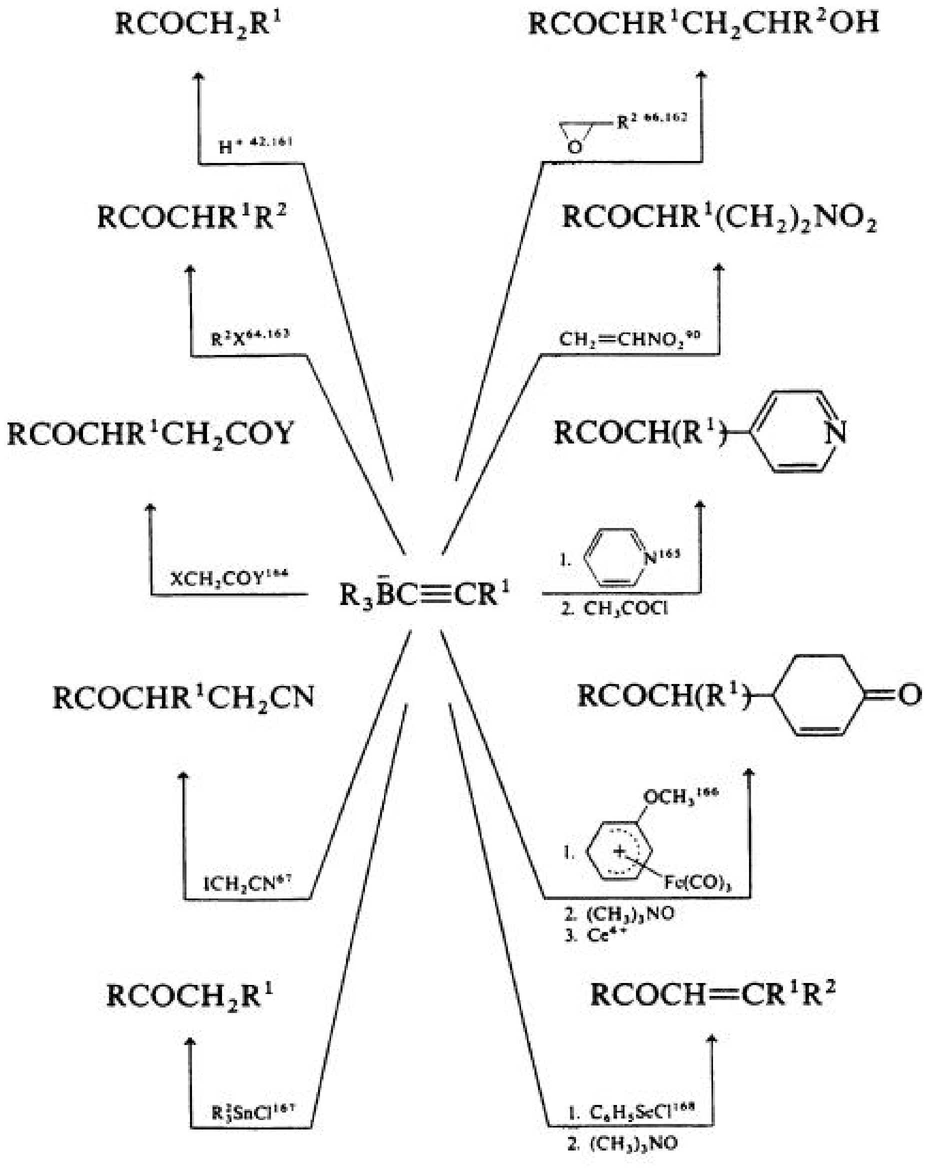
Closely related to the carbonylation reaction are the cyanoborate process (41) (Eq. 61) and the DCME reaction. (38, 40, 160) One distinct advantage of the DCME reaction over the other two reactions is that, whereas both the carbonylation reaction and the cyanoborate process require triorganoboranes, the DCME reaction proceeds readily with dialkylalkoxyboranes.



Another group of organoboron reactions applicable to the synthesis of ketones by carbon homologations involves treatment of alkynyltrialkylborates with electrophiles (E^+) and proceeds according to Eq. 69.

$$R_3\bar{B}C{\equiv}CR^1 \xrightarrow{E^+} R_2BC(R){=}CR^1E \xrightarrow{[O]} RCOCHR^1E \qquad (69)$$

A wide variety of electrophiles participate in this reaction as summarized in Eq. 70.

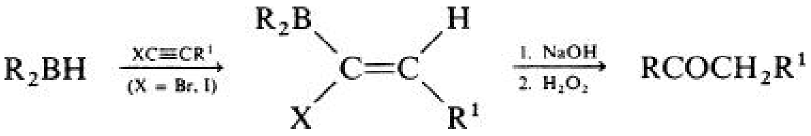


(70)

$(Y = CH_3, C_6H_5, OC_2H_5)$

Most of these reactions can be readily explained in terms of Eq. 69. The reaction with a trialkyltin chloride presumably produces α-stanno ketones that, under hydrolytic conditions, readily lose the trialkyltin group. (167) Pyridine itself is not sufficiently electrophilic, but *N*-acetylpyridinium salts react readily with alkynylborates to form *N*-acetyldihydropyridine derivatives that can subsequently be oxidized to produce 4-substituted pyridines. (165) The reaction of phenylselenyl chloride provides β -selenoalkenylboranes that, on oxidation with trimethylamine oxide, produce α, β -unsaturated ketones. (168) The intramolecular alkylation of alkynylborates followed by oxidation before isomerization of the alkenylborane intermediates gives cyclopropyl ketones. (95)

α-Hetero-substituted alkenylborates can undergo single-migration reactions leading to new alkenylboranes that can be converted into ketones by oxidation. The reactions shown in Eq. 71 (29) and Eq. 72 (125) are representative.



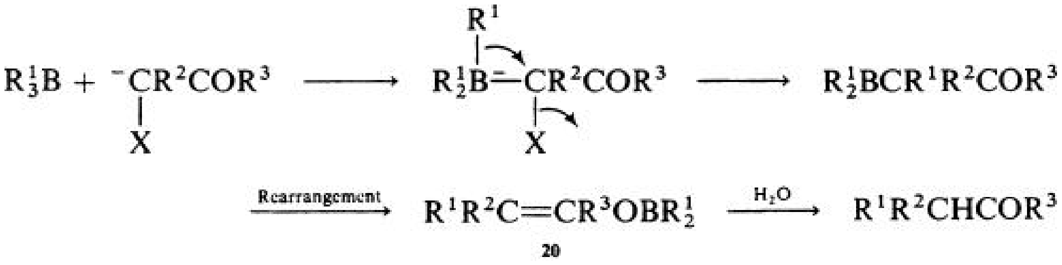
(71)

$$R_3B \xrightarrow{LiC(OCH_3)=CH_2} R_2BC(R)=CH_2 \xrightarrow{[O]} RCOCH_3 \qquad (72)$$

The reactions of organoboranes withα, α-bis(phenylthio)alkyllithiums (Eq. 59) and lithioaldimines (Eq. 60) can be stopped after a single migration to produceα-thioorganoboranes (169) andα-aminoorganoboranes, (20) respectively. Their oxidation provides the corresponding ketones.

3.4.1.2. Ketones via Two-Carbon Homologation

A few useful syntheses of ketones via two-carbon homologation follow the general equation shown in Eq. 73.

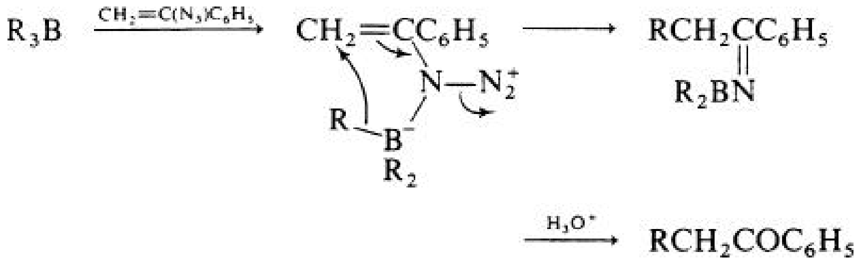


(73)

(Y = Br, Cl, or N_2^+)

The base-induced reactions ofα-haloketones with organoboranes (170) have been reviewed in detail. (171) The 9-BBN group serves as a satisfactory “dummy” group in the reaction ofα-haloketones (172-174) but not in the reaction ofα-diazoketones. (18, 175) The enoxyborane intermediates **20** can be trapped by various other reagents as well. Their deuteration producesα-deuterioketones. Treatment with *N*-bromosuccinimide and *N*-chlorosuccinimide produces α-bromo-and α-chloroketones, respectively. (176) It is also possible to alkylate the alpha position with alkyl halides. (177) The reaction shown in Eq. 73 provides a useful route to enolate anion equivalents.

Another method for the synthesis of ketones by two-carbon homologation of organoboranes involves treatment of organoboranes with vinyl azides, (178) which presumably proceeds as in Eq. 74.



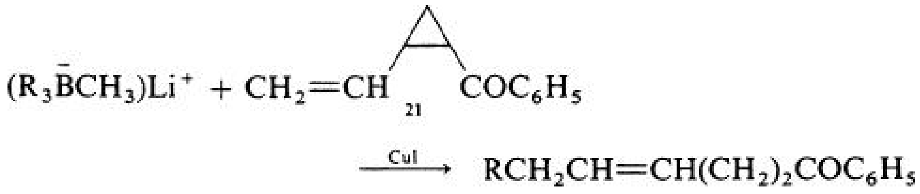
(74)

3.4.1.3. *Ketones via Three-Carbon Homologation*

The conjugate addition of organoboranes toα, β -unsaturated ketones (Eqs. 35–39) is a general and useful route to ketones. Its scope and limitations as well as mechanistic aspects were discussed in the preceding section. Regardless of whether the reaction proceeds by a free-radical mechanism (Eq. 35) or by a six-centered mechanism (Eq. 39), it produces enoxyboranes as intermediates. Thus this reaction also serves as a route to enolate anion equivalents that can be trapped by bromine, (179) alkyl halides, (177) aldehydes, (135) or iminium salts (180) to produce the correspondingα-substituted ketones.

3.4.1.4. *Ketones via Four-or-More-Carbon Homologation*

The homoconjugate addition of organoboranes or organoborates to the cyclopropane derivative **21** provides an unusual route to ketones by six-carbon homologation. (181) The preferred procedure involves reaction of lithium tetraalkylborates with **21** in the presence of cuprous iodide (Eq. 75).

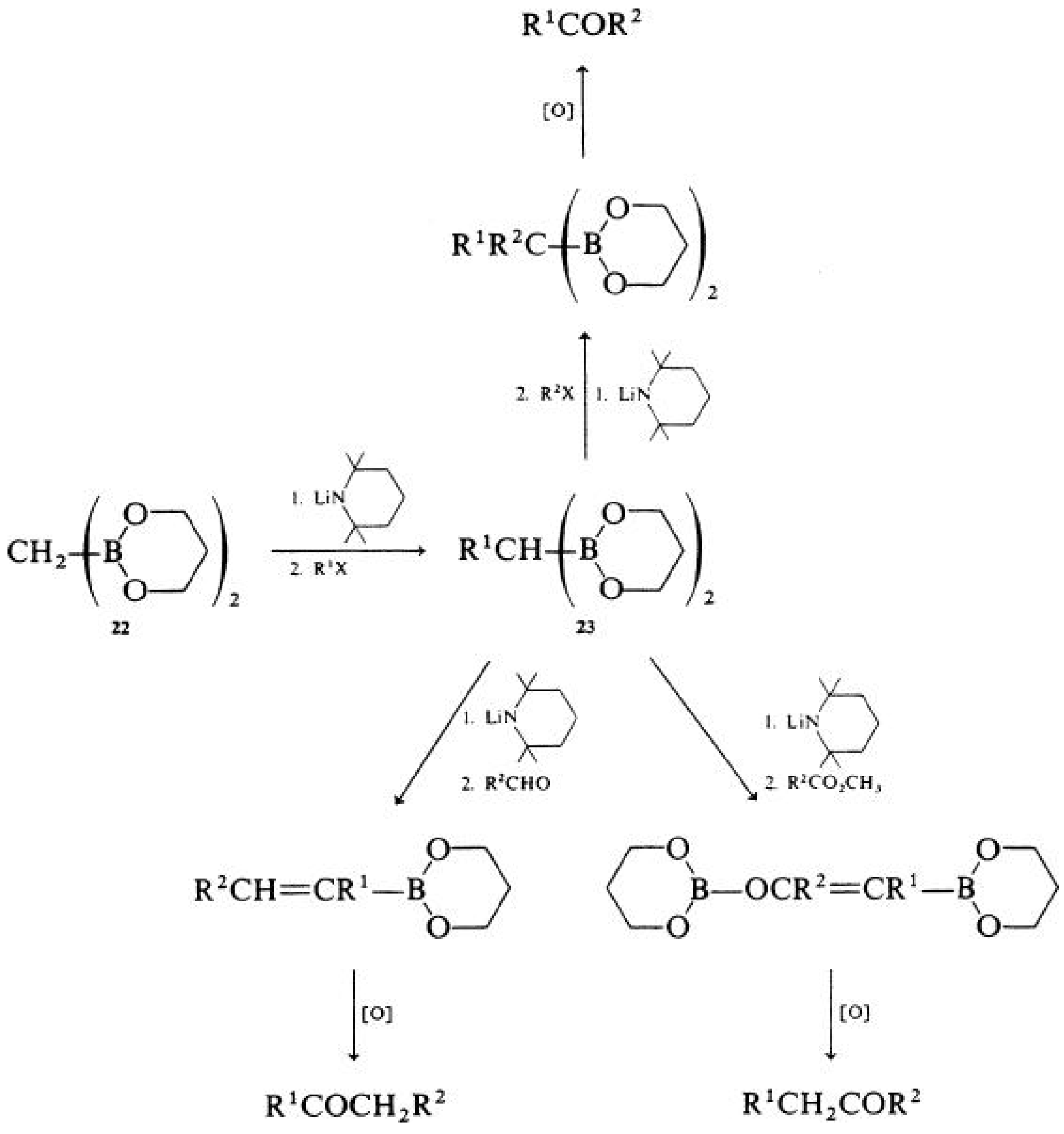


(75)

The reactions of alkynylborates withα-haloketones (164) also produce four-carbon homologated ketones (Eq. 70).

3.4.1.5. Miscellaneous Preparations of Ketones

Diboramethane derivatives (e.g., **22**) can serve as carbonyl dianion equivalents. Single alkylation converts **22** into **23**, which can then be deprotonated and reacted with alkyl halides, aldehydes, or esters to produce ketones. (182)



(76)

3.5. Aldehydes

Many of the procedures for the preparation of ketones are also applicable to the preparation of aldehydes. Such procedures are only briefly discussed, whereas those that are specific to aldehyde synthesis are discussed in greater detail.

3.5.1.1. *Aldehydes via One-Carbon Homologation*

Carbonylation of organoboranes in the presence of an appropriate metal hydride, such as $LiAlH(OCH_3)_3$ or $LiAlH(OC_4H_9\text{-}t)_3$, followed by oxidation with hydrogen peroxide and a NaH_2PO_4 – K_2HPO_4 buffer solution, (15, 183-185) is probably the single most useful route to aldehydes by one-carbon homologation. The use of 9-BBN has been effective in achieving a high yield of an aldehyde based on the starting olefin. (184) A wide variety of functional groups, including ester and cyanide, can be tolerated.

Although there are many double-migration reactions that are suitable for the synthesis of ketones, it has been difficult to stop these reactions after single migration. As a result, most of these reactions cannot readily be adapted to aldehyde synthesis. The 1,2-migration reaction ofα, α-bis(phenylthio)borates **8**, however, can be stopped after single migration. Oxidation of the organoborane intermediates gives aldehydes in good yields. (169)

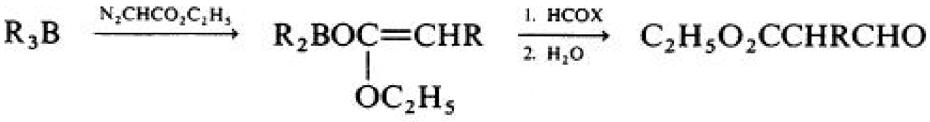
$$\underset{\mathbf{8}}{R_3\bar{B}CH(SC_6H_5)_2} \xrightarrow[-30^\circ]{} R_2BCHR(SC_6H_5) \xrightarrow{[O]} RCHO$$

3.5.1.2. *Aldehydes via Two-Carbon Homologation*

There are only a few procedures for the synthesis of aldehydes by two-carbon homologation. The reaction of organoboranes withα-diazoketones (Eq. 73) can be adapted to the synthesis of aldehydes by replacing the diazoketone with a diazoaldehyde. (186)

$$R_3B + N_2CHCHO \longrightarrow RCH_2CHO$$

The reaction of enoxyboranes with formic acid esters or amides gives the Claisen condensation products in low to moderate yields. (135)



$$R_3B \xrightarrow{N_2CHCO_2C_2H_5} \underset{\displaystyle OC_2H_5}{R_2BOC{=}CHR} \xrightarrow[2.\ H_2O]{1.\ HCOX} C_2H_5O_2CCHRCHO$$

(X = alkoxy, aryloxy, NH_2)

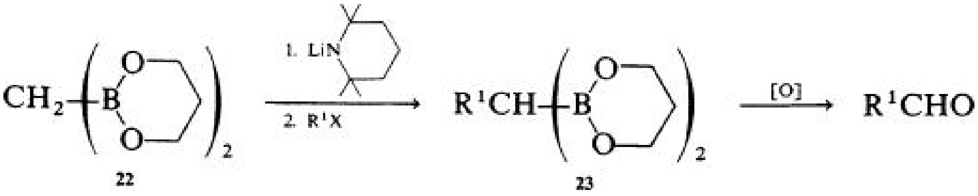
3.5.1.3. Aldehydes via Three-Carbon Homologation

The synthesis of aldehydes by three-carbon homologation has been achieved by the reaction of organoboranes withα, β -unsaturated aldehydes. (80, 81, 187, 188) The free-radical chain mechanism shown in Eq. 35 appears to operate in this reaction as well. (83, 84) The use ofα, β -unsaturatedα-bromoaldehydes providesα-bromoaldehydes. (81)

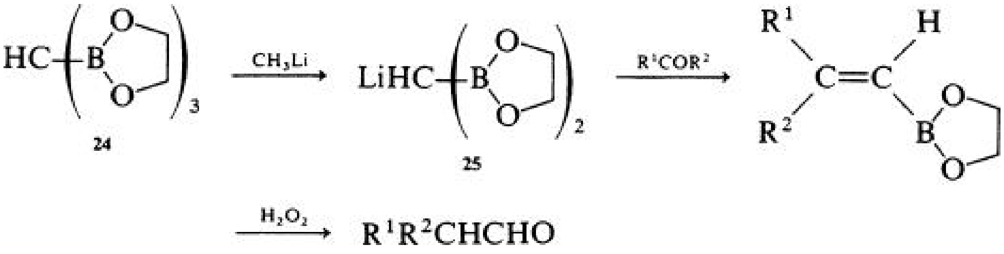
$$(C_6H_{11})_3B \xrightarrow[H_2O]{CH_2{=}CBrCHO} C_6H_{11}CH_2CHBrCHO$$

3.5.1.4. Miscellaneous Preparations of Aldehydes

The ketone synthesis with **22** (Eq. 76) can also be applied to the preparation of aldehydes. (182)



The reaction of **24** with methyllithium involves lithium–boron exchange to produce **25**. Its reaction with aldehydes and ketones followed by hydrogen peroxide oxidation gives aldehydes in good yields. (99)



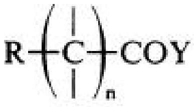
The reaction of dichloromethaneboronic esters with organolithiums or Grignard reagents producesα-chloroalkaneboronic esters that can be oxidized at pH 8.8 to produce the corresponding aldehydes. (189)

$$Cl_2CHB[OC_3H_7\text{-}i]_2 \xrightarrow[M\,=\,Li\text{ or }MgBr]{RM} RCH(Cl)B[OC_3H_7\text{-}i]_2$$

$$\xrightarrow[pH\ 8.8]{[O]} RCHO$$

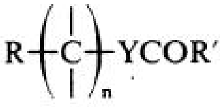
3.6. Carboxylic Acids and Their Derivatives

Organoboranes (RBX_2) can be converted into carboxylic acids and their derivatives **26**, where Y is hydroxy, alkoxy, or thioalkyl. Amides **26** ($Y = NR_2$) do not appear to have been synthesized directly. The preparation of esters and amides **27** is discussed in sections describing the synthesis of alcohols and amines, respectively.



$$R\left(\begin{matrix}|\\C\\|\end{matrix}\right)_n COY$$

26



$$R\left(\begin{matrix}|\\C\\|\end{matrix}\right)_n YCOR'$$

27

(R, R′ = carbon groups; Y = OH, OR, SR, or NR_2; n = 0, 1, 2, . . .)

3.6.1.1. Carboxylic Acids and Their Derivatives via One-Carbon Homologation

Unlike organolithiums and Grignard reagents, organoboron compounds do not normally react with carbon dioxide to produce carboxylic acids. 1,1-Dibora compounds can, however, be converted into malonic acid derivatives by treatment with an organolithium and carbon dioxide. (98)

3.6.1.2. Carboxylic Acids and Their Derivatives via Two-Carbon Homologation

The methods available for the synthesis of esters by two-carbon homologation are quite similar to those for the preparation of ketones by two-carbon homologation. Thus the reaction of organoboranes with (a) potassium salts ofα-halo esters (Eq. 13), (171, 190) (b) alkali metal salts ofα-phenoxycarboxylic acids, (191) (c) α-diazo esters (Eq. 15), (18) or (d) sulfur ylides derived from acetates (Eq. 16) (19) yields carboxylic acids or their esters. The mechanism, the stereochemistry, and the intermediacy of enoxyboranes are discussed in the preceding section.

Although these reactions can often be used interchangeably, there are some differences among them. Whereas the use of *B*-alkyl-9-BBN's is effective for a high-yield conversion of a boron-bound alkyl group into two-carbon homologated carboxylic acid esters by reaction with the potassium salt of anα-bromo ester, (Eq. 77), (192) it is ineffective in the reaction withα-diazo esters. (175)

(77)

In the latter reaction, however, monochlorodialkylboranes (193) or preferably dihaloorganoboranes (194, 195) (Eqs. 78 and 79) have been shown to be effective.

$$RBCl_2 \xrightarrow{N_2CHCO_2C_2H_5} RCH_2CO_2C_2H_5 \tag{78}$$

$$RC{\equiv}CBF_2 \xrightarrow{N_2CHCO_2C_2H_5} RC{\equiv}CCH_2CO_2C_2H_5 \tag{79}$$

As shown in Eq. 14, α, α-dibromo esters can be converted into eitherα-bromo, α-alkyl, orα, α-dialkyl derivatives. (16, 173) The use of potassium 2,6-di-*t*-butylphenoxide is advantageous in these reactions. (196) α-Bromo-α-alkyl derivatives of ethyl acetate can also be prepared by trapping the enoxyborane intermediates formed from organoboranes, ethyl diazoacetate, and bromine. (179)

3.6.1.3. Carboxylic Acids and Their Derivatives via Three-Carbon Homologation

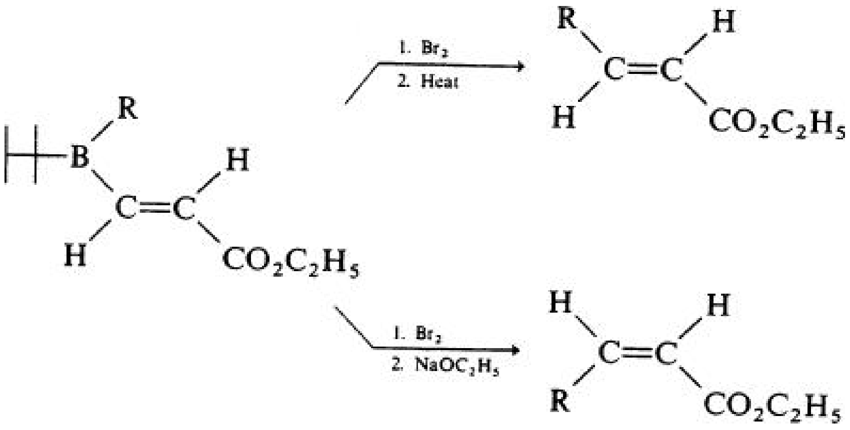
Unlikeα, β -unsaturated ketones and aldehydes, α, β -unsaturated carboxylic acids and esters do not readily undergo conjugate addition with organoboranes. Under electrolytic conditions, however, ethyl acrylate and ethyl methacrylate react with organoboranes to form the conjugate addition products. (197)

$$R_3B + CH_2{=}CR^1CO_2C_2H_5 \xrightarrow[CH_3CN,\ R'_4NX]{\text{Electrolysis}} RCH_2CHR^1CO_2C_2H_5$$

$$(R^1 = H \text{ or } CH_3)$$

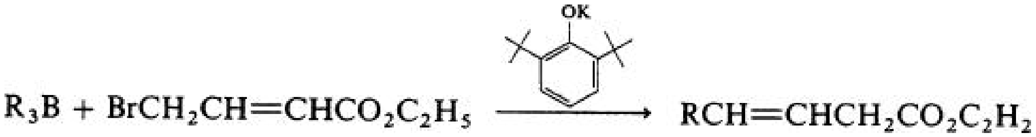
Alternatively, organoboranes can be converted into their ate complexes with methyllithium, and these can be allowed to react withα, β -unsaturated esters in the presence of cuprous iodide. (63) This reaction presumably involves cuprous trialkylmethylborates. This method is also effective in related reactions with ethyl propiolate (198) or ethyl β -bromoacrylate. (61) The stoichiometry of these reactions has not been resolved.

The intramolecular conjugate addition reaction of thexylalkylboranes (89) (Eq. 40), which after oxidation produces β -hydroxycarboxylic acids, can be modified to produce either (*E*)- or (*Z*)- β -alkylacrylic esters. (48)



3.6.1.4. Carboxylic Acids and Their Derivatives via Four-or-More-Carbon Homologation

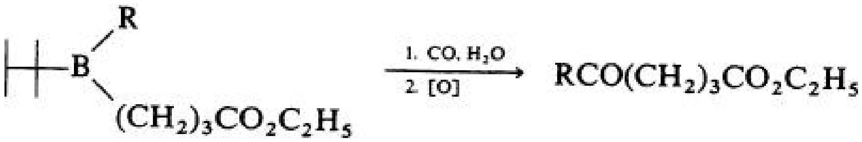
The potassium salt of ethyl γ -bromocrotonate reacts with organoboranes to form γ -alkyl- β , γ -unsaturated esters. (199)



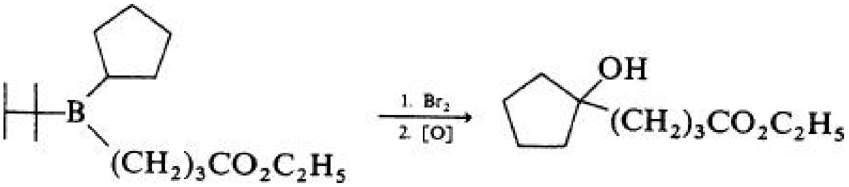
$$R_3B + BrCH_2CH{=}CHCO_2C_2H_5 \longrightarrow RCH{=}CHCH_2CO_2C_2H_2$$

In principle, organoboron reactions involving the use of ester-containing reagents or organoboron compounds can produce esters. The ketone syntheses by the reaction of organoborates with acyl halides (56) (Eq. 68) as well as by the carbonylation of organoboranes (154) can be applied to the synthesis of keto esters provided the two carbonyl functionalities are separated by at least two carbon atoms.

$$R\bar{B}(C_5H_9)_3\,Li^+ \xrightarrow{ClCO(CH_2)_2CO_2CH_3} RCO(CH_2)_2CO_2CH_3$$



Two other similar examples are shown in Eq. 80 (26) and Eq. 70. (164)



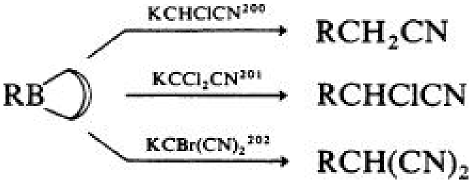
(80)

3.7. Nitriles

No procedure for the synthesis of nitriles by one-carbon homologation of organoboranes appears to have been reported.

3.7.1.1. Nitriles via Two-Carbon Homologation

The preparation of nitriles by two-carbon homologation has been achieved mostly by reactions of organoboranes with potassium salts ofα-halo nitriles, (200) which proceed in a manner similar to those with potassium salts ofα-halo esters. α-Halo nitriles that have been successfully utilized include chloroacetonitrile, (200) dichloroacetonitrile, (201) bromomalononitrile, (202) and ethyl bromocyanoacetate. (202) Potassium 2,6-di-*t*-butylphenoxide has been the most satisfactory reagent for generating the potassium salts ofα-halo nitriles. The 9-BBN moiety is an effective “dummy” group for most, if not all, of these reactions. (201, 202)



Diazoacetonitrile can serve as a substitute for the potassium salt of chloroacetonitrile. (203) For this reaction to be useful, however, it would be necessary to find a suitable “dummy” group that would permit the high-yield preparation of nitriles based on the alkyl group. The use of dichloroorganoboranes is promising but has not yet been tested.

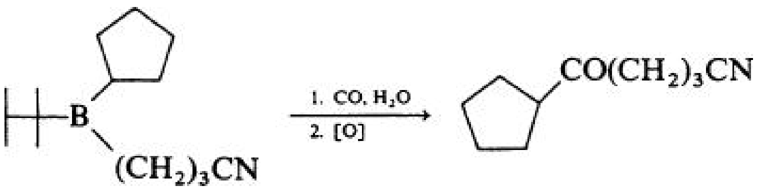
Electrolysis of organoboranes in the presence of acetonitrile and tetraethylammonium iodide followed by oxidation gives two-carbon homologated nitriles. (103) Approximately one and a half out of three alkyl groups are utilized in this reaction.

3.7.1.2. Nitriles via Three-Carbon Homologation

The conjugate addition reaction of cuprous methyltrialkylborates with acrylonitrile appears to be the only currently available method for preparing nitriles by three-carbon homologation (Eq. 30a). (63)

3.7.1.3. *Nitriles via Four-or-More-Carbon Homologation*

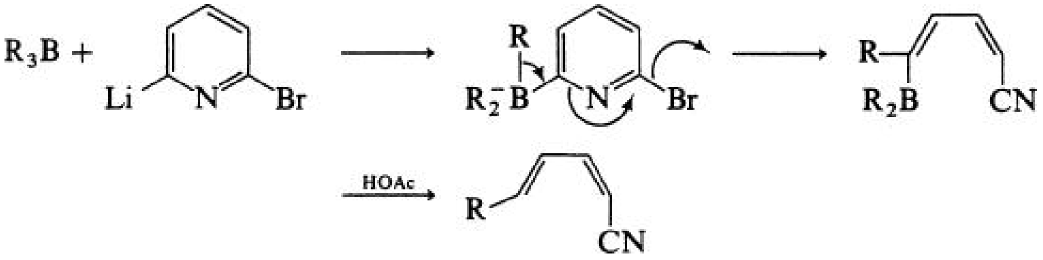
Organoboron reactions of either cyano organoboron compounds or cyano reagents are, in principle, applicable to the synthesis of nitriles by multicarbon homologation. In addition to the four-carbon homologation procedure shown in Eq. 31, (67) the reactions shown in Eq. 81 and Eq. 82 provide examples of such syntheses. (154, 57)



(81)

(82)

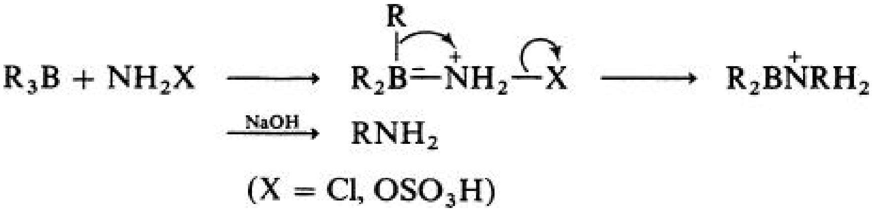
The only reaction of organoboron compounds that generates the cyano group involves treatment of organoboranes with 2-lithio-6-bromopyridine, (204) which produces (*Z,E*)-dienylnitriles.



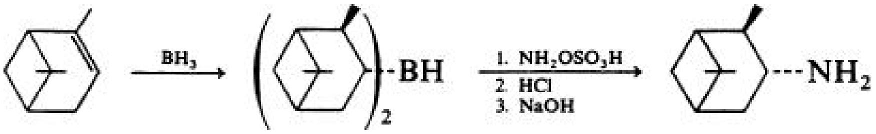
3.8. Amines

3.8.1.1. *Amines via Direct Functionalization*

Organoboranes react with chloramine or, more conveniently, hydroxylamine-*O*-sulfonic acid to produce primary amines (Eq. 83). (205) Conversion of hindered organoboranes into amines is difficult, but favorable results have been observed in diglyme at about 100° (Eq. 84). (206) The reactions proceed with complete retention of configuration. (206)



(83)



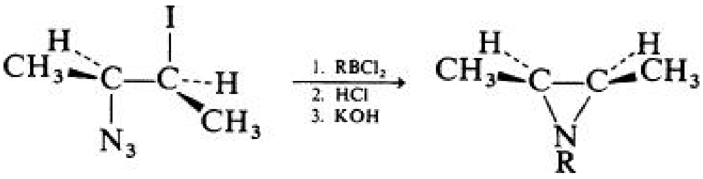
(84)

Only two of the three alkyl groups participate in these reactions, limiting the maximum yield to 67%. As yet, no satisfactory solution to this problem has been provided. Hydroxylamine *O*-mesitylenesulfonate has also been used for amination of organoboranes, (207) but it is not clear that this reagent offers any advantage over the others. The reaction of chloramine-T with organoboranes gives alkyl toluenesulfonamides. (208)

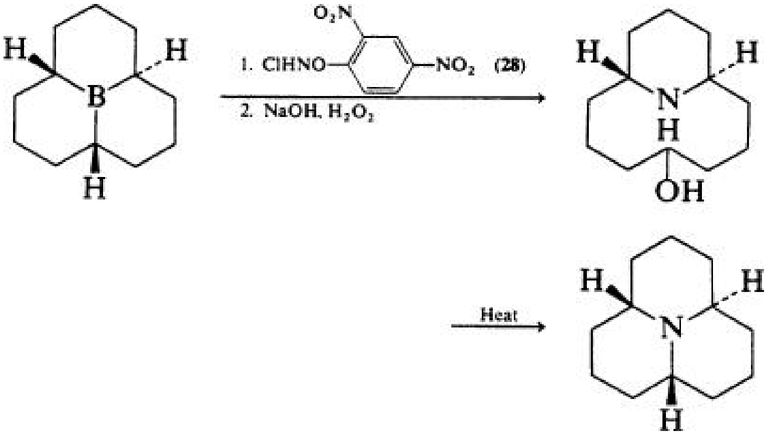
Secondary amines are readily prepared from organoboranes and azides. (209) As only one of the three organic groups participates in this reaction, it is advantageous to use monoalkyldichloroboranes. (210) The latter organoboranes react with azides much more readily (below room temperature) than trialkylboranes. This fact seems to rule out a nitrene mechanism that involves thermal generation of nitrenes as the first step, but supports the 1,2-migration mechanism shown in Eq. 85.

(85)

A useful modification of the reaction involves the use of -iodoazides, which convert organoboranes into aziridines. (113)



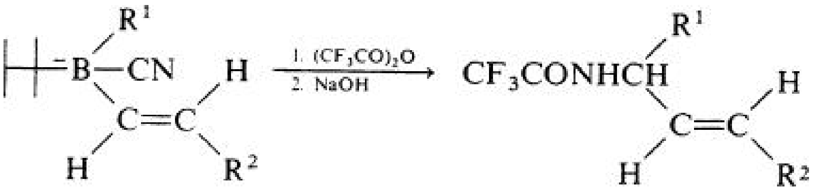
In principle, secondary amines can be prepared by double-migration reactions. In practice, however, generation of amine reagents containing two good leaving groups represents a major challenge. Nitric oxide reacts with organoboranes to give dialkylamines in low yields. (211) The only noteworthy example of the synthesis of a secondary amine involving double migration is the reaction of organoboranes with hydroxylamine derivative **28**, which is generated *in situ* from *O*-(2,4-dinitrophenyl)hydroxylamine and *t*-butyl hypochlorite. (212)



The reaction of dialkylchloramines with organoboranes gives tertiary amines if the competitive free-radical reaction leading to the formation of alkyl chlorides is suppressed by the addition of a radical scavenger such as galvinoxyl. (213)

3.8.1.2. Other Preparations of Amines

Treatment of thexylalkylalkenylcyanoborates with trifluoroacetic anhydride (TFAA) does not lead to ketones but produces the trifluoroacetyl derivatives of alkylalkenylamines **29** in good yields. (214)



29

Enoxyborane intermediates obtained from organoboranes and diazo ketones react with iminium salts to give β -amino ketones. (180)

$$R_3B \xrightarrow{N_2CHCOR^1} R_2BOCR^1{=}CHR$$
$$\xrightarrow{CH_2{=}N^+(CH_3)_2I^-} R^1COCHRCH_2N(CH_3)_2$$

The oxygen-induced conjugate addition of organoboranes toα, β -unsaturated imines produces β -alkylimines. (215) In an analogous manner, the photochemically induced reaction of organoboranes with acridines gives 9-alkyl-9,10-dihydroacridines. (129, 130)

3.9. Miscellaneous Nitrogen Compounds

Organoboranes react with sodium azide in the presence of ferric sulfate and hydrogen peroxide to produce alkyl azides. (216) The reaction presumably proceeds by a free-radical mechanism.

$$R_3B \xrightarrow[2.\ H_2O_2]{1.\ NaN_3,\ Fe_2(SO_4)_3} RN_3$$

Trialkylboranes are electrolyzed between platinum electrodes in nitromethane containing tetraethylammonium iodide to give higher nitroalkanes. (104)

$$R_3B \xrightarrow[(C_2H_5)_4NI,\ CH_3NO_2]{\text{Pt}-\text{Pt electrodes}} RCH_2NO_2$$

The reaction of lithium alkynyltrialkylborates with nitroethylene produces γ -nitro ketones (Eq. 70). (90)

3.10. Halides

3.10.1.1. Halides via Direct Functionalization

3.10.1.1.1. Alkyl Halides

Organoboranes are relatively inert to iodine, bromine, or chlorine. On the other hand, organoborates are very reactive toward iodine and bromine, and the reactions are convenient methods for the synthesis of organic iodides and bromides. Treatment of organoboranes with iodine in the presence of sodium hydroxide (217) or sodium methoxide (218) involves organoborates as reactive species. (218)

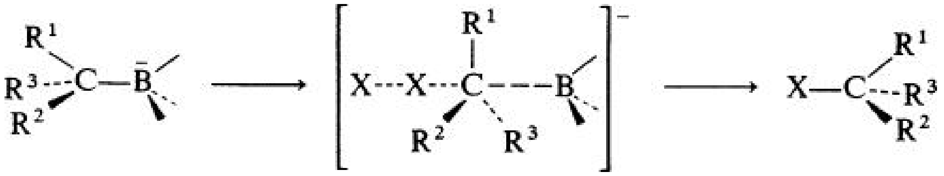
$$R_3B \xrightarrow{NaOH} R_3\overset{-}{B}OHNa^+ \xrightarrow{I_2} RI \qquad (86)$$

When this reaction is run in the presence of excess sodium hydroxide or sodium methoxide, two of three alkyl groups are converted into the corresponding alkyl iodide. Primary alkyl groups are more reactive toward iodine than secondary alkyl groups. Thus iodination of disiamylalkylboranes * containing a primary alkyl group gives the primary alkyl iodides in quantitative yields. (217)

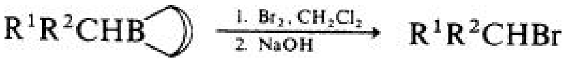
There are at least two distinct paths for bromination of organoboranes. In the presence of a suitable base, such as sodium methoxide, bromination presumably proceeds in the same manner as the iodination in Eq. 86. In the bromination, however, water must be avoided to prevent generation of hypobromite, which converts organoboranes into alcohols. Accordingly, use of sodium methoxide in methanol is recommended. (219) All three primary alkyl groups can be converted into the corresponding bromides according to Eq. 87.

$$R_3B + 3Br_2 + 4NaOCH_3 \longrightarrow 3RBr + 3NaBr + NaB(OCH_3)_4 \qquad (87)$$

The base-induced iodination and bromination of *exo*-norbornylborane gives predominantly *endo*-norbornyl iodide (220) and *endo*-norbornyl bromide, (221) respectively. The inversion of configuration can be explained in terms of an S_E2 mechanism.

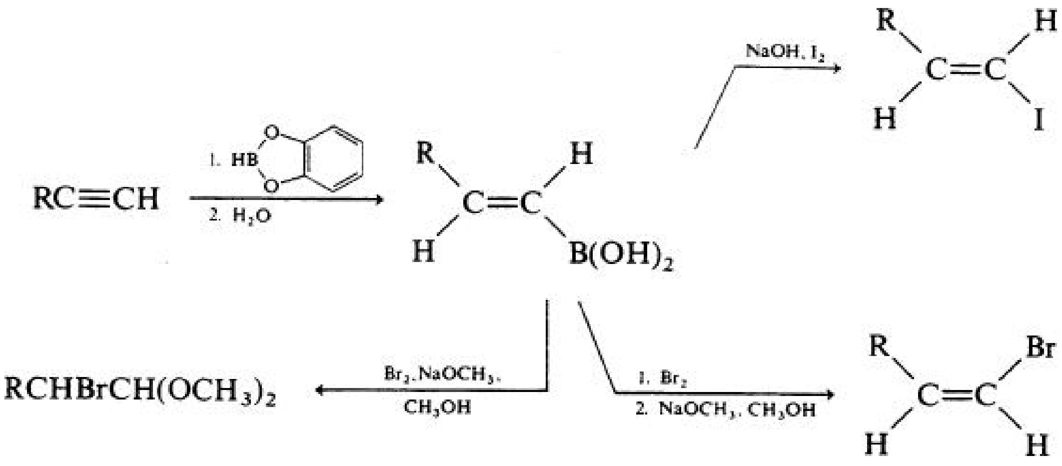


Organoboranes containing secondary alkyl groups are more difficult to brominate by the ionic procedure shown in Eq. 87. Fortunately, these organoboranes readily undergo a free-radical bromination to formα-bromoorganoboranes (Eqs. 11 and 12), which protonolize to give secondary alkyl bromides. (222) The 9-BBN moiety is effective as a “dummy” group because the bridgehead carbon — hydrogen bond, which is orthogonal to the empty *p* orbital of the boron atom, does not react readily with bromine. (223)



A wide variety of chlorine compounds can convert organoboranes into organic chlorides. Such reagents include ferrous chloride, (224) cupric chloride, (225) and nitrogen trichloride. (226) Most, if not all, of these reactions appear to proceed by free-radical mechanisms.

Iodination and bromination of alkenylboranes are not as straightforward as the corresponding reactions of alkenylalanes. When there is another carbon group on the boron atom, treatment with iodine or bromine tends to induce migration of the carbon group from the boron atom to theα-carbon atom of the alkenyl group. Such complications do not exist in the halogenation of alkeneboronic acids, which can be obtained by hydroboration of acetylenes with catecholborane. Thus treatment of alkeneboronic acids with iodine and sodium hydroxide gives alkenyl iodides with retention of configuration, (227) whereas their reaction with bromine followed by treatment with sodium methoxide in methanol produces configurationally inverted alkenyl bromides. (228) When the same alkeneboronic acids are treated simultaneously with bromine and sodium methoxide in methanol, α-bromoaldehyde dimethylacetals are obtained in good yields. (148)



The opposite stereochemical results observed in the bromination and iodination reactions are puzzling, and the mechanisms of these reactions remain to be established.

3.10.1.2. Halides via One-Carbon Homologation

All reported examples of the preparation of organic halides by one-carbon homologation involve either the reaction of organoboranes with the alkali metal salts ofα, α-dihalo ketones, esters, (16) or nitriles, (20) or trapping the enoxyborane intermediates with bromine, *N*-bromosuccinimide, or *N*-chlorosuccinimide. (176)

3.10.1.3. Halides via Two–Carbon Homologation

The conjugate addition of organoboranes withα-bromo-α, β -unsaturated aldehydes (81) formsα-bromoaldehydes by two-carbon homologation. Treatment of enoxyboranes with bromine gives, after methanolysis, α-bromoketones. (179)

3.10.1.4. Miscellaneous Preparations of Halides

Organoboron compounds, especially organoboranes, are relatively unreactive toward organic halides. Thus reactions that involve organoboron compounds containing remote halogen atoms and/or halogen-containing reagents tend to give products containing these halogen atoms. Dichloroalkylboranes containing at least one γ -chlorine atom can be converted into chlorine-containing cyclopropane derivatives. (93)

3.11. Sulfur Derivatives

The current scope of the synthesis of organosulfur derivatives using organoboron compounds is rather modest. Trialkylboranes react with organic disulfides in the presence of a free-radical source to produce the corresponding symmetrical or unsymmetrical sulfides. (229) The reaction has been shown to proceed by a free-radical mechanism.

$$\begin{aligned}
\mathrm{R^1_3B} &\xrightarrow{\text{initiator}} \mathrm{R^1\cdot} \\
\mathrm{R^1\cdot + R^2SSR^2} &\longrightarrow \mathrm{R^1SR^2 + R^2S\cdot} \\
\mathrm{R^2S\cdot + R^1_3B} &\longrightarrow \mathrm{R^2SBR^1_2 + R^1\cdot} \\
&(\mathrm{R^1 = alkyl,\ R^2 = CH_3\ or\ C_6H_5})
\end{aligned}$$

α-Bromo sulfones, sulfonates, and sulfonamides can be alkylated with trialkylboranes under the influence of a base such as potassium *t*-butoxide (Eq. 88). (230) The reaction appears to proceed in a manner analogous to those ofα-halo ketones and esters discussed earlier.

$$\mathrm{R_3B + KCHBrSO_2Y \xrightarrow{R^1OH} RCH_2SO_2Y + R_2BOR^1 + KBr} \qquad (88)$$

$$(\mathrm{Y = alkyl,\ alkoxy,\ or\ amino})$$

3.12. Alkanes, Cycloalkanes, and Arenes

3.12.1.1. Alkanes

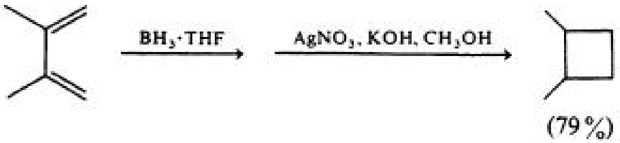
Treatment of trialkylboranes with silver nitrate and sodium hydroxide or potassium hydroxide gives the dimers of the alkyl groups. (231, 232) Two different organoboranes give a statistical mixture of the cross and homo dimers

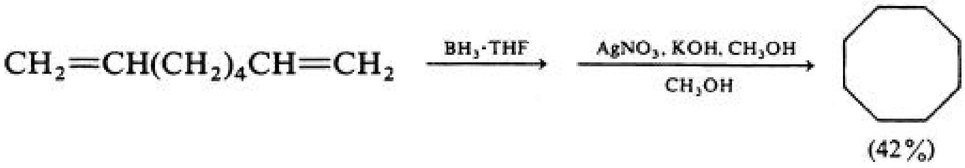
$$R^1_3B + R^2_3B \xrightarrow{AgNO_3,\ KOH} R^1R^1 + R^1R^2 + R^2R^2$$

Although the mechanism of the reaction is not clear, it is likely that the reaction involves organosilver intermediates that decompose by free-radical or other mechanisms to produce the alkyl dimers. In reactions where one alkyl group (R^1) is much more expensive than the other (R^2), the use of a large excess of the latter will allow formation of the cross dimer (R^1R^2) in high yield based on the R^1 group. Another closely related coupling reaction involves electrolysis of trialkylboranes in methanolic potassium hydroxide using platinum plate electrodes. (233)

3.12.1.2. Cycloalkanes

The coupling reaction discussed above can also be applied to the synthesis of cycloalkane dimers. (232) Furthermore, hydroboration of dienes followed by basic silver nitrate treatment produces cycloalkanes. (234) Common rings are obtained in good yields, and some small and medium rings are obtained in fair to good yields.





Boracyclobutanes are not readily available, so the silver nitrate procedure is not suitable for the synthesis of cyclopropanes. Cyclopropanes can, however, be obtained by treating γ -haloorganoboranes with a base (Eq. 41). (91, 97)

Favorable results have been obtained by treating allylic halides with 9-BBN and then with aqueous sodium hydroxide. (93)

$(CH_3)_2C(Cl)CH{=}CH_2 \longrightarrow (CH_3)_2C(Cl)(CH_2)_2B$

Closely related is the reaction ofα, α-dibora- ω-haloalkanes and related ω -sulfonyloxy derivatives with a base such as methyllithium to produce cycloalkylboranes. Oxidation of the products gives the corresponding cycloalkanols such as cyclopropanol and cyclobutanol (Eq. 65). (94)

3.12.1.3. Arenes

The basic silver nitrate treatment of organoboranes is also applicable to the synthesis of bibenzyls and biaryls. (235) Benzyl derivatives such as benzyl bromide can be converted into higher alkyl homologs by reaction of either lithium methyltrialkylborates with benzyl bromide in the presence of cuprous iodide (60) (Eq. 89) or organoboranes withα-lithiobenzyl sulfides followed by treatment with cuprous iodide (Eq. 90). (236)

$$R_3\bar{B}CH_3Li^+ + C_6H_5CH_2Br \xrightarrow{CuI} C_6H_5CH_2R \qquad (89)$$

$$R_3B \xrightarrow{LiCH(SC_6H_5)C_6H_5} R_3\bar{B}\underset{\displaystyle C_6H_5S}{\underset{|}{C}}HC_6H_5 \xrightarrow[2.\ NaOH,\ H_2O_2]{1.\ CuI} RCH_2C_6H_5 \qquad (90)$$

The reaction of lithium 1-naphthyltributylborate with methyl fluorosulfonate produces, after oxidation, the double alkylation product **4** in 70% yields, or, after hydrolysis, the *trans*-dihydroaromatic derivative **5** in 56% yield along with 22% of **4** (see p. 21). (70) The results can be interpreted in terms of an intramolecular 1,2 migration (Eq. 6). Although the scope of the double alkylation reaction is very limited, it holds considerable promise as a route to arenes.

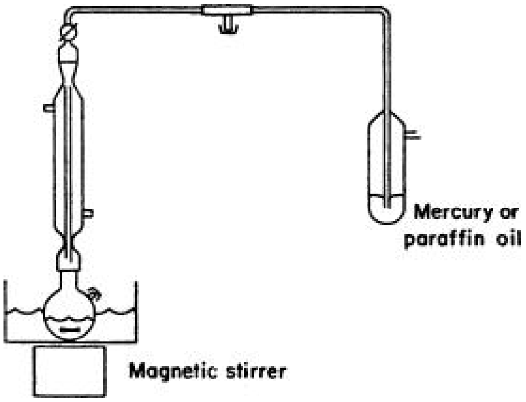
4. Experimental Factors

4.1. Handling Organoboron Compounds

Most organoboranes are air sensitive, and the volatile ones such as triethylborane are usually spontaneously inflammable in air. They should thus be handled in an inert atmosphere. Prepurified nitrogen (99.998%) is satisfactory in essentially all cases. Handling of air-sensitive compounds has been described in detail in a few monographs. 2c, 237 In this section only the most frequently used syringe technique is described.

A large number of the reactions discussed in this review can be carried out by use of the setup shown in Figure 1. After the system is swept with nitrogen, solvents, neat liquid reactants, and/or solutions containing liquid or solid reactants are introduced into the system by means of hypodermic syringes through the side arm that is capped with a septum. It is advisable to use syringes with a Luer lock. The use of relatively long (6–8-in.) needles (16–20 gauge) permits transfer of a liquid from an air-tight vessel to a syringe without the need to introduce a gas into the syringe.

Figure 1. A convenient reaction setup.



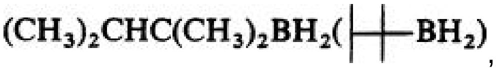
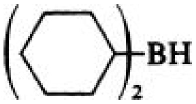
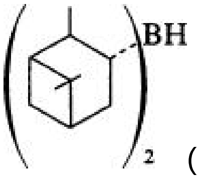
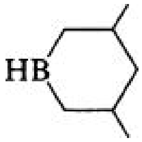
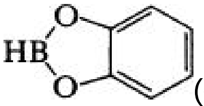
Disposal of organoboron compounds requires special precautions. Unlike most other air-sensitive organometallic compounds such as organolithiums and organoaluminums, organoboranes cannot readily be quenched with water. It is thus advisable to destroy organoboranes by oxidation with hydrogen peroxide before transferring waste mixtures into a waste container. Oxidation of organoborane byproducts also facilitates the isolation and purification of desired organic products. Therefore, unless it is essential to recycle organoborane byproducts, it is a generally useful practice to oxidize and convert them into boric acid or its esters before workup. Typical organoboranes do not show any sign of explosiveness under ordinary conditions. When boron hydrides are mixed with hydrogen peroxide, however, an explosion may result. It is thus important to destroy completely the boron — hydrogen bond by hydrolysis or other suitable means before the addition of hydrogen peroxide. Although most organoboranes that contain boron — hydrogen bonds can be destroyed with water, some of them as well as certain borohydrides require more vigorous methods such as treatment with an aqueous acid.

4.2. Preparation of Organoboron Compounds

A detailed discussion of the preparation of organoboron compounds is beyond the scope of this review. The reader is referred to pertinent monographs, (2) reviews (3, 238-242) and original papers cited therein. Hydroboration (3) and transmetalation (171) are the two most generally applicable methods for the preparation of organoboranes, and the complexation reaction of boranes with organolithium and related organometallic compounds is the only satisfactory method for the preparation of organoborates. (2)

4.3. Selection of Boron-Containing Reagents

A wide variety of boron-containing reagents has been developed. Judicious selection of boron-containing reagents is often essential to obtaining successful results. The following are some of the readily available hydroborating agents that are widely used:

1. Nonsubstituted boranes: BH_3-tetrahydrofuran (THF), (3) BH_3 generated in bis-(2-methoxyethyl) ether (diglyme, DG), (3) $BH_3 \cdot N(C_2H_5)_3$, (240) BH_3-dimethyl sulfide (DMS). (243)
2. Monosubstituted boranes: , (238) $ClBH_2 \cdot O(C_2H_5)_2$, (244) $ClBH_2$ — DMS. (245)
3. Disubstituted boranes: [$(CH_3)_2CHCH(CH_3)_2BH(Sia_2BH)$, (3)  (dicyclohexylborane), (3)  (dipinanylborane), (246)  (9-borabicyclo[3.3.1]nonane, 9-BBN), (241)  (3,5-dimethylborinane), (239)  (catecholborane), (242) $HBCl_2 \cdot O(C_2H_5)_2$, (247) $HBCl_2$ — DMS. (248)

The early hydroboration experiments were carried out with diborane generated *in situ* in diglyme. (3) Since both borane in THF and borane–dimethyl sulfide are now commercially available (Aldrich), they are convenient hydroborating agents. Borane–triethylamine and other borane–amine complexes are much less reactive than borane–THF and borane–DMS. In the hydroboration of dienes and polyenes, however, the use of borane-amine complexes can be advantageous in that the formation of intractable polymeric material can be minimized.

Thexylborane (238) offers a number of advantages. Unsymmetrically substituted organoboranes (thexylBR^{1}R^2) are readily obtainable and are useful intermediates for preparing ketones and alcohols. Thexylborane and chloroborane are convenient cyclic hydroboration reagents. (239)

Disubstituted boranes permit highly regioselective hydroboration of olefins, dienes and acetylenes. (3) Dipinanylborane (246) can be obtained in an optically active form and can serve as an asymmetric hydroborating agent.

The 9-BBN moiety can serve as a nonparticipating "dummy" group in several types of reaction, including aldehyde synthesis via carbonylation, ester synthesis via α -bromo esters, and secondary alkyl bromide synthesis. Catecholborane (242) is a relatively weak hydroborating agent but provides a convenient entry into boronic acids that have only one carbon group bonded directly to boron. When these boronic acids are sufficiently reactive, they permit a high yield conversion of the organic group bonded to boron into the desired product. Dichloroborane (247, 248) appears to be even more promising. Its reactivity is considerably higher than that of catecholborane, and the chlorine atoms often serve as convenient "dummy" groups, as in ester synthesis via α -diazo esters and azide synthesis.

4.4. Other Factors

A large number of organoboron reactions proceed readily in THF at room temperature. Chloroboranes, however, tend to form strong complexes with THF that are inert in many reactions. The use of diethyl ether and other less polar solvents circumvents such a difficulty.

5. Experimental Procedures

5.1.1.1. Perhydro-9b-phenalenol (Carbonylation. Preparation of Alcohols via One-Carbon Homologation) (249)

A 1-L flask fitted with a septum inlet, magnetic stirring bar, short Vigreux column connected to a distillation setup, and a mercury bubbler was assembled, flushed with nitrogen, and then maintained under a static pressure of the gas. In the flask was placed 500 mL (0.50 mol) of 1.0*M* borane–tetrahydrofuran complex. The flask was immersed in an ice-water bath, and the borane–triethylamine complex was prepared *in situ* by the slow addition of 50.6 g (0.50 mol) of triethylamine. Most of the tetrahydrofuran was removed by distillation at atmospheric pressure. Pure, dry diglyme (300 mL) was added and the temperature was maintained at 130–140° as a solution of 81 g (0.50 mol) of (*E,E,E*)-1,5,9-cyclododecatriene in 100 mL of diglyme was added over 2 hours by means of a syringe pump. After most of the diglyme had been removed by distillation at atmospheric pressure, the product was heated at 200° for 6 hours. After cooling, the product was transferred under nitrogen to a smaller distillation setup. Distillation provided 74.6 g (85%) of a 92:8 mixture of (*Z,E*)- and all (*Z*)-perhydro-9b-boraphenalene, bp 115–117° (10 mm).

A 250-mL autoclave was flushed with nitrogen. The autoclave was then maintained under a static pressure of nitrogen as it was charged with 17.6 g (0.10 mol) of (*Z,E*)-perhydro-9b-boraphenalene, 50 mL of tetrahydrofuran, and 18.6 g (16.8 m, 0.30 mol) of ethylene glycol. The autoclave was pressured to 1000 psi with carbon monoxide, and the temperature was then raised to 150° and maintained there for 2 hours. The apparatus was brought to room temperature and opened to the air. The reaction mixture was diluted with 100 mL of pentane, washed with water, and dried ($MgSO_4$). Removal of the solvents under reduced pressure provided crude (*Z,Z,E*)-2-(perhydro-9¢b-phenalyl)-1,3,2-dioxaborole in 87% yield.

A solution of 24.8 g (0.10 mol) of (*Z,Z,E*)-2-(perhydro-9¢b-phenalyl)-1,3,2-dioxaborole in 100 mL of tetrahydrofuran and 100 mL of 95% ethanol was stirred with 37 mL (0.20 mol) of 6 *M* sodium hydroxide followed by the slow addition of 37 mL of 30% hydrogen peroxide at a rate such that the temperature did not exceed 40°. After the original reaction subsided, the reaction mixture was maintained at 50° for 3 hours to complete the reaction. The reaction mixture was brought to 25°, an equal volume of pentane added, and the organic phase separated. The organic phase was washed with water and then dried ($MgSO_4$). Removal of the pentane gave 13.6 g (70%) of pure (*Z,Z,E*)-perhydro-9b-phenalenol, mp 78–78.5°.

5.1.1.2. Thexylcyclohexylcyclopentylcarbinol (DCME Reaction. Preparation of Alcohols via One-Carbon Homologation) (39)

A 1.0 *M* solution of thexylborane in tetrahydrofuran (100 mL) (238) was cooled to –25° followed by the addition of 8.2 g (0.10 mol) of cyclohexene. After 1 hour, 8.4 g (0.10 mol) of 2,3-dimethyl-2-butene was added, followed by 6.8 g (0.10 mol) of cyclopentene. The reaction mixture was maintained at –25° for 24 hours.

The solution was brought to 0°, and 25.3 g (0.22 mol, 120% excess) of dichloromethyl methyl ether was added. In a dropping funnel was placed 111 mL of a 1.80 *M* solution of lithium triethylcarboxide (0.20 mol, 100% excess, prepared by the dropwise addition of one equivalent of triethylcarbinol to one equivalent of *n*-butyllithium at 0° under nitrogen). The base was added to the reaction mixture at 0° over 20–30 minutes, and the mixture was then maintained at room temperature for 30 minutes. A heavy precipitate of lithium chloride formed. To the reaction mixture was added 12.4 g (0.20 mol, 100% excess) of ethylene glycol, and the volatile materials were removed by distillation. To the residue was added 50 mL of 95% ethanol and 25 mL of tetrahydrofuran, followed by 24 g (0.60 mol) of solid sodium hydroxide. When most of the sodium hydroxide had dissolved, 50 mL of 30% hydrogen peroxide was cautiously added dropwise to the solution during 2 hours while the temperature was maintained below 50°. The reaction was then maintained at 55–60° for an additional 2 hours. After it had been brought to 25°, the aqueous phase was saturated with sodium chloride and the organic phase separated. The aqueous phase and salts were extracted with ether, and the combined organic phase was dried ($MgSO_4$). Following removal of the solvents, the triethylcarbinol was distilled at 50° (0.2 mm) and the product was obtained as a very thick oil. In order to minimize dehydration, it was distilled rapidly in two portions in a Kügelrohr to yield a total of 17.4 g (66%) of thexylcyclohexyl-cyclopentylcarbinol; bp 115–120° (0.5 mm); $n_{\mathrm{D}}^{20}1.5060$.

5.1.1.3. Methyl 11-(2,5-Dihydroxyphenyl)undecanoate (Synthesis of Substituted Hydroquinones. Preparation of Alcohols via Two-, Three-Carbon Homologation) (136, 137)

To 29.7 g (150 mmol) of methyl 10-undecenoate was added 25 mL of a 2 *M* borane solution in tetrahydrofuran. After the hydroboration was complete, 0.91 mL (50 mmol) of water was added followed by 5.4 g (50 mmol) of *p*-benzoquinone in 20 mL of tetrahydrofuran. Air was added at a rate of 0.1 mL/minute until the reaction was complete. Nuclear magnetic resonance analysis at this point showed an isomer distribution of 78% methyl 11-(2,5-dihydroxyphenyl)undecanoate and 22% methyl 10-(2,5-dihydroxy-phenyl)undecanoate, with an overall yield of 95% of the isomeric products.

Methyl 11-(2,5-dihydroxyphenyl)undecanoate was converted to the acid for characterization as follows. The reaction mixture was maintained under nitrogen, and 8.0 g (200 mmol) of sodium hydroxide was added. The mixture was stirred for 3 hours. The mixture was extracted with two 25-mL aliquots of ether to remove the organic, nonacidic byproducts. The alkaline water layer was then neutralized with hydrochloric acid and the organic layer was extracted into ether. The resultant oil was comprised chiefly of the isomeric undecanoic acids. The recovery of crude product was approximately 80%. The 11-(2,5-dihydroxyphenyl)undecanoic acid was purified by recrystallization from ether–hexane; mp 110–111°; NMR (D_2O – CD_3COCD_3): δ 1.20–1.70 (m, 18 *H*, $-CH_2CO_2-$ and alkyl *H*), 2.1–2.4 (m, 2 *H*, $ArCH_2-$), 6.75 (broad s, 3 *H*, ArH).

5.1.1.4. 7-Methyl-5-pentyl-5-(E)-octen-3-ol (Reaction of Lithium Trialkylalkynylborates with Oxiranes. Preparation of Alcohols via Four-Carbon Homologation) (66)

To a stirred solution of 0.48 g (5 mmol) of 1-heptyne in 5 mL of tetrahydrofuran at 0° maintained under nitrogen was added 5 mL of a 1.0 *M n*-butyllithium solution in hexane and the mixture was stirred at room temperature for 30 minutes. The mixture was cooled to 0°, and 0.7 g (5 mmol) of triisopropylborane was added, followed by stirring at room temperature for 1 hour. To the reaction was added 0.43 g (6 mmol) of ethyloxirane and the reaction mixture was heated at reflux for 15 hours.

The reaction was cooled to room temperature, and 4 mL of acetic acid was added. The resulting mixture was heated at reflux for 10 hours. The mixture was then treated with 10 mL of a 4 *N* sodium hydroxide solution followed by extraction with hexane. The solution was dried (Na_2SO_4) and concentrated under reduced pressure. The yield of 7-methyl-5-pentyl-5-(*E*)-octen-3-ol on distillation was 1.04 g (98%); bp 118–120° (6 mm); IR (neat): 3420, 1468, 1383, 1101 cm^{-1}; mass spectrum *m/e* 212 (M^+).

5.1.1.5. Methyl 4-Oxooctanoate (Reaction of Lithium Tetraorganoborates with Acyl Halides. Preparation of Ketones via One-Carbon Homologation) (56)

To a dry 250-mL flask equipped with a septum inlet, reflux condenser, and a stirring bar were introduced at 0° 10.9 g (50 mmol) of tricyclopentylborane in tetrahydrofuran and 20.8 mL (50 mmol) of 2.4 *M n*-butyllithium in hexane. After 1 hour, 7.52 g (50 mmol) of 3-carbomethoxypropionyl chloride was added at 0°. The reaction was stirred at 0° for 30 minutes, followed by stirring at 40–45° for 24 hours. After evaporation of the volatile compounds, distillation provided 6.54 g (76%) of methyl 4-oxooctanoate; bp 57–61° (0.27 mm); $n_D^{22} 1.4372$; NMR (CCl_4): δ 0.91 (t, *J* = 6.5 Hz, 3 *H*), 1.1–1.8 (m, 4 *H*), 2.3–2.8 (m, 6 *H*), 3.63 (s, 3 *H*), IR (neat): 1720, 1210, 1160 cm^{-1}.

5.1.1.6. 5-Methyltetradecan-6-one (Alkylation of Alkynyltrialkylborate Salts. Preparation of Ketones via One-Carbon Homologation) (163)

A solution containing 5 mmol of tri-*n*-octylborane in tetrahydrofuran was prepared under nitrogen in a dropping funnel. To a stirred solution containing 0.41 g (5 mmol) of 1-hexyne in 5 mL of petroleum ether (bp 40–60°) in an ice bath was added dropwise 5 mmol of *n*-butyllithium in hexane. The alkynyllithium precipitated as a white solid, and butane was evolved. The ice bath was removed and the mixture stirred thoroughly for 30 minutes. The flask was recooled to 0°, and the solution of tri-*n*-octylborane was added dropwise. Diglyme (5 mL) was added, and the residual trialkylborane solution was washed into the flask with diglyme. After 2–3 minutes the precipitate had dissolved completely, and volatile materials were pumped off. Stirring was continued for a further 15 minutes at ambient temperature to complete formation of the salt. The solution was then cooled to –78°, and 0.63 g (5 mmol) of dimethyl sulfate was added.

After 10 minutes at –78°, the reaction flask was cooled in ice and 1.5 mL of a 5 *M* aqueous solution of sodium hydroxide was added. Hydrogen peroxide (1.5 mL of a 50% solution) was carefully added dropwise, the ice bath was removed, and the mixture was left for at least 3 hours. The product was extracted into ether, and the extract was washed with water, dried ($MgSO_4$), filtered, and evaporated to give a syrupy residue. 5-Methyltetradecan-6-one was obtained pure in 85% yield by column chromatography; bp 87–90° (1.5 mm); $n_D^{22}1.4338$; mass spectrum *m/e* 226.2 (M^+).

5.1.1.7. Cyclopentyl 8-Iodooctyl Ketone (Reaction of Trialkylcyanoborates with Trifluoroacetic Anhydride. Preparation of Ketones via One-Carbon Homologation) (250)

Into a 100-mL flask equipped with a sealed tube bent to an angle of approximately 100° containing 0.53 g (11 mmol) of sodium cyanide was charged in succession 15 mL of tetrahydrofuran, 6.7 mL of a 1.5 *M* tetrahydrofuran solution of borane (10 mmol), 0.84 g (10 mmol) of 2,3-dimethylbut-2-ene, 0.68 g (10 mmol) of cyclopentene, and 2.38 g (10 mmol) of 8-iodooct-1-ene. The bent tube was rotated, allowing the cyanide to enter the reaction, and vigorous stirring was maintained for 1 hour at 35°. The flask was cooled to –78°, and 2.53 g (12 mmol) of trifluoroacetic anhydride was added with stirring. The cooling bath was removed and the mixture was allowed to come to room temperature over 1 hour. The mixture was then cooled to 0° and 12 mL of 3 *N* sodium hydroxide followed by 8 mL of 50% hydrogen peroxide were slowly added. After the initial vigorous reaction subsided, the cooling bath was removed, and oxidation was completed over 3 hours at 25° and 15 minutes at 50°. The mixture was extracted into 150 mL of pentane. The extract was washed with 2 *N* sodium hydroxide, 2 *N* hydrochloric acid and water, dried ($MgSO_4$), filtered, and evaporated. By elution through a silica column using benzene, 2.55 g (76%) of cyclopentyl 8-iodooctyl ketone was isolated; bp 130° (0.5 mm); $n_{\mathrm{D}}^{19}1.5150$; IR (film): 1702 cm^{-1}; mass spectrum *m/e* 336 (M^{+}).

5.1.1.8. 7,7-Dimethyl-(E)-5-octen-2-one (Conjugate Addition of B-Alkenyl-9-BBN to Methyl Vinyl Ketone. Preparation of Ketones via Three-Carbon Homologation) (86)

To an oven-dried, 500-mL flask flushed with nitrogen and equipped with a reflux condenser and magnetic stirring bar was added 208 mL of 0.48 *M* 9-borabicyclo[3.3.1]nonane (100 mmol) in tetrahydrofuran. 2c The solution was cooled in an ice-water bath, and 9.1 g (110 mmol) of 3,3-dimethyl-1-butyne was added over 5 minutes. The mixture was then stirred overnight at room temperature to ensure complete hydroboration. Methyl vinyl ketone (7.7 g, 110 mmol) was added, and the solution was heated under reflux for 16 hours. After it had been cooled to room temperature, the residual organoborane was oxidized by adding 40 mL of 3 *N* sodium hydroxide, followed by the slow addition of 40 mL of 30% hydrogen peroxide. The reaction mixture was maintained at 50° for 1 hour to ensure complete oxidation. The aqueous layer was saturated with anhydrous potassium carbonate, separated, and extracted with hexane. After drying ($MgSO_4$), the combined organic layer was distilled to provide 13.1 g (85%) of 7,7-dimethyl-(*E*)-5-octen-2-one; bp 80–82° (12 mm), $n_{\mathrm{D}}^{20}1.4355$; NMR (CCl_4): δ 0.95 (s, 9 *H*), 2.05 (s, 3 *H*), 2.2–2.4 (m, 4 *H*), 5.4 (m, 2 *H*); IR (neat): 1720, 975 cm^{-1}.

5.1.1.9. Cyclopentanecarboxaldehyde (Carbonylation of Organoboranes in the Presence of Potassium Triisopropoxyborohydride. Preparation of Aldehydes via One-Carbon Homologation) (251)

A Brown automatic gasimeter was set up for carbonylation as described 2c and fitted with a 128-mL reaction flask. The apparatus was flushed with nitrogen and charged with 10.0 mL of a 0.5 *M* solution of 9-borabicyclo[3.3.1]nonane in tetrahydrofuran and 0.34 g (5 mmol) of cyclopentene. The mixture was stirred at 25° in order to complete the hydroboration; then it was cooled to 0°, and the stirrer was stopped. Potassium triisopropoxyborohydride (5.0 mL of a 1.0 *M* solution in tetrahydrofuran) was added, and the apparatus was flushed with carbon monoxide by forcing 2 mL of formic acid into the generator flask by means of a rubber bulb attached to the top of the buret. The stirrer was started and the uptake of carbon monoxide was monitored by the intake of formic acid. The uptake was complete within minutes. After 15 minutes, the stirrer was stopped, the buret was closed, and the system was flushed with nitrogen.

The stirrer was started, and to the vigorously stirred mixture 10 mL of a pH 7 buffer and 2.0 mL of 30% hydrogen peroxide were added. After the initial vigorous reaction, the cooling bath was removed and the stirring was maintained for 15 minutes. Potassium carbonate (13 g) was added and the upper tetrahydrofuran layer was separated. This solution was dried (Na_2CO_3) and analyzed by GLC with hexadecane as an internal standard using a Carbowax-20 M column to give cyclopentanecarboxaldehyde in 92% yield. A large-scale (20 mmol) reaction was run, and the cyclopentanecarboxaldehyde was isolated in 94% yield, bp 80–81° (50 mm).

5.1.1.10. 2-Bromo-4-methylhexanal (Reaction of Organoboranes with 2-Bromoacrolein. Preparation of Aldehydes via Three-Carbon Homologation) (81)

A 100-mL flask fitted with a rubber septum cap, a magnetic stirring bar, and a condenser was flushed with nitrogen. In the flask was placed 50 mL of a 2.0 *M* solution of borane–tetrahydrofuran at room temperature. Then the solution was cooled to –10° and 16.8 g (0.30 mol) of 2-butene was added. The reaction mixture was stirred for 1 hour at 0° and then brought to room temperature. Water, 1.8 mL (0.10 mol), was added. Then 13.5 g (0.1 mol) of 2-bromoacrolein was added. The reaction was exothermic, and the temperature rose spontaneously to 40°. The reaction mixture was cooled to room temperature. Examination of an aliquot indicated a yield of 90%. Distillation gave 15.4 g (80%) of 2-bromo-4-methylhexanal, bp 60° (4.8 mm).

5.1.1.11. Ethyl p-Chlorophenylacetate (Reaction of Aryldichloroboranes with Ethyl Diazoacetate. Preparation of Esters via Two-Carbon Homologation) (194)

A dry 50-mL flask equipped with a magnetic stirring bar and septum inlet was flushed with nitrogen. The flask was then cooled to –25° and charged with 1.89 g (10 mmol) of *p*-chlorophenyldichloroborane (252) in 10 mL of tetrahydrofuran. To this solution was added dropwise 1.25 g (11 mmol) of ethyl diazoacetate in 10 mL of tetrahydrofuran at such a rate (1 mL/3–5 minutes) that nitrogen was evolved smoothly (approximately 1.5 hours). At this temperature, 5 mL of water and 5 mL of methanol were added. Finally the cooling bath was removed. The mixture was poured into saturated aqueous sodium carbonate (75 mL) and extracted with three 50-mL portions of ether. Distillation of the dried ($MgSO_4$), concentrated residue gave 1.80 g (91%) of ethyl *p*-chlorophenylacetate; bp 106–107° (3.5 mm); mp 31–32°.

5.1.1.12. Ethyl [trans-2-Methylcyclopentyl]acetate (Reaction of B-Organo-9-BBN Derivatives with α-Halo Esters in the Presence of Base. Preparation of Esters via Two-Carbon Homologation) 2c

Into a 500-mL flask equipped with a septum inlet, dropping funnel, and magnetic stirring bar was charged 8.2 g (0.1 mol) of 1-methylcyclopentene and 12.2 g (0.1 mol) of 9-borabicyclo[3.3.1]-nonane in tetrahydrofuran. The reaction mixture was refluxed. To the stirred solution at 0° were added 50 mL of dry *t*-butyl alcohol and 16.7 g (0.1 mol) of ethyl bromoacetate. The reaction was induced by the slow dropwise addition of 100 mL of a 1.0 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol over a 30-minute period. The reaction mixture was brought to room temperature. To the mixture was added 33 mL of 3 *M* sodium acetate, followed by the dropwise addition of 22 mL of 30% hydrogen peroxide while the temperature was maintained at 40–50°. The reaction mixture was stirred at room temperature for 30 minutes, and then the aqueous phase was saturated with sodium chloride. The organic layer was separated, dried ($MgSO_4$), and distilled to give 9.7 g (57%) of ethyl [(*E*)-2-methylcyclopentyl]acetate; bp 80° (10 mm); $n_D^{20}1.4383$.

5.1.1.13. 3-Hydroxy-3-[trans-2-methylcyclopentyl]propionic Acid (Intramolecular Michael Reaction Involving Borate Complexes. Preparation of Carboxylic Acids via Three-Carbon Homologation) (89)

A dry 250-mL flask equipped with a septum inlet, reflux condenser, and a magnetic stirring bar was flushed with nitrogen, and in it was placed 16.8 mL (30 mmol) of 1.78 *M* thexylborane in tetrahydrofuran. (238) To the reaction was added 3.2 mL (30 mmol) of 1-methylcyclopentene. After 1 hour of stirring at –25 to –30°, 3.2 mL (30 mmol) of ethyl propiolate was added. This was also stirred for 1 hour at –25 to –30°, followed by the addition of 25 mL (75 mmol) of 3 *N* sodium hydroxide. The reaction was stirred for 5 minutes at –25° and then at room temperature for 1 hour. The reaction mixture was oxidized with 10 mL of 30% hydrogen peroxide and heated for 2 hours at 40–50° to complete oxidation and hydrolysis. After workup, 4.1 g (79%) of crude product (*ca.* 90% pure) was obtained. After recrystallization (ether–pentane), 3.2 g (62%) of 3-hydroxy-3-[(*E*)-2-methylcyclopentyl]propionic acid was obtained; mp 69.5–70°; NMR (CCl_4): δ 1.05 (d, *J* = 6 Hz, 3 *H*), 1.2–2.2 (m. 8 *H*), 2.45 (d, *J* = 6 Hz, 2 *H*), 3.6–4.2 (m. 1 *H*), 7.62 (s, 2 *H*), IR (Nujol): 3150, 1690 cm^{-1}.

5.1.1.14. Ethyl (E)-2-Heptenoate (Reaction of Copper(I) Methyltrialkylborates with Ethyl β -Bromoacrylates. Preparation of Esters via Three-Carbon Homologation) (61)

A dry 25-mL flask was charged under nitrogen with 1.425 g (7.5 mmol) of copper(I) iodide and 5 mL of anhydrous tetrahydrofuran. To this solution was added 7.5 mmol of lithium methyltributylborate (prepared by the reaction of methyllithium with tributylborane) in tetrahydrofuran at 0°. After 5 minutes of stirring, 0.895 g (5 mmol) of ethyl (*E*)- β -bromoacrylate was gradually added and the reaction mixture was stirred for 2 hours at 0°. The residual organoborane was oxidized by alkaline hydrogen peroxide. 2c The product was extracted with ether, and the extracts were analyzed by GLC, revealing ethyl (*E*)-2-heptenoate in 98% yield. An analytically pure sample was obtained by preparative GLC (20% Silicone SE-30 on Uniport-B, 2 m), $n_D^{23}1.4382$.

5.1.1.15. N-[trans-2-Methylcyclohexyl]cyclohexylamine (Reaction of Dichloro-organoboranes with Organic Azides. Preparation of Amines via Direct Functionalization) 2c

A dry 500-mL flask equipped with a septum inlet, reflux condenser, magnetic stirring bar, and mercury bubbler was flushed with nitrogen. The flask was charged with 100 mL of benzene and 17.8 g (0.10 mol) of (*E*)-2-methylcyclohexyldichloroborane (prepared by the reaction of dichloroborane with 1-methylcyclohexene). Then 12.5 g (0.10 mol) of cyclohexyl azide was added dropwise over 30 minutes at 20°. The solution was stirred for an additional 15 minutes, and the temperature was brought to 80° over 45 minutes. A gentle reflux was maintained until nitrogen evolution was complete. The reaction was cooled to 0–5°, and the reaction product was carefully hydrolyzed by slowly adding 10 mL of water. An additional 90 mL of water was added, and the precipitate was removed by filtration. The organic phase was separated and washed with 50 mL of 2 *M* hydrochloric acid. The combined aqueous layer and precipitate was made strongly alkaline with 40% potassium hydroxide. The amine was taken up in ether and dried (K_2CO_3), followed by removal of the ether under reduced pressure. Distillation gave 16.8 g (86%) of *N*-[(*E*)-2-methylcyclohexyl]cyclohexylamine ; bp 102–104° (1.5 mm); $n_D^{20}1.4790$.

5.1.1.16. 3-Hexyl-2-methyl-1-nitrodec-3-ene (Michael Reaction of Lithium Trialkylalkynylborates. Preparation of Nitroalkenes via Three-Carbon Homologation) (90)

To 5 mmol of lithium tri-*n*-hexyloctynylborate (prepared by the reaction of octynyllithium with tri-*n*-hexylborane) was added 0.435 g (5 mmol) of 1-nitropropene in 10 mL of dry tetrahydrofuran at 0°, followed by warming the reaction mixture to 20°. After 20 minutes, the reaction mixture was allowed to stand with 2 mL of degassed isobutyric acid for 17 hours at 20°. Oxidation was achieved by the addition of 5 mL of a 5 *M* aqueous sodium acetate solution followed by 5 mL of 50% hydrogen peroxide. After at least 3 hours at 20°, the solution was acidified with 6 mL of 5 *M* aqueous hydrochloric acid and the crude product was extracted with ether. Column chromatography gave 3-hexyl-2-methyl-1-nitrodec-3-ene in 82% yield.

5.1.1.17. endo-2-Iodonorbornane (Base-Induced Reaction of Iodine with Organoboranes. Preparation of Organic Halides via Direct Functionalization) (220)

A dry nitrogen-flushed, 400-mL flask was charged with 29.25 g (0.30 mol) of norbornene in 200 mL of dry tetrahydrofuran and hydroborated by the dropwise addition of 41 mL of 2.45 *M* borane–tetrahydrofuran (0.10 mol) at 0°. After 1 hour at 25°, 1 mL of methanol was added to destroy traces of residual hydride. The flask was wrapped in aluminum foil and cooled to 0°. Then 56 g (0.22 mol) of iodine was added under nitrogen, followed by 46.5 mL of a 4.72

M solution of sodium methoxide in methanol over 10 minutes. Excess iodine was decolorized with 10 mL of saturated aqueous sodium thiosulfate. Extraction with pentane and distillation yielded 17.2 g (78%) of 2-iodonorbornane, bp 54–55° (1.8 mm). Analysis by ^{1}H NMR revealed the mixture to be 80% *endo*- and 20% *exo*-iodonorbornane. Refluxing the isomeric mixture in 200 mL of 80% aqueous methanol (v/v) containing 5 g of potassium carbonate for 3 hours selectively destroyed the *exo* isomer. Extraction with pentane and distillation gave 12.0 g of pure *endo*-2-iodonorbornane; bp 51.5–52.0° (1.2 mm); $n_D^{20}1.5650$.

5.1.1.18. (E)-1-Iodo-1-octene (Reaction of Vinylboronic Acid with Iodine and Base. Preparation of Alkenyl Halides via Direct Functionalization) 2c

Into a 200-mL flask under a nitrogen atmosphere was placed 11.0 g (0.10 mol) of 1-octyne, followed by 12.2 g (0.10 mol) of catecholborane. The stirred mixture was heated for 2 hours at 70°. The flask and its contents were then cooled to 25° and 100 mL of water added. The mixture was stirred for 2 hours at 25° to effect hydrolysis of the ester. The mixture was cooled to 0°, and the white solid, (*E*)-1-octenylboronic acid, was collected by filtration. It was washed several times with ice-cold water.

The (*E*)-1-octenylboronic acid was dissolved in 100 mL of ether in a 1-L flask and cooled to 0° in an ice bath. To the stirred solution was added 100 mL of 3 *M* sodium hydroxide, followed by 30.5 g (0.12 mol) of iodine in 300 mL of ether. The stirring was continued for 0.5 hour following completion of addition of the iodine. A few drops of a saturated solution of sodium thiosulfate in water were then added to destroy residual iodine, as indicated by disappearance of the color. The ether solution was separated from the aqueous phase and dried ($MgSO_4$). The ether was removed under reduced pressure and the product distilled to give 16.9 g (71%) of (*E*)-1-iodo-1-octene, bp 58° (0.2 mm).

5.1.1.19. 2-Bromo-4-methylpentane (Reaction of B-sec-Alkyl-9-BBN with Bromine. Preparation of Alkyl Halides via Direct Functionalization) (223)

A dry 500-mL flask equipped with septum inlet, gas outlet tube with stopcock, reflux condenser, and magnetic stirring bar was flushed with nitrogen and then maintained under a positive nitrogen pressure. The flask was charged with 190 mL of a 0.57 *M* solution of 9-borabicyclo[3.3.1]nonane in tetrahydrofuran. 4-Methyl-2-pentene (8.4 g, 12.5 mL, 100 mmol) was added and the solution was heated to reflux and maintained at reflux for 1 hour. The tetrahydrofuran was then removed under reduced pressure and replaced with 100 mL of methylene chloride. The solution was cooled to 0° and the outlet tube stopcock closed. The entire reaction flask was covered with aluminum foil, and 5.6 mL (110 mmol) of bromine was added through the septum inlet over a period of 1 minute using an all-glass syringe equipped with a Teflon needle. The reaction was then allowed to stir for 30 minutes at 0° followed by 1 hour at 25°. After removing the aluminum foil and venting the flask to a trap containing alkali, the *B*-bromoborabicyclo[3.3.1]nonane and any excess bromine were destroyed by the dropwise addition of 75 mL of a 3 *M* sodium hydroxide solution at 0°. After 15 minutes of stirring, the lower organic layer was removed, dried (K_2CO_3), and filtered through Celite. Following removal of the methylene chloride on a rotary evaporator, vacuum distillation gave 12.2 g (74%) of

2-bromo-4-methylpentane; bp 58–60° (54 mm); $n_{\mathrm{D}}^{21}1.4415$.

5.1.1.20. Cyclopentylmethyl Phenyl Sulfone (Alkylation of α -Bromosulfonyl Compounds with Trialkylboranes. Preparation of Sulfones via One-Carbon Homologation) (230)

A dry 50-mL flask equipped with a septum inlet, a magnetic stirring bar, and a nitrogen inlet was flushed with nitrogen and maintained under a constant pressure of nitrogen. The flask was charged with 4.25 mL of a 2.35 *M* solution of borane in tetrahydrofuran. The solution was cooled to 0° with stirring, and 2.04 g (30 mmol) of cyclopentene was added dropwise with a syringe over 3 minutes; then the clear solution was stirred at room temperature for 1 hour. The mixture was cooled to 0°, and a solution of 2.35 g (10 mmol) of bromo-methyl phenyl sulfone in 10 mL of tetrahydrofuran was added with a cannula. Potassium *t*-butoxide (9.1 mL of a 1.10 *M* solution in *t*-butyl alcohol) was added dropwise with a syringe over 20 minutes while the reaction was stirred at 0°.

After the reaction mixture had been stirred for an additional 30 minutes at 0°, 5 mL of a 3 *N* aqueous solution of sodium hydroxide was added, followed by the slow, dropwise addition of 5.0 mL of 30% hydrogen peroxide. The mixture was stirred for 2 hours at 55°, cooled to room temperature, and extracted with ether. The organic layer was washed with two 10-mL portions of water and one 10-mL portion of brine, dried ($MgSO_4$), and filtered. Concentration under reduced pressure yielded a residue that was recrystallized from an ether–pentane mixture to yield 1.85 g (82%) of cyclopentylmethyl phenyl sulfone, mp 37–38°.

6. Tabular Survey

An attempt has been made to include all carbon —carbon and carbon — heteroatom bond-forming reactions via organoboranes and organoborates, except for olefin- and acetylene-forming reactions and the alcohol synthesis by direct hydroxylation, reported in the literature through December 1979.

The reactions are listed in Tables I–XII. In general, a reaction is listed under the type of compound formed only if the functionality is not present in the starting organoborane. Exceptions are made where there is an intramolecular rearrangement. If more than one functional group is introduced, the reaction is listed in all pertinent tables. In each table, the reactions are listed in order of increasing number of carbon atoms in the principal product. A dash (—) in the borane, reaction conditions, or yield columns indicates that either nothing was reported, or in the borane column, the borane is listed in the reactant column. A borane is listed as a reactant if any group in it is incorporated into the product. For reactions carried out in tetrahydrofuran at room temperature; these conditions are given only under special circumstances.

Abbreviations used in the tables are as follows:

	9-Borabicyclo[3.3.1]nonyl
9-BBN	9-Borabicyclo[3.3.1]nonane
CATBH	Catecholborane
COD	Cyclooctadiene
DCHB	Dicyclohexylborane
DG	Bis(methoxyethyl) ether (diglyme)
DIPCB	Diisopinocamphenylborane
DIPEA	Diisopropylethylamine
DME	Dimethoxyethane
DMF	*N,N*,-Dimethylformamide
DMS	Dimethyl sulfide
DMSO	Dimethyl sulfoxide
e^-	Electrolysis
EDA	Ethylenediamine
EG	Ethylene glycol
Ether	Diethyl ether
HMPT	Hexamethylphosphortriamide
LDA	Lithium diisopropylamide

LTMP	Lithium tetramethylpiperidide
MCPBA	*m*-Chloroperbenzoic acid
Ms	Methanesulfonyl
NBS	*N*-Bromosuccinimide
NCS	*N*-Chlorosuccinimide
Sia_2BH	Bis(3-methyl-2-*n*-butyl)borane (disiamylborane)
Tf	Trifluoroacetyl
TFAA	Trifluoroacetic anhydride
$ThexylBH_2$	2,3-Dimethyl-2-*n*-butylborane (thexylborane)
THF	Tetrahydrofuran
THP	Tetrahydropyranyl
Ts	Toluenesulfonyl (tosyl)

Many of the reactions reported involve a sequence of steps in which the final step is use of a reagent to decompose an intermediate borate or boronate. To save space in the reactions conditions column, reagents most commonly used for this purpose are indicated by an abbreviation after a semicolon in the penultimate step:

EA	Ethanolamine
[O]	Oxidation with alkaline hydrogen peroxide
TEA	Triethanolamine

In the products column, yields are based on either GLC analysis or isolation techniques. The first entry in parentheses is the GLC yield and the second is the isolated yield.

Table IA. Alcohols A. One-Carbon Homologation

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Table IB. Alcohols B. Two-Carbon Homologation

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Table IC. Alcohols C. Three-Carbon Homologation

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Table ID. Alcohols D. Four-or-More-Carbon Homologation

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Table IE. Alcohols E. Miscellaneous Preparations

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Table IIA. Ethers A. Direct Functionalization

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Table IIB. Ethers B. One-Carbon Homologation

View PDF

Table IIC. Ethers C. Three-Carbon Homologation

View PDF

Table IID. Ethers D. Four-or-More-Carbon Homologation

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Table III. Organic Peroxides

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Table IVA. Ketones. A. One-Carbon Homologation

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Table IVB. Ketones. B. Two-Carbon Homologation

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Table IVC. Ketones. C. Three-Carbon Homologation

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Table IVD. Ketones. D. Four-or-More-Carbon Homologation

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Table IVE. Ketones. E. Miscellaneous Preparations

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Table VA. Aldehydes. A. One-Carbon Homologation

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Table VB. Aldehydes. B. Two-Carbon Homologation

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Table VC. Aldehydes. C. Three-Carbon Homologation

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Table VD. Aldehydes. D. Miscellaneous Preparations

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Table VIA. Carboxylic Acids and Derivatives A. One-Carbon Homologation

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Table VIB. Carboxylic Acids and Derivatives B. Two-Carbon Homologation

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Table VIC. Carboxylic Acids and Derivatives C. Three-Carbon Homologation

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Table VID. Carboxylic Acids and Derivatives D. Four-or-More-Carbon Homologation

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Table VIE. Carboxylic Acids and Derivatives E. Miscellaneous Preparations

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Table VIIA. Nitriles A. Two-Carbon Homologation

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Table VIIB. Nitriles B. Three-Carbon Homologation

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Table VIIC. Nitriles C. Four-or-More-Carbon Homologation

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Table VIIIA. Amines A. Direct Functionalization

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Table VIIIB. Amines B. One-Carbon Homologation

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Table VIIIC. Amines C. Two-Carbon Homologation

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Table VIIID. Amines D. Three-or-More-Carbon Homologation

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Table IX. Miscellaneous Nitrogen Compounds

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Table XA. Halides. A. Direct Functionalization

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Table XB. Halides. B. One-Carbon Homologation

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Table XC. Halides. C. Two-Carbon Homologation

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Table XD. Halides. D. Three-or-More-Carbon Homologation

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Table XE. Halides. E. Miscellaneous Preparations

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Table XIA. Sulfur Derivatives A. Direct Functionalization

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Table XIB. Sulfur Derivatives B. One-Carbon Homologation

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Table XIC. Sulfur Derivatives C. Two-or-More-Carbon Homologation

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Table XII. Alkanes, Cycloalkanes, and Arenes

View PDF

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION

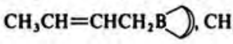
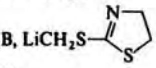
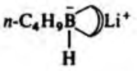
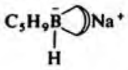
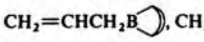
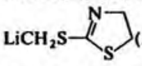
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
3	CH$_2$=CH$_2$	BH$_3$-THF	CO, MBH$_4$;^{b} KOH	n-C$_3$H$_7$OH (80, –)	115
	(C$_2$H$_5$)$_3\bar{\text{B}}$HLi$^+$	(C$_2$H$_5$)$_3$B	1. CO, –25° 2. NaOH, reflux; [O]	" (92, –)	253
	(C$_2$H$_5$)$_3\bar{\text{B}}$HNa$^+$	(C$_2$H$_5$)$_3$B	CO, NaOH, reflux; [O]	" (71, –)	253
	(C$_2$H$_5$)$_3\bar{\text{B}}$HK$^+$	(C$_2$H$_5$)$_3$B	"	" (80, –)	253
4	CH$_3$C≡CH, CH$_2$O	9-BBN	Heat; [O]	CH$_3$CH=CHCH$_2$OH (48, –)	77
	(C$_2$H$_5$)$_3$B, Cl$_2$CHOCH$_3$	—	CH$_3$Li (3 eq), ether; [O]	C$_2$H$_5$CHOHCH$_3$ (50, –)	120
5	CH$_2$=CHCH$_2$B(C$_2$H$_5$)$_2$, CH$_3$CHO	—	0°; TEA	CH$_2$=CHCHOHCH$_3$ (–, 88)	254
	, CH$_2$O	—	n-Pentane; EA	CH$_2$=CHCH(CH$_3$)CH$_2$OH (88, –)	114
	CH$_2$=CH$_2$	BH$_3$-THF	1. LiAlH(OCH$_3$)$_3$ 2. CO 3. CH$_3$CO$_2$H; [O]	(C$_2$H$_5$)$_2$CHOH (98, –)	116
	C$_2$H$_5$CH=CH$_2$	"	CO, MBH$_4$;^{b} KOH	n-C$_5$H$_{11}$OH (72, –)	115
	(C$_2$H$_5$)$_3$B	—	CO, 700 atm, 50°, H$_2$O; [O]	(C$_2$H$_5$)$_2$CHOH (–, 71)^c	119
	(n-C$_3$H$_7$)$_3$B, CH$_2$O	—	O$_2$, heat; [O]	n-C$_5$H$_{11}$OH (26, –)	76
	(s-C$_4$H$_9$)$_3$B, CH$_2$O	—	"	s-C$_4$H$_9$CH$_2$OH (45, –)	76
	(s-C$_4$H$_9$)$_3\bar{\text{B}}$HLi$^+$	(s-C$_4$H$_9$)$_3$B	1. CO, –25° 2. NaOH, reflux; [O]	" (94, –)	253
	(s-C$_4$H$_9$)$_3\bar{\text{B}}$HK$^+$	"	"	" (87, –)	253
	(i-C$_4$H$_9$)$_3$B, CH$_2$O	—	O$_2$, heat; [O]	i-C$_5$H$_{11}$OH (29, –)	76
	(n-C$_4$H$_9$)$_3$B, LiCH$_2$SCH$_3$	—	CH$_3$I, 0°; [O]	n-C$_5$H$_{11}$OH (97, –)	59
	(n-C$_4$H$_9$)$_3$B, 	—	"	" (89, –)	59
		(n-C$_4$H$_9$)$_3$B	1. CO, 0° 2. NaOH, C$_2$H$_5$OH, reflux; [O]	" (98, –)	253
6	CH$_2$=CHCH$_2$B(C$_2$H$_5$)$_2$, CF$_3$COCF$_3$	—	0°; TEA	CH$_2$=CHCH$_2$COH(CF$_3$)$_2$ (–, 78)	254
	(CH$_2$=CHCH$_2$)$_3$B, CF$_3$COCF$_3$	—	HC≡CC$_3$H$_7$-n; TEA	" (–, 83)	254
	(CH$_2$=CHCH$_2$)$_3$B, CH$_2$=CHCHO	—	Ether; EA	CH$_2$=CHCH$_2$CHOHCH=CH$_2$ (–, 75)	255
	Cyclopentene	BH$_3$-THF	CO, MBH$_4$;^{b} KOH	C$_5$H$_9$CH$_2$OH (69, –)	115
	(C$_5$H$_9$)$_3\bar{\text{B}}$HLi$^+$	(C$_5$H$_9$)$_3$B	CO, NaOH, reflux; [O]	C$_5$H$_9$CH$_2$OH (90, –)	253
		"	1. CO, –25° 2. NaOH, C$_2$H$_5$OH, reflux; [O]	" (86, –)	253
	n-C$_3$H$_7$C≡CH, CH$_2$O	9-BBN	Heat; [O]	n-C$_3$H$_7$CH=CHCH$_2$OH (–, 36)	77
	CH$_2$=CHCH$_2$B(C$_2$H$_5$)$_2$, CH$_3$COCH$_3$	—	0°; TEA	CH$_2$=CHCH$_2$COH(CH$_3$)$_2$ (–, 90)	254
	(CH$_2$=CHCH$_2$)$_3$B, C$_2$H$_5$CHO	—	HC≡CC$_3$H$_7$-n; TEA	CH$_2$=CHCH$_2$CHOHC$_2$H$_5$ (–, 90)	254
	(CH$_2$=CHCH$_2$)$_3$B, CH$_3$COCH$_3$	—	"	CH$_2$=CHCH$_2$COH(CH$_3$)$_2$ (–, 92)	254
	CH$_2$=C(CH$_3$)CH$_2$B(C$_3$H$_7$-n)$_2$, CH$_3$CHO	—	0°; TEA	CH$_2$=C(CH$_3$)CH$_2$CHOHCH$_3$ (–, 92)	254
	, CH$_3$COCH$_3$	—	n-Pentane; EA	CH$_2$=CHCH$_2$COH(CH$_3$)$_2$ (99, –)	114
	CH$_2$=CHCH$_2$B(C$_4$H$_9$-n)$_2$, C$_2$H$_5$CHO	—	0°; TEA	CH$_2$=CHCH$_2$CHOHC$_2$H$_5$ (–, 92)	244
	[CH$_2$=C(CH$_3$)CH$_2$]$_3$B, CH$_3$CHO	—	"	CH$_2$=C(CH$_3$)CH$_2$CHOHCH$_3$ (–, 93)	254
	CH$_3$CH=CHCH$_2$B(C$_4$H$_9$-n)$_2$, CH$_3$CHO	--	"	CH$_2$=CHCH(CH$_3$)CHOHCH$_3$ (–, 92)	254
	(C$_5$H$_9$)$_3$B, (3 eq)	—	CH$_3$I, 0°; [O]	C$_5$H$_9$CH$_2$OH (97, –)	59
	(i-C$_3$H$_7$)$_3$B, LiCH=CH$_2$, CH$_2$O	—	1. 0°, ether 2. 45°; [O]	i-C$_3$H$_7$CHOH(CH$_2$)$_2$OH (–, 74)	68
	(n-C$_3$H$_7$)$_3$B, Cl$_2$CHOCH$_3$	—	CH$_3$Li (10 eq), ether; [O]	n-C$_3$H$_7$CHOHC$_2$H$_5$ (45, –)	120
	(n-C$_4$H$_9$)$_3$B, LiCH=CH$_2$	—	–78°, HCl; [O]	n-C$_4$H$_9$CHOHCH$_3$ (91, –)	42
	(s-C$_4$H$_9$)$_3$B, LiCH=CH$_2$	—	"	s-C$_4$H$_9$CHOHCH$_3$ (87, –)	42
	(i-C$_4$H$_9$)$_3$B, LiCH=CH$_2$	—	"	i-C$_4$H$_9$CHOHCH$_3$ (87, –)	42
	(n-C$_5$H$_{11}$)$_2$BC(CH$_3$)$_2$C$_3$H$_7$-i, LiCH$_2$SCH$_3$ (2 eq)	—	CH$_3$I, 0°; [O]	n-C$_6$H$_{13}$OH (88, –)	59
7	, LiCH$_2$SCH$_3$ (3 eq)	—	"	C$_6$H$_5$CH$_2$OH (73, –)	59
	(C$_6$H$_5$)$_3$B, (CH$_3$)$_2\overset{+}{\text{S}}\overset{-}{\text{C}}H_2$	—	–10°; [O]	" (94, –)	118
	CH$_2$=C(CH$_3$)CH$_2$B(C$_3$H$_7$-n)$_2$, CF$_3$COCF$_3$	—	0°; TEA	CH$_2$=C(CH$_3$)CH$_2$COH(CF$_3$)$_2$ (–, 89)	254
	(CH$_3$CH=CHCH$_2$)$_3$B, CF$_3$COCF$_3$	—	0°; n-C$_9$H$_{19}$OH	CH$_2$=CHCH(CH$_3$)COH(CF$_3$)$_2$ (–, 87)	254
	[CH$_2$=C(CH$_3$)CH$_2$]$_3$B, CF$_3$COCF$_3$	—	HC≡CH, 140°; TEA	CH$_2$=C(CH$_3$)CH$_2$COH(CF$_3$)$_2$ (–, 69)	254

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

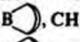
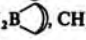
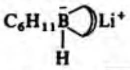
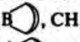
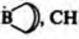
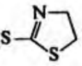
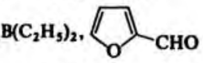
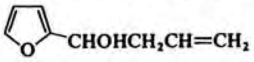
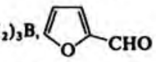
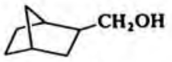
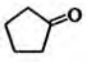
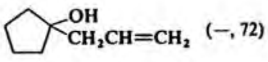
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$CH_3CH=CHCH_2B(C_4H_9\text{-}n)_2, CF_3COCF_3$	—	0°; $n\text{-}C_9H_{19}OH$	$CH_2=CHCH(CH_3)COH(CF_3)_2$ (−, 88)	254
	$CH_2=C=CHB(OC_4H_9\text{-}n)_2,$ $CH_3CH=CHCHO$	—	Ether; HCl	$HC\equiv CCH_2CHOHCH=CHCH_3$ (−, 30) "	256
	$CH_2=CHCH_2B(C_2H_5)_2, CH_3COCH=CHCl$	—	0°; [O]	$CH_2=CHCH_2COH(CH_3)CH=CHCl$ (−, 73)	254
	$CH_2=CHCH_2B(C_2H_5)_2, CH_3CH=CHCHO$	—	"	$CH_2=CHCH_2CHOHCH=CHCH_3$ (−, 82)	254
		—	0°; TEA	" (−, 89)	254
	$CH_2=CHCH_2B(C_2H_5)_2, CH_3COCH=CH_2$	—	"	$CH_2=CHCH_2COH(CH_3)CH=CH_2$ (−, 77)	254
	$(CH_2=CHCH_2)_3B,$ 	—	−70 to 20°; [O]	$(CH_2=CHCH_2)_2CHOH$ (−, −)	257
	$(CH_2=CHCH_2)_3B, CH_3CH=CHCHO$	—	Ether; EA	$CH_2=CHCH_2CHOHCH=CHCH_3$ (−, 74)	255
	$CH_2=CHCH_2B$, $CH_3CH=CHCHO$	—	*n*-Pentane; EA	" (91, −)	114
	$CH_2=CHCH_2B$, $CH_3COCH=CH_2$	—	"	$CH_2=CHCH_2COH(CH_3)CH=CH_2$ (94, −)	114
	$CH_2=C=CHB(OC_4H_9\text{-}n)_2, n\text{-}C_3H_7CHO$	—	Ether; HCl	$HC\equiv CCH_2CHOHC_3H_7\text{-}n$ (−, 60)	256
	Cyclohexene	BH_3–THF	CO, MBH_4;[b] KOH	$C_6H_{11}CH_2OH$ (80, −)	115
	$(C_6H_{11})_3\bar{B}HNa^+$	$(C_6H_{11})_3B$	CO, NaOH, reflux; [O]	" (88, −)	253
		"	CO, KOH, C_2H_5OH, reflux; [O]	" (79, −)	253
	$(n\text{-}C_3H_7)_3B,$ 	—	−70 to 20°; [O]	$n\text{-}C_3H_7CHOHCH_2CH=CH_2$ (−, 79)	257
	$CH_2=C(CH_3)CH_2B(C_3H_7\text{-}n)_2, CH_3COCH_3$	—	0°; TEA	$CH_2=C(CH_3)CH_2COH(CH_3)_2$ (−, 94)	254
	$CH_3CH=CHCH_2B$, CH_3COCH_3	—	*n*-Pentane; EA	$CH_2=CHCH(CH_3)COH(CH_3)_2$ (100, −)	114
	$CH_2=C(CH_3)CH_2B$, CH_3COCH_3	—	"	$CH_2=C(CH_3)CH_2COH(CH_3)_2$ (95, −)	114
	$[CH_2=C(CH_3)CH_2]_3B, CH_3COCH_3$	—	0°; TEA	" (−, 90)	254
		—	$HC\equiv CH$, 140°; TEA	" (−, 73)	254
	$CH_3CH=CHCH_2B(C_4H_9\text{-}n)_2, CH_3COCH_3$	—	0°; TEA	$CH_2=CHCH(CH_3)COH(CH_3)_2$ (−, 85)	254
	$(C_5H_9)_3B, LiCH=CH_2$	—	−78°, HCl; [O]	$C_5H_9CHOHCH_3$ (90, −)	42
	$(E)\text{-}n\text{-}C_4H_9CH=CHB[CH(CH_3)C_3H_7\text{-}i]_2,$ $LiCH_2SCH_3$ (3 eq)	—	CH_3I, 0°; [O]	$(E)\text{-}n\text{-}C_4H_9CH=CHCH_2OH$ (72, −)	59
	$(n\text{-}C_4H_9)_3B, LiCH=CH_2, CH_2O$	—	1. 45° 2. PCl_3, −15°; [O]	$n\text{-}C_4H_9CHOH(CH_2)_2Cl$ (−, 53)	68
	$CH_3CH=CH_2$	BH_3–THF	CO, Na, EG, DG (3 eq); [O]	$(n\text{-}C_3H_7)_2CHOH$ (−, 39)	258
	$CH_3CH=CH_2, Cl_2CHOCH_3$	"	CH_3Li (10 eq); [O]	" (40, −)	259
	$(C_2H_5)_3B$	—	CO, 650 atm, 150°, EG; [O]	$(C_2H_5)_3COH$ (−, 77)	260
		—	CO, 700 atm, 150°, H_2O; [O]	" (−, 90)	119
	$(n\text{-}C_3H_7)_3B, Cl_2CHOCH_3$	—	CH_3Li (10 eq), ether; [O]	$(n\text{-}C_3H_7)_2CHOH$ (40, −)	120
	$[n\text{-}C_3H_7CH(CH_3)CH_2]_3B, LiCH_2S$ (3 eq)	—	CH_3I, 0°; [O]	$n\text{-}C_4H_9CH(CH_3)CH_2OH$ (92, −)	59
	$(n\text{-}C_6H_{13})_3B, (CH_3)_2\overset{+}{S}\overset{-}{C}H_2$	—	−10°; [O]	$n\text{-}C_7H_{15}OH$ (91, −)	118
	$[i\text{-}C_3H_7(CH_2)_3]_3B, (CH_3)_2\overset{+}{S}\overset{-}{C}H_2$	—	"	$i\text{-}C_3H_7(CH_2)_4OH$ (96, −)	118
	$(n\text{-}C_6H_{13})_3B, (CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	—	0°; [O]	$n\text{-}C_7H_{15}OH$ (79, −)	117
	$[i\text{-}C_3H_7(CH_2)_3]_3B, (CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	—	"	$i\text{-}C_3H_7(CH_2)_4OH$ (79, −)	117
	$(i\text{-}C_3H_7)_3B, LiCH=CH_2, CH_3CHO$	—	0–45°; [O]	$i\text{-}C_3H_7CHOHCH_2CHOHCH_3$ (−, 52)	68
	$(n\text{-}C_4H_9)_3B, LiCH=CH_2, CH_2O$	—	"	$n\text{-}C_4H_9CHOH(CH_2)_2OH$ (−, 80)	68
8	$CH_2=CHCH_2B(C_2H_5)_2,$ 	—	0°; TEA	 (−, 92)	254
	$(CH_2=CHCH_2)_3B,$ 	—	$HC\equiv CC_3H_7\text{-}n$; TEA	" (−, 71)	254
	$p\text{-}CH_3OC_6H_4B$, $LiCH_2SCH_3$ (2 eq)	—	CH_3I, 0°; [O]	$p\text{-}CH_3OC_6H_4CH_2OH$ (84, −)	59
	$n\text{-}C_3H_7CH=C=CHB(OC_4H_9\text{-}n)_2, Cl_3CCHO$	—	Ether, HCl	$HC\equiv CCH(C_3H_7\text{-}n)CHOHCCl_3$ (−, 72)	261
		BH_3–THF	CO, MBH_4;[b] KOH	 (85, −)	115
	$CH_2=CHCH_2B(C_2H_5)_2,$ 	—	0°; TEA	 (−, 72)	254

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

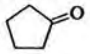
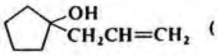
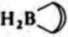
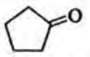
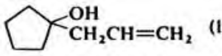
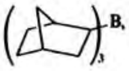
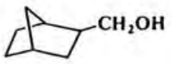
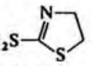
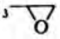
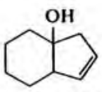
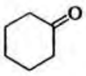
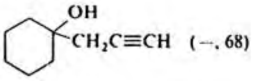
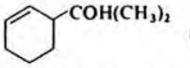
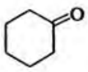
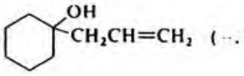
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(CH_2{=}CHCH_2)_3B$, CH_3CO_2H	—	0°, H_2O	$(CH_2{=}CHCH_2)_2COHCH_3$ (—, 80)	254
	", $CH_3CO_2C_2H_5$	—	0°; TEA	" (—, 70)	254
	", 	—	$HC{\equiv}CC_3H_7$-*n*; TEA	 (—, 77)	254
	$CH_2{=}CHCH_2B$(2 eq), CH_3COCl	—	*n*-Pentane; EA	$(CH_2{=}CHCH_2)_2COHCH_3$ (95, —)	114
	", $(CH_3CO)_2O$	—	"	" (95, —)	114
	", $CH_3CO_2C_2H_5$	—	—	" (90, —)	114
	", $CH_3CON(CH_3)_2$	—	"	" (50–57, —)	114
	", $CH_3COCH{=}CHCH_3$	—	"	$CH_2{=}CHCH_2COH(CH_3)CH{=}CHCH_3$ (96, —)	114
	", 	—	"	 (102, —)	114
	", CH_3CO_2B(2 eq)	—	"	$(CH_2{=}CHCH_2)_2COHCH_3$ (91, —)	114
	$CH_2{=}C{=}CHB(C_4H_9\text{-}n)_2$, *t*-$C_4H_9CHO$	—	Ether; HCl	$HC{\equiv}CCH_2CHOHC_4H_9$-*t* (—, 50)	262
	", $C_2H_5COC_2H_5$	—	"	$HC{\equiv}CCH_2COH(C_2H_5)_2$ (—, 60)	262
	$CH_2{=}CHCH_2B(C_4H_9\text{-}n)_2$ (2 eq), $CH_3CO_2C_4H_9$-*n*	—	0°; TEA	$(CH_2{=}CHCH_2)_2COHCH_3$ (—, 85)	254
	$(CH_3CH{=}CHCH_2)_3B$, $CH_2{=}C(CH_3)CHO$	—	1. −10° 2. 8-Quinolinol	$CH_2{=}CHCH(CH_3)CHOHC(CH_3){=}CH_2$ (—, 23)	187
	$(CH_3CH{=}CHCH_2)_3B$, 	—	−70 to 20°; [O]	(*E*)-$CH_3CH{=}CHCH_2CHOHCH_2CH{=}CH_2$ (—, 63) (*Z*) " (—, 27)	257
	$(CH_2{=}CHCH_2)_2BC_6H_{13}$-*n*, $CH_3CO_2C_2H_5$	—	0°; TEA	$(CH_2{=}CHCH_2)_2COHCH_3$ (—, 88)	254
	n-$C_3H_7CH{=}C{=}CHB(OC_4H_9\text{-}n)_2$, CH_3CHO	—	Ether; HCl	$HC{\equiv}CCH(C_3H_7\text{-}n)CHOHCH_3$ (—, 65)	261
	 B, $LiCH_2SCH_3$ (2 eq)		CH_3I, 0°; [O]	 (83, —)	59
	", $LiCH_2S$—	—	"	" (66, —)	59
	", $(CH_3)_2\overset{+}{S}\overset{-}{C}H_2$	—	−10°; [O]	" (76, —)	118
	", $(CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	—	0°; [O]	" (79, —)	117
	$Cl(CH_2)_3C{\equiv}CH$, C_2H_5CHO	9-BBN	Heat; [O]	$Cl(CH_2)_3CH{=}CHCHOHC_2H_5$ (*E*)-(47, —)	77
	$CH_2{=}C{=}C(CH_3)_2$, CH_3COCH_3	"	*n*-Pentane; EA	$CH_2{=}CHC(CH_3)_2COH(CH_3)_2$ (80, —)	114
	$CH_2{=}CHCH_2B$, *t*-C_4H_9CHO	—	"	$CH_2{=}CHCH_2CHOHC_4H_9$-*t* (97, —)	114
	i-$C_3H_7CH(CH_3)B(C_3H_7\text{-}i)_2$, $HC{\equiv}CCO_2C_2H_5$	—	NaOR;[d] [O]	*i*-$C_3H_7CH(CH_3)CHOHCH_2CO_2H$ (72, 68)	89
	$(CH_3)_2C{=}CHCH_2B$, CH_3COCH_3	—	*n*-Pentane; EA	$CH_2{=}CHC(CH_3)_2COH(CH_3)_2$ (93, —)	114
	$(C_6H_{11})_3B$, $LiCH{=}CH_2$	—	HCl, −78°; [O]	$C_6H_{11}CHOHCH_3$ (93, —)	42
	$(C_2H_5)_3B$, furan	—	1. *n*-C_4H_9Li, ether 2. CH_3CO_2H; [O]	$(C_2H_5)_2COHCH{=}CHCH_2OH$ (*E*)-(90, —)	23
	$(n\text{-}C_7H_{15})_3B$, $(CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	—	0°; [O]	*n*-$C_8H_{17}OH$ (79, —)	117
	$(i\text{-}C_3H_7)_3B$, $LiCH{=}CH_2$, CH_3—	—	0°, ether; [O]	*i*-$C_3H_7CHOH(CH_2)_2CHOHCH_3$ (, 100)	69
	$(n\text{-}C_4H_9)_3B$, $LiCH{=}CH_2$, 	—	0°, ether; [O]	*n*-$C_4H_9CHOH(CH_2)_2CH_2OH$ (, 100)	69
9	$CH_2{=}CHCH{=}CH(CH_2)_2CH{=}CH_2$	BH_3-DG	CO, 1000 psi, 150°, EG; [O]	 (33, —)	263
	$CH_2{=}C{=}CHB(OC_4H_9\text{-}n)_2$, 	—	Ether, HCl; K_2CO_3	 (—, 68)	262
	 CH_3COCH_3	9-BBN	*n*-Pentane; EA	 (68, —)	114
	t-$C_4H_9C{\equiv}CCH_3$, CH_3CHO	"	Heat; [O]	(*E*)-*t*-$C_4H_9CH{=}C(CH_3)CHOHCH_3$ (69, 56)	77
	$CH_2{=}CHCH_2B(C_2H_5)_2$, 	—	0°; TEA	 (—, 75)	254

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

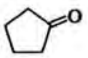
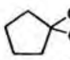
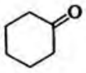
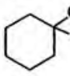
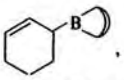
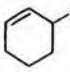
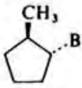
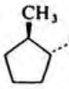
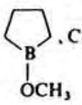
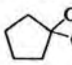
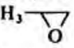
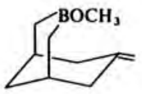
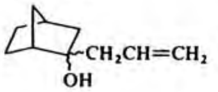
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(CH_2=CHCH_2)_3B$, "	—	$HC\equiv CC_3H_7$-*n*; TEA	" (—, 88)	254
	", $CH_3COCH=C(CH_3)_2$	—	Ether; EA	$CH_2=CHCH_2COH(CH_3)CH=C(CH_3)_2$ (—, 78)	264
	$CH_2=CHCH_2B(C_3H_7\text{-}n)_2$, $CH_3COCH=C(CH_3)_2$	—	0°; [O]	" (—, 73)	254
	$CH_2=C(CH_3)CH_2B(C_3H_7\text{-}n)_2$, 	—	0°; TEA	 OH $CH_2C(CH_3)=CH_2$ (—, 82)	254
	$CH_2=CHCH_2B$, 	—	*n*-Pentane; EA	 OH $CH_2CH=CH_2$ (100, —)	114
	", $CH_3COCH=CH_2$	—	"	$CH_2=CHCH_2COH(CH_3)CH=C(CH_3)_2$ (94, —)	114
	$(n\text{-}C_4H_9)_3B$, $CH_3COCH_2COCH_3$	—	*hν*, C_6H_6; [O]	*n*-$C_4H_9C(CH_3)=CHCOCH_3$ (—, 45), *n*-$C_4H_9COH(CH_3)CH_2COCH_3$ (—, 45)	265
	, CH_3COCH_3	—	*n*-Pentane; EA	 $COH(CH_3)_2$ (86, —)	114
	n-$C_3H_7CH=C=CHB(OC_4H_9\text{-}n)_2$, C_2H_5CHO	—	Ether; HCl	$HC\equiv CCH(C_3H_7\text{-}n)CHOHC_2H_5$ (—, 70)	261
	 $LiCH=CH_2$	—	HCl, −78°; [O]	 $CHOHCH_3$ (94, —)	124
	 $BHC(CH_3)_2C_3H_7$-*i*, $HC\equiv CCO_2C_2H_5$		NaOR;[e] [O]	 $CHOHCH_2CO_2H$ (81, 69)	89
	$C_6H_{11}BHC(CH_3)_2C_3H_7$-*i*, $HC\equiv CCO_2C_2H_5$	—	NaOR;[f] [O]	$C_6H_{11}CHOHCH_2CO_2H$ (74, 60)	
	, $CH_2=CHC_2H_5$	—	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 OH C_4H_9-*n* (91, 85)	266
	$CH_2=CHCH_2B$, *n*-$C_5H_{11}CHO$	—	*n*-Pentane; EA	$CH_2=CHCH_2CHOHC_5H_{11}$-*n* (92, —)	114
	", $CH_3COC_4H_9$-*t*	—	"	$CH_2=CHCH_2COH(CH_3)C_4H_9$-*t* (101, —)	114
	$(CH_3)_2C=CHCH_2B(C_3H_7\text{-}n)_2$, *n*-$C_3H_7CHO$	—	60°; TEA	$CH_2=CHC(CH_3)_2CHOHC_3H_7$-*n* (—, —)	254
	$(i\text{-}C_3H_7)_3B$, $LiCH=CH_2$, $CH_3CH=CHCHO$	—	0–45°; [O]	*i*-$C_3H_7CHOHCH_2CHOHCH=CHCH_3$ (—, 28)	68
	n-$C_3H_7CH(CH_3)CH_2BHC(CH_3)_2C_3H_7$-*i*, $HC\equiv CCO_2C_2H_5$	—	NaOR;[g] [O]	*n*-$C_3H_7CH(CH_3)CH_2CHOHCH_2CO_2H$ (46, —)	89
	$CH_3CH=CHCH_3$	BH_3–THF	1. $LiAlH(OCH_3)_3$, CO, 2. HCl; [O]	$(s\text{-}C_4H_9)_2CHOH$ (88, 82)	116
	$(CH_3)_2C=CH_2$	"	"	$(i\text{-}C_4H_9)_2CHOH$ (84, —)	116
	"	"	1. $LiAlH(OCH_3)_3$, CO, 0° 2. CH_3CO_2H; [O]	" (81, —)	116
	n-$C_6H_{13}CH=CH_2$	"	CO, MBH_4;[h] KOH	*n*-$C_9H_{19}OH$ (70, —)	115
	$(n\text{-}C_8H_{17})_3B$, CH_2O	—	O_2, heat; [O]	" (79, —)	76
	$[t\text{-}C_4H_9CH_2CH(CH_3)CH_2]_3B$, $(CH_3)_2\overset{+}{S}\overset{-}{C}H_2$	—	−10°; [O]	*t*-$C_4H_9CH_2CH(CH_3)(CH_2)_2OH$ (78, —)	118
	", $(CH_3)_2\overset{+}{S}O\overset{-}{C}H_2$	—	0°; [O]	" (76, —)	117
	$(C_5H_9)_3B$, $Br_2CHSi(CH_3)_3$	—	Li, 0°; [O]	$C_5H_9CHOHSi(CH_3)_3$ (63, —)	267,268
	$(i\text{-}C_3H_7)_3B$, $LiCH=CH_2$, *i*-C_3H_7CHO	—	0–45°; [O]	*i*-$C_3H_7CHOHCH_2CHOHC_3H_7$-*i* (—, 73)	68
	$(n\text{-}C_4H_9)_3B$, $LiCH=CH_2$, CH_3	—	Ether, 0°; [O]	*n*-$C_4H_9CHOH(CH_2)_2CHOHCH_3$ (—, 93)	69
	$(n\text{-}C_5H_{11})_3B$, $Br_2CHSi(CH_3)_3$	—	Li (2 eq), 0°; [O]	*n*-$C_5H_{11}CHOHSi(CH_3)_3$ (79, —)	267,268
10	$CH_2=C=CHB(OC_4H_9\text{-}n)_2$, C_6H_5CHO	—	Ether; HCl	$HC\equiv CCH_2CHOHC_6H_5$ (—, 72)	262
	$CH_2=CHCH_2B$, "	—	*n*-Pentane; EA	$CH_2=CHCH_2CHOHC_6H_5$ (96, —)	114
	$CH_2=CHCH_2B(C_4H_9\text{-}n)_2$, "	—	0°; TEA	" (—, 95)	254
	$(C_6H_5)_3B$, $CH_2=C(CH_3)CHO$	—	−10°, $(CH_3)_3NO$, CH_3OH	$C_6H_5CHOHC(CH_3)=CH_2$ (—, 80)	187
		—	1. $(C_2H_5)_4B_2H_4$, ether 2. CO, 50 atm, EG; [O]	 (—, —)	269
	$CH_2=CHCH_2B$, 	—	*n*-Pentane; EA	 *endo*-(96, —) *exo*-(4, —)	114

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

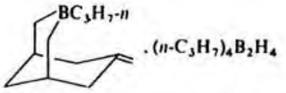
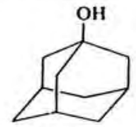
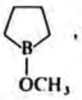
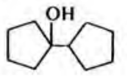
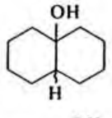
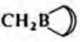
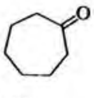
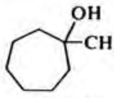
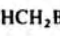
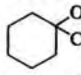
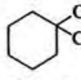
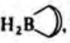
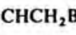
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	 . $(n\text{-}C_3H_7)_4B_2H_4$		CO, 500 atm, 100°, ether; [O]	 (—, —)	270
	 $BHC(CH_3)_2C_3H_7$-i, $HC{\equiv}CCO_2C_2H_5$		NaOR;[b] [O]	 $CHOHCH_2CO_2H$ (57, 51)	89
	 , cyclopentene		1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 (89, 81)	266
	$CH_2=CHCH_2CH=CH(CH_2)_2CH=CH_2$	BH_3-DG	CO, 1000 psi, 150°, EG; [O]	 *cis*-(58, –) *trans*-(15, —)	263
	$CH_2=CHCH_2B$, 	—	*n*-Pentane; EA	 $CH_2CH=CH_2$ (94, —)	114
	i-$C_3H_7C(CH_3)_2(C_5H_9)BH$, $HC{\equiv}CC(CH_3)=CH_2$	—	1. *hv* 2. CH_3CO_2H; [O]	$C_5H_9CHOHCH_2C(CH_3)=CH_2$ (—, 70)	271
	i-$C_3H_7C(CH_3)_2(C_5H_9)BH$, $CH_2=C(CH_3)C{\equiv}CI$	—	1. $KB(C_4H_9\text{-}s)_3H$ 2. CH_3CO_2H; [O]	" (—, 77)	271
	$CH_3CH=CHCH_2B$ (2 eq), CH_3COCl	—	*n*-Pentane; EA	$[CH_2=CHCH(CH_3)]_2COHCH_3$ (93, —)	114
	" (4 eq), $(CH_3CO)_2O$	—	"	" (97, —)	114
	$CH_3CH=CHCH_2B(C_4H_9\text{-}n)_2$, $CH_3COCH=C(CH_3)_2$	—	0°; TEA	$CH_2=CHCH(CH_3)COH(CH_3)CH=C(CH_3)_2$ (—, 81)	254
	n-$C_3H_7CH=C=CHB(OC_4H_9\text{-}n)_2$, *i*-$C_3H_7CHO$	—	Ether; HCl	$HC{\equiv}CCH(C_3H_7\text{-}n)CHOHC_3H_7$-*i* (—, 78)	261
	t-$C_4H_9C{\equiv}CH$, *n*-C_3H_7CHO	9-BBN	Heat; [O]	*t*-$C_4H_9CH=CHCHOHC_3H_7$-*n* (—, 55)	77
	$C_6H_{11}BOCH_3$, $CH_3CH=CHCH_3$	—	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 OH C_4H_9-*s* (90, 85)	266
	$C_6H_{11}BOCH_3$, LiC_4H_9-*t*		CO, 70 atm, 50°, H_2O, EG	 OH C_4H_9-*t* (87, 72)	272
	$CH_2=CHCH_2B$, *i*-$C_3H_7COC_3H_7$-*i*	—	*n*-Pentane, EA	$CH_2=CHCH_2COH(C_3H_7\text{-}i)_2$ (98, —)	114
	$(CH_3)_2C=CHCH_2B(C_3H_7\text{-}n)_2$, *i*-$C_4H_9CHO$	—	60°; TEA	$CH_2=CHC(CH_3)_2CHOHC_4H_9$-*i* (—, 65)	254
	$CH_3CH=CHCH_2B$, *n*-$C_5H_{11}CHO$	—	*n*-Pentane, EA	$CH_2=CHCH(CH_3)CHOHC_5H_{11}$-*n* (89, —)	114
	$(n\text{-}C_3H_7)_3B$, furan	— —	1. *n*-C_4H_9Li, ether 2. CH_3CO_2H; [O]	$(n\text{-}C_3H_7)_2COHCH=CHCH_2OH$ (*E*)-(98, —)	23
	$(n\text{-}C_4H_9)_3B$, $LiCH=CH_2$, $CH_3CH=CHCHO$	—	0-45°; [O]	*n*-$C_4H_9CHOHCH_2CHOHCH=CHCH_3$ (—, 48)	68
	$(n\text{-}C_4H_9)_3B$, $CH_3COCH_2CO_2C_2H_5$ (3 eq)	—	*hv*, C_6H_6; [O]	*n*-$C_4H_9COH(CH_3)CH_2CO_2C_2H_5$ (—, 60)	265
	$CH_3CH=CH_2$	BH_3-THF	CO, EG, DG (3 eq); [O]	$(n\text{-}C_3H_7)_3COH$ (—, 74)	258
	$C_2H_5CH=CH_2$, $HC{\equiv}CH$	"	1. *n*-C_4H_9Li 2. HCl, −78°-reflux 3. KOH; [O]	$(n\text{-}C_4H_9)_2COHCH_3$ (82, –)	124
	$CH_3CH=CHCH_3$, "	"	"	$(s\text{-}C_4H_9)_2COHCH_3$ (68, —)	124
	$(CH_3)_2C=CH_2$, "	"	"	$(i\text{-}C_4H_9)_2COHCH_3$ (72, —)	124
	$C_2H_5CH=CH_2$, $LiC{\equiv}CH$-EDA	BH_3-THF	"	$(n\text{-}C_4H_9)_2COHCH_3$ (80, —)	124
	$CH_3CH=CHCH_3$, "	"	"	$(s\text{-}C_4H_9)_2COHCH_3$ (55, —)	124
	$(CH_3)_2C=CH_2$, "	"	"	$(i\text{-}C_4H_9)_2COHCH_3$ (72, —)	124
	$(s\text{-}C_4H_9)_3B$, $CH_3OCH=CH_2$	—	1. *t*-C_4H_9Li, −70° 2. HCl; [O]	$(s\text{-}C_4H_9)_2COHCH_3$ (92, —)	22
	$(i\text{-}C_4H_9)_3B$, "	—	"	$(i\text{-}C_4H_9)_2COHCH_3$ (94, 77)	22
	$(n\text{-}C_5H_{11})_3B$, Cl_2CHOCH_3	—	CH_3Li (10 eq), ether; [O]	*n*-$C_5H_{11}CHOHC_4H_9$-*n* (54, —)	120
	$(C_6H_{11})_3B$, $Br_2CHSi(CH_3)_3$	—	Li (2 eq), 0°; [O]	$C_6H_{11}CHOHSi(CH_3)_3$ (43, —)	267,268
	$(n\text{-}C_4H_9)_3B$, $LiCH=CH_2$, *i*-C_3H_7CHO	—	1. 0°, ether 2. 45°; [O]	*n*-$C_4H_9CHOHCH_2CHOHC_3H_7$-*i* (—, 74)	68

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

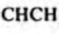
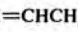
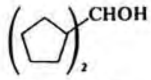
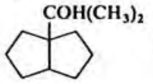
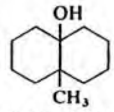
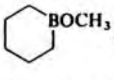
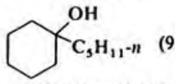
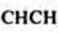
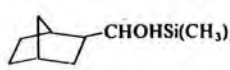
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_6H_{13})_3B$, $LiCH=CH_2$, 	–	Ether, 0°; [O]	$n\text{-}C_6H_{13}CHOH(CH_2)_3OH$ (–, 89)	128
	$(n\text{-}C_6H_{13})_3B$, $Br_2CHSi(CH_3)_3$		Li (2 eq), 0°; [O]	$n\text{-}C_6H_{13}CHOHSi(CH_3)_3$ (72, –)	267,268
	$(C_2H_5)_2BH$, $(S)\text{-}HC\equiv CCH(O_2CCH_3)C_5H_{11}\text{-}n$	–	NaOH, –20°; [O]	$C_2H_5CHOHCH=CHC_5H_{11}\text{-}n$ (*R,E*)-(38, –) (*S,E*)-(12, –)	273
11	$CH_2=C=CHB(OC_4H_9\text{-}n)_2$, $CH_3COC_6H_5$	–	Ether; HCl	$HC\equiv CCH_2COH(CH_3)C_6H_5$ (–, 44)	262
	$CH_2=C(CH_3)CH_2B(C_3H_7\text{-}n)_2$, C_6H_5CHO	–	0°; TEA	$CH_2=C(CH_3)CH_2CHOHC_6H_5$ (–, 89)	254
	$CH_2=CHCH_2B$, $CH_3COC_6H_5$	–	*n*-Pentane; EA	$CH_2=CHCH_2COH(CH_3)C_6H_5$ (101, –)	114
	$CH_3CH=CHCH_2B$, C_6H_5CHO	–	"	$CH_2=CHCH(CH_3)CHOHC_6H_5$ (87, –)	114
	$[CH_2=C(CH_3)CH_2]_3B$, "	–	0°; TEA	$CH_2=C(CH_3)CH_2CHOHC_6H_5$ (–, 78)	254
	$N_2CHCO_2C_2H_5$, "	9-BBN	–	$C_6H_5CHOHCH_2CO_2C_2H_5$ (–, 43)	135
	$(C_2H_5)_3B$, $LiCH=CH_2$, "	–	1. 0°, ether 2. 45°; [O]	$C_2H_5CHOHCH_2CHOHC_6H_5$ (–, 78)	68
	Cyclopentene, Cl_2CHOCH_3	BH_3-THF	CH_3Li; (10 eq); [O]	 (50, –)	259
	", $(C_6H_5S)_2CH_2$	"	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), –78 to 0°; [O]	" (–, 88)	121,122
	HB, $CH_2=CH_2$	–	CO, 150°, EG; [O]	$COHC_2H_5$ (–, 90)	274
	CH_3B, $LiCH_3$	–	"	 (–, 62)	275
	$CH_2=CHCH_2CH=C(CH_3)(CH_2)_2CH=CH_2$	BH_3-DG	CO, 1000 psi, 150°, EG; [O]	 (46, –)	274
	$(C_6H_{11})_2BH$, $HC\equiv CC(CH_3)=CH_2$	–	1. *hv* 2. CH_3CO_2H; [O]	$C_6H_{11}CHOHCH_2C(CH_3)=CH_2$ (–, 71)	276
	", $IC\equiv CC(CH_3)=CH_2$	–	1. $KB(C_4H_9\text{-}s)_3H$ 2. CH_3CO_2H; [O]	" (77, –)	271
	$(C_5H_9)_3B$, Cl_2CHOCH_3	–	CH_3Li, (10 eq), ether; [O]	$(C_5H_9)_2CHOH$ (50, –)	120
	$(C_5H_9)_2BC(CH_3)_2C_3H_7\text{-}i$, $(C_6H_5S)_2CH_2$	–	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), –78 to 0°; [O]	" (–, 80)	122
	$(C_6H_{11})_2BH$, $HC\equiv CC(CH_3)=CH_2$	–	*hv*; [O]	$C_6H_{11}CHOHCH=C(CH_3)CH_2OH$ (–, 58)	276
	, $CH_2=CHC_3H_7\text{-}n$	–	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 (95, 88)	266
	$(CH_3)_2C=CHCH=C(CH_3)_2$, CH_3COCH_3	9-BBN	*n*-Pentane; EA	$i\text{-}C_3H_7CH=CHC(CH_3)_2COH(CH_3)_2$ (80, –)	114
	$n\text{-}C_6H_{13}C\equiv CH$, CH_3COCH_3	Sia_2BH	1. LTMP 2. $C_2H_5CO_2H$, heat	$n\text{-}C_5H_{11}CH(CH=CH_2)COH(CH_3)_2$ (72, –)	277
	$CH_2=CHCH_2B$, $t\text{-}C_4H_9COC_3H_7\text{-}n$	–	*n*-Pentane; EA	$CH_2=CHCH_2COH(C_4H_9\text{-}t)C_3H_7\text{-}n$ (97, –)	114
	$CH_2=CHCH_2B$, $t\text{-}C_4H_9COC_3H_7\text{-}i$	–	*n*-Pentane; EA	$CH_2=CHCH_2COH(C_4H_9\text{-}t)C_3H_7\text{-}i$ (74, –)	114
	$n\text{-}C_3H_7CH(CH_3)CH_2BH[C(CH_3)_2C_3H_7\text{-}i]$, $HC\equiv CC(CH_3)=CH_2$	–	1. *hv* 2. CH_3CO_2H; [O]	$n\text{-}C_3H_7CH(CH_3)CH_2CHOHCH_2C(CH_3)=CH_2$ (–, 68)	271
	$(CH_3)_2C=CHCH(C_3H_7\text{-}i)B$, CH_3COCH_3	–	*n*-Pentane; EA	$i\text{-}C_3H_7CH=CHC(CH_3)_2COH(CH_3)_2$ (85, –)	114
	, $Br_2CHSi(CH_3)_3$	–	Li (2 eq), 0°; [O]	 (46, –)	267,268
	$n\text{-}C_3H_7COCH_3$, $n\text{-}C_5H_{11}CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, –78°, ether 2. CH_3OH, H_2O_2	$n\text{-}C_3H_7COCH_2CHOHC_5H_{11}\text{-}n$ (–, 65)	74
	", "	TfOB	"	$n\text{-}C_3H_7(COCH_3)CHOHC_5H_{11}\text{-}n$ (–, 67)	278

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

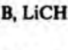
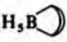
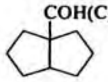
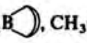
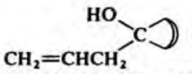
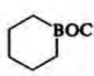
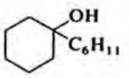
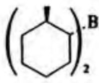
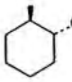
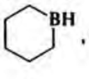
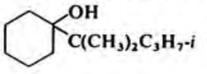
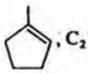
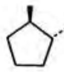
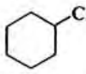
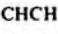
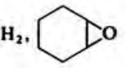
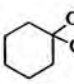
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_6H_{13})_3B$, $LiCH{=}CH_2$,  CH_3	—	Ether, 0–45°; [O]	$n\text{-}C_6H_{13}CHOH(CH_2)_2CHOHCH_3$ (—, 85)	69
	$C_2H_5CH{=}CH_2$, $CH_3OCH{=}CH_2$, CH_3I	BH_3-DMS	$t\text{-}C_4H_9Li$, −78°; [O]	$(n\text{-}C_4H_9)_2COHC_2H_5$ (70, —)	125
	$C_2H_5CH{=}CH_2$, $CH_3OCH{=}CH_2$, CH_3OSO_2F	"	"	" (81, —)	125
	$CH_3CH{=}CHCH_3$, $CH_3OCH{=}CH_2$, CH_3I	"	"	$(s\text{-}C_4H_9)_2COHC_2H_5$ (84, —)	125
	$CH_3CH{=}CHCH_3$, $CH_3OCH{=}CH_2$, CH_3OSO_2F	"	"	" (97, —)	125
	$(CH_3)_2C{=}CHCH_3$, $HC\equiv CC_4H_9\text{-}n$	BH_3-THF	1. CH_3Li, −70° 2. HCl, ether; [O]	$i\text{-}C_3H_7CH(CH_3)CHOHC_5H_{11}\text{-}n$ (—, 76)	43
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH{=}CH_2$, CH_3I	—	$t\text{-}C_4H_9Li$, −78°; [O]	$(i\text{-}C_4H_9)_2COHC_2H_5$ (89, —)	125
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH{=}CH_2$, CH_3OSO_2F	—	"	" (98, —)	125
12	$(CH_2{=}CHCH_2)_3B$, $C_6H_5CH{=}CHCHO$	—	Ether; EA	$CH_2{=}CHCH_2CHOHCH{=}CHC_6H_5$ (—, 78)	255
	$C_6H_5C\equiv CCH_2B(OC_4H_9\text{-}n)_2$, C_2H_5CHO	—	Ether, HCl	$CH_2{=}C{=}C(C_6H_5)CHOHC_2H_5$ (—, 52)	256
	C_2H_5B, CH_3Li	—	1. CH_3COCl (2 eq), 0° 2. $LiOC(C_2H_5)_3$, Cl_2CHOCH_3; [O]	 (—, —)	293
	$CH_3CH{=}CHCH_2B$, $CH_3COC_6H_5$	—	*n*-Pentane; EA	$CH_2{=}CHCH(CH_3)COH(CH_3)C_6H_5$ (97, —)	114
	$(i\text{-}C_3H_7)_3B$, $LiCH{=}CH_2$, C_6H_5CHO	—	Ether, 0–45°; [O]	$i\text{-}C_3H_7CHOHCH_2CHOHC_6H_5$ (—, 65)	68
	$CH_2{=}CHCH_2B$, OC	—	*n*-Pentane; EA	 (85, —)	114
	Cyclopentene, $HC\equiv CH$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$(C_5H_9)_2COHCH_3$ (72, —)	124
	", $LiC\equiv CH$-EDA	"	"	" (72, —)	124
	 $BOCH_3$, cyclohexene	—	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 (98, 90)	266
	 BC_6H_{11}, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$; [O]	" (71, —)	37
	 BH, $HC\equiv CC(CH_3){=}CH_2$	—	1. *hν* 2. CH_3CO_2H; [O]	 $CHOHCH_2C(CH_3){=}CH_2$ (—, 66)	271
	", $IC\equiv CC(CH_3){=}CH_2$	—	1. $LiB(C_2H_5)_3H$ 2. CH_3CO_2H; [O]	" (—, 64)	271
	$(C_5H_9)_3B$, $CH_3OCH{=}CH_2$	—	1. $t\text{-}C_4H_9Li$, −70° 2. HCl; [O]	$(C_5H_9)_2COHCH_3$ (87, —)	22
	$(C_6H_{11})_3B$, $CH_3COCH_2CO_2C_2H_5$	—	*hν*, C_6H_6; [O]	$C_6H_{11}COH(CH_3)CH_2CO_2C_2H_5$ (—, 33)	265
	, $(CH_3)_2C{=}C(CH_3)_2$	—	CO, 70 atm, 50°, H_2O, EG	 (68, 61)	272
	, $C_2H_5C\equiv CC_2H_5$	BH_3-THF	1. CH_3Li, −70° 2. HCl, ether; [O]	 $COH(C_2H_5)C_3H_7\text{-}n$ (—, 72)	43
	Cyclohexene, $HC\equiv CC_4H_9\text{-}n$	"	"	 $CHOHC_5H_{11}\text{-}n$ (—, 69)	43
	$CH_2{=}CHCH_2B$, $t\text{-}C_4H_9COC_4H_9\text{-}t$	—	*n*-Pentane; EA	$CH_2{=}CHCH_2COH(C_4H_9\text{-}t)_2$ (<25, —)	114
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH{=}CH_2$, $BrCH_2CH{=}CH_2$	—	$t\text{-}C_4H_9Li$, −78°; [O]	$(i\text{-}C_4H_9)_2COHCH_2CH{=}CH_2$ (74, —)	125
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH{=}CH_2$, $ClCH_2CH{=}CH_2$	—	"	" (77, 52)	125
	$i\text{-}C_4H_9COCH_3$, $n\text{-}C_5H_{11}CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, −78°, ether 2. CH_3OH, H_2O_2	$i\text{-}C_4H_9COCH_2CHOHC_5H_{11}\text{-}n$ (—, 70)	74
	"	TfOB	"	$i\text{-}C_4H_9(COCH_3)CHOHC_5H_{11}\text{-}n$ (—, 57)	278
	$(n\text{-}C_4H_9)_3B$, $LiCH{=}CH_2$, 	—	Ether, 0°; [O]	 $CH_2CHOHC_4H_9\text{-}n$ (—, 77)	69
	$(n\text{-}C_8H_{17})_3B$. $Br_2CHSi(CH_3)_3$	—	Li (2 eq), 0°; [O]	$n\text{-}C_8H_{17}CHOHSi(CH_3)_3$ (69, —)	267,268

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

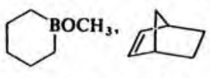
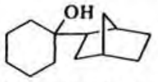
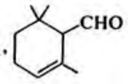
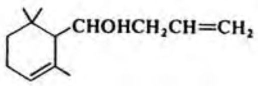
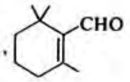
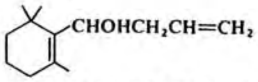
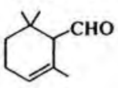
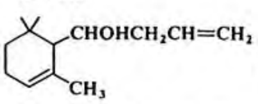
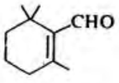
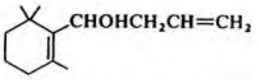
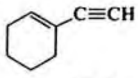
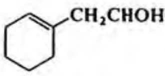
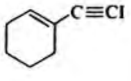
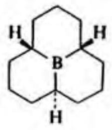
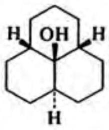
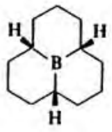
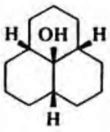
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
13	$CH_2=CHCH_2B(C_2H_5)_2$, $CH_3COCH=CHC_6H_5$	—	0°; [O]	$CH_2=CHCH_2COH(CH_3)CH=CHC_6H_5$ (−, 92)	254
	"	—	0°; TEA	" (−, 97)	254
	$C_6H_5C(CH_3)=CH_2$, $CH_2=CHCHO$	Sia_2BH	NaOH, H_2O_2	$C_6H_5C(CH_3)(CH=CH_2)CHOHCH=CH_2$ (−, 60)	279
	$CH_2=CHCH_2B$(2 eq), C_6H_5COCl	—	*n*-Pentane; EA	$(CH_2=CHCH_2)_2COHC_6H_5$ (89, −)	114
	$CH_2=CHCH_2B$(2 eq), $C_6H_5CO_2C_2H_5$	—	"	" (82,)	114
	$CH_2=CHCH_2B$(2 eq), $C_6H_5COC(CH_3)_2$	—	"	" (91, −)	114
	$CH_2=CHCH_2B$(4 eq), $(C_6H_5CO)_2O$	—	"	" (82, −)	114
	$(CH_2=CHCH_2)_3B$, $CH_3COCH=CHC_6H_5$	—	Ether; EA	$CH_2=CHCH_2COH(CH_3)CH=CHC_6H_5$ (, 78)	265
	n-$C_3H_7CH=C=CHB(OC_4H_9$-*n*$)_2$, C_6H_5CHO	—	1. Ether 2. HCl	$HC\equiv CCH(C_3H_7$-*n*$)CHOHC_6H_5$ (−, 79)	261
	$C_6H_5C\equiv CCH(CH_3)B(OC_4H_9$-*n*$)_2$, C_2H_5CHO	—	"	$CH_3CH=C=C(C_6H_5)CHOHC_2H_5$ (−, 50)	256
	n-$C_4H_9C\equiv CH$, C_6H_5CHO	9-BBN	Heat; [O]	*n*-$C_4H_9CH=CHCHOHC_6H_5$ (86, −)	77
	$C_6H_5C(CH_3)=C=CH_2$, CH_3COCH_3	Sia_2BH	NaOH, H_2O_2	$C_6H_5C(CH_3)(CH=CH_2)COH(CH_3)_2$ (−, 60)	279
	$C_6H_5(CH_2)_2COCH_3$, CH_3COCH_3	TfOB	1. 2,6-Lutidine, −78°, ether 2. CH_3OH, H_2O_2	$C_6H_5CH_2CH(COCH_3)COH(CH_3)_2$ (−, 63)	278
	$(n$-$C_4H_9)_3B$, $LiCH=CH_2$, C_6H_5CHO	—	Ether, 0 45°; [O]	*n*-$C_4H_9CHOHCH_2CHOHC_6H_5$ (−, 72)	68
		—	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	 (93, 82)	266
	$CH_2=CHCH_2B(C_2H_5)_2$, $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCHO$	—	0°; [O]	$CH_2=CHCH_2CHOHCH=C(CH_3)(CH_2)_2CH=C(CH_3)_2$ (−, 73)	254
	$CH_2=CHCH_2B(C_2H_5)_2$, 	—	0°; [O]	 (−, 84)	254
	$CH_2=CHCH_2B(C_2H_5)_2$, 	—	0°; [O]	 (−, 80)	254
	$(CH_2=CHCH_2)_3B$, $(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCHO$	—	Ether, EA	$CH_2=CHCH_2CHOHCH=C(CH_3)(CH_2)_2CH=C(CH_3)_2$ (−, 66)	255
	$(CH_2=CHCH_2)_3B$, 	—	Ether, EA	 (−, 28)	255
	$(CH_2=CHCH_2)_3B$, 	—	Ether; EA	 (−, 73)	255
	$C_5H_9BH[C(CH_3)_2C_3H_7$-*i*$]$, 	—	1. *hv* 2. CH_3CO_2H; [O]	 (−, <10)	271
	$C_5H_9BH[C(CH_3)_2C_3H_7$-*i*$]$, 	—	1. $KB(C_4H_9$-*s*$)_3H$ 2. CH_3CO_2H; [O]	" (−, 73)	271
		—	CO, 150°, EG; [O]	 (−, 70)	249
		—	"	 (−, −)	126

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

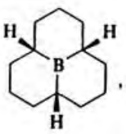
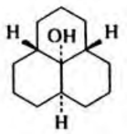
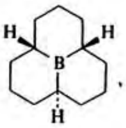
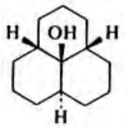
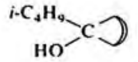
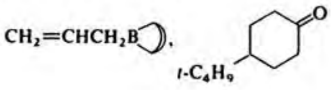
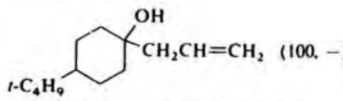
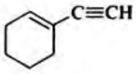
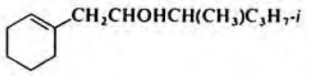
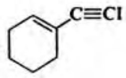
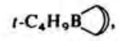
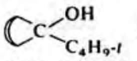
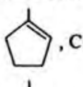
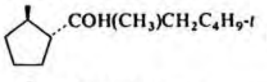
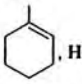
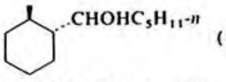
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	 , KCN	—	TFAA; [O]	 (−, 41)	127
	 , "	—	"	 (, 75)	127
	Cyclopentene, $CH_3OCH=CH_2$, CH_3I	BH_3-DMS	t-C_4H_9Li, −78°; [O]	$(C_5H_9)_2COHC_2H_5$ (86,)	125
	", ", CH_3OSO_2F	"	"	" (80, −)	125
	Cyclohexene	BH_3-THF	1. $LiAl(OCH_3)_3H$ 2. CO, 0° 3. CH_3CO_2H or HCl; [O]	$(C_6H_{11})_2CHOH$ (85,) or (86, 80)	116
	", $(C_6H_5S)_2CH_2$	"	1. n-C_4H_9Li 2. $HgCl_2$ (3 eq), −78 to 0°; [O]	" (−, 88)	121,122
	 , $CH_2=C(CH_3)_2$		CO, 150°, EG; [O]	 (−, 86)	274
		—	n-Pentane; EA	 (100, −)	114
	$[i$-$C_3H_7CH(CH_3)]_2BH$, 	—	1. $h\nu$ 2. CH_3CO_2H; [O]	 (−, 62)	271
	", 		1. $KB(C_4H_9$-$s)_3H$ 2. CH_3CO_2H; [O]	" (−, 74)	271
	 , Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$, 15°; [O]	 (83, −)	39
	$(C_6H_{11})_3B$	—	CO, Na, EG, DG; [O]	$(C_6H_{11})_2CHOH$ (−, −)	280
	 , $CH_3C\equiv CC_4H_9$-t	BH_3-THF	1. CH_3Li, −70° 2. HCl, ether; [O]	 (−, 79)	43
	 , $HC\equiv CC_4H_9$-n	"	"	 (−, 71)	43
	$C_2H_5CH=CH_2$	BH_3-DG	CO; [O]	$(n$-$C_4H_9)_3COH$ (−, 90)	281
	$CH_3CH=CHCH_3$	BH_3-DG	CO; [O]	$(s$-$C_4H_9)_3COH$ (−, 87)	281
	$(CH_3)_2C=CH_2$	BH_3-DG	CO; [O]	$(i$-$C_4H_9)_3COH$ (−, 90)	281
	$C_2H_5CH=CH_2$, KCN	BH_3-THF	TFAA (3 eq), 0-20°; [O]	$(n$-$C_4H_9)_3COH$ (89, −)	282
	", NaCN	"	TFAA, −78 to 45°; [O]	" (−, 73)	283
	n-$C_4H_9CH=CH_2$, $(C_6H_5S)_2CH_2$	"	1. n-C_4H_9Li 2. $HgCl_2$ (3 eq), −78-0°; [O]	n-$C_6H_{13}CHOH$ (−, 85)	121,122
	t-$C_4H_9BH_2$, $CH_3CH=CHCH_3$,	—	CO, 70 atm, 50°, H_2O, EG	t-$C_4H_9COH(C_4H_9$-$s)C_4H_9$-n (49, 43)	272
	$(n$-$C_4H_9)_2BOCH_3$, LiC_4H_9-t	—	"	$(n$-$C_4H_9)_2COHC_4H_9$-t (85, 81)	272
	$(n$-$C_4H_9)_3B$	—	CO, 700 atm, 150°, H_2O; [O]	$(n$-$C_4H_9)_3COH$ (−, 96)	119
	$(n$-$C_4H_9)_2BC_4H_9$-t	—	CO; [O]	$(n$-$C_4H_9)_2COHC_4H_9$-t (−, −)	284
	$(n$-$C_4H_9)_3B$, $HCClF_2$	—	$LiOC(C_2H_5)_3$ (2 eq), 65°, NaO_2CCH_3; [O]	$(n$-$C_4H_9)_3COH$ (98, −)	35
	", $HCCl_2F$	—	"	" (79, −)	35
	", $HCCl_3$	—	"	" (85, −)	35
	$(s$-$C_4H_9)_3B$, $HCClF_2$	—	"	$(s$-$C_4H_9)_3COH$ (21, −)	36
	", "	—	1. $LiOC(C_2H_5)_3$ (2 eq) 2. CH_3SO_3H; [O]	" (90, −)	36
	", $HCCl_2F$	—	1. $LiOC(C_2H_5)_3$, (2 eq) 2. NaO_2CCH_3; [O]	" (25, −)	36

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

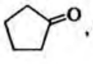
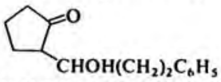
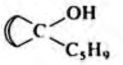
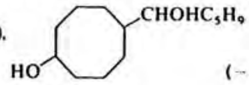
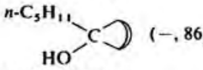
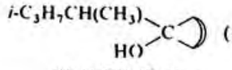
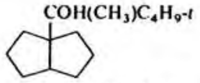
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(s\text{-}C_4H_9)_3B$, $HCCl_2F$	—	1. $LiOC(C_2H_5)_3$, (2 eq) 2. CH_3SO_3H; [O]	" (75, —)	36
	", $HCCl_3$	—	1. $LiOC(C_2H_5)_3$, (2 eq), 65° 2. NaO_2CCH_3; [O]	" (33, —)	36
	", "	—	1. $LiOC(C_2H_5)_3$ (2 eq) 2. CH_3SO_3H; [O]	" (27, —)	36
	$(i\text{-}C_4H_9)_3B$, $HCClF_2$	—	"	$(i\text{-}C_4H_9)_3COH$ (93, —)	36
	$(n\text{-}C_4H_9)_3B$, Cl_2CHOCH_3 (1.3 eq)	—	$LiOC(C_2H_5)_3$, (10 eq); [O]	$(n\text{-}C_4H_9)_3COH$ (94, —)	35,37
	$(s\text{-}C_4H_9)_3B$, "	—	"	$(s\text{-}C_4H_9)_3COH$ (95, 85)	37
	$(i\text{-}C_4H_9)_3B$, "	—	"	$(i\text{-}C_4H_9)_3COH$ (99, —)	37
	", $CH_3OCH{=}CH_2$, $i\text{-}C_3H_7CH_2I$	—	$t\text{-}C_4H_9Li$, −78°; [O]	" (24, —)	125
	$(n\text{-}C_4H_9)_3B$, $C_6H_5Si(CH_3)_2CH_2Cl$	—	LTMP, 0–20°; [O]	$C_6H_5Si(CH_3)_2CHOHC_4H_9\text{-}n$ (—, 60)	268
14	, $C_6H_5(CH_2)_2CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, ether, −78° 2. CH_3OH, H_2O_2	 (—, 80)	74
	$CH_3CH{=}CHCH_2B(C_4H_9\text{-}n)_2$, $C_6H_5CH{=}CHCOCH_3$	—	0^c; [O]	$C_6H_5CH{=}CHCOH(CH_3)CH(CH_3)CH{=}CH_2$ (—, 77)	254
	$C_6H_5C(CH_3){=}C{=}CH_2$, $n\text{-}C_3H_7CHO$	Sia_2BH	[O]	$C_6H_5C(CH_3)(CH{=}CH_2)CHOHC_3H_7\text{-}n$ (—, 60)	279
	$CH_2{=}CHCH_2B$, $C_6H_5COC_4H_9\text{-}t$	—	*n*-Pentane; EA	$C_6H_5COH(C_4H_9\text{-}t)(CH_2)_2CH{=}CH_2$ (82, —)	114
	HB, cyclopentene	—	CO, 150°, EG; [O]	 (—, 46),  (—, 46)	274
	Cyclopentene, $(C_6H_5S)_2CHC_3H_7\text{-}n$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), −78–0°; [O]	$(C_5H_9)_2COHC_3H_7\text{-}n$ (—, 85)	121,285
	Cyclohexene, $HC{\equiv}CH$	"	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$(C_6H_{11})_2COHCH_3$ (72, —)	124
	", $LiC{\equiv}CH\cdot EDA$	"	"	" (86, —)	124
	HB, $CH_2{=}CHC_3H_7\text{-}n$	—	CO, 150°, EG; [O]	 (—, 86)	274
	", $CH_3CH{=}C(CH_3)_2$	—	"	 (—, 31)	274
	CH_3B, $LiC_4H_9\text{-}t$	—	—	 (—, 41)	275
	$(C_5H_9)_2BCl$, $LiC_3H_7\text{-}i$, $t\text{-}C_4H_9NC$	—	1. $HSCH_2CO_2H$, −78 to 20° 2. NaOH, reflux, DG; [O]	$(C_5H_9)_2COHC_3H_7\text{-}i$ (77, —)	21
	$(C_6H_{11})_2BCH_3$	—	CO; [O]	$(C_6H_{11})_2COHCH_3$ (—, —)	284
	$(C_6H_{11})_3B$, $CH_3OCH{=}CH_2$	—	1. $t\text{-}C_4H_9Li$, −70° 2. HCl; [O]	" (94, —)	22
	$(E)\text{-}(C_6H_{11})_2(C_6H_{11}CH{=}CH)\bar{B}(C_4H_9\text{-}n)Li^+$	—	HCl	$C_6H_{11}CH_2CHOHC_6H_{11}$ (44, —)	45
	$(n\text{-}C_4H_9)_2BCl$, $Li(CH_2)_3CH{=}CH_2$, $t\text{-}C_4H_9NC$	—	1. $HSCH_2CO_2H$, −78 to 20° 2. NaOH, reflux, DG; [O]	$(n\text{-}C_4H_9)_2COH(CH_2)_3CH{=}CH_2$ (—, 46)	21
	$(n\text{-}C_5H_{11})_3B$, furan	—	1. $n\text{-}C_4H_9Li$, ether 2. CH_3CO_2H; [O]	$(n\text{-}C_5H_{11})_2COHCH{=}CHCH_2OH$ (*E*)-(100, —)	23
	$C_2H_5CH{=}CH_2$, $HC{\equiv}CC_4H_9\text{-}n$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$(n\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (86, —)	124
	", $HC{\equiv}CC_4H_9\text{-}t$	"	"	$(n\text{-}C_4H_9)_2COHCH_2C_4H_9\text{-}t$ (86, —)	124
	$CH_3CH{=}CHCH_3$, $HC{\equiv}CC_4H_9\text{-}n$	"	"	$(s\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (86, —)	124
	", $HC{\equiv}CC_4H_9\text{-}t$	"	"	$(s\text{-}C_4H_9)_2COHCH_2C_4H_9\text{-}t$ (30, —)	124
	$(CH_3)_2C{=}CH_2$, $HC{\equiv}CC_4H_9\text{-}n$	"	"	$(i\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (81, —)	124
	", $HC{\equiv}CC_4H_9\text{-}t$	"	"	$(i\text{-}C_4H_9)_2COHCH_2C_4H_9\text{-}t$ (75, —)	124
	$[i\text{-}C_3H_7CH(CH_3)]_2BC_3H_7\text{-}i$		CO; [O]	$[i\text{-}C_3H_7CH(CH_3)]_2COHC_3H_7\text{-}i$ (—, —)	284

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

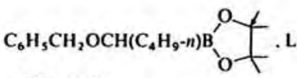
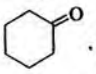
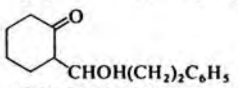
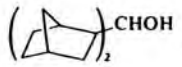
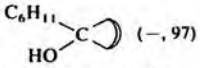
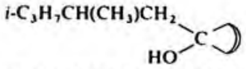
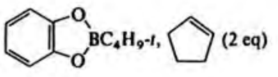
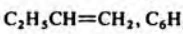
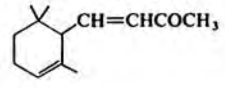
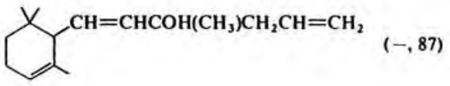
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_4H_9)_2BOCH_3$, $CH_2{=}CHC_3H_7\text{-}n$	–	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	$(n\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (75, 62)	266
	$(s\text{-}C_4H_9)_2BOCH_3$, $CH_2{=}CHC_3H_7\text{-}n$	–	"	$(s\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (88, 76)	266
	$(i\text{-}C_4H_9)_2BOCH_3$, "	–	"	$(i\text{-}C_4H_9)_2COHC_5H_{11}\text{-}n$ (84, 70)	266
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH{=}CH_2$, $n\text{-}C_4H_9Br$ or $n\text{-}C_4H_9I$	–	$t\text{-}C_4H_9Li$, −78°; [O]	" (63, –) or (88, –)	125
	$(n\text{-}C_6H_{13})_2BCl$, $LiCH_3$, $t\text{-}C_4H_9NC$	–	1. $HSCH_2CO_2H$, −78 to 20° 2. NaOH, reflux, DG; [O]	$(n\text{-}C_6H_{13})_2COHCH_3$ (–, 45)	21
	$(n\text{-}C_4H_9)_2BCH(CH_3)C_3H_7\text{-}i$, Cl_2CHOCH_3	–	$LiOC(C_2H_5)_3$, 15°; [O]	$(n\text{-}C_4H_9)_2COHCH(CH_3)C_3H_7\text{-}i$ (84, –)	39
	$(n\text{-}C_6H_{13})_3B$, $CH_3OCH{=}CH_2$	–	1. $t\text{-}C_4H_9Li$, −70° 2. HCl; [O]	$(n\text{-}C_6H_{13})_2COHCH_3$ (100, –)	22
	 C6H5CH2OCH(C4H9-n)B, $LiCHCl_2$, CH_3MgBr	–	1. −100° to room temp 2. NaOH, $NaBO_3$	$C_6H_5CH_2OCH(C_4H_9\text{-}n)CHOHCH_3$ (–, 71)	286
	$(C_5H_9)_3B$, $C_6H_5Si(CH_3)_2CH_2Cl$	–	LTMP, 0–20°; [O]	$C_6H_5Si(CH_3)_2CHOHC_5H_9$ (–, 72)	268
	$(C_6H_{11})_2BH$, $(S)\text{-}HC{\equiv}CCH(O_2CCH_3)C_5H_{11}\text{-}n$	–	NaOH, −20°; [O]	$C_6H_{11}CHOHCH{=}CHC_5H_{11}\text{-}n$ (*R,E*)-(86, 75) (*S,E*)-(13, 11)	273
15	$(C_6H_5)_2BOCH_3$, $CH_2{=}CH_2$, Cl_2CHOCH_3	–	1. $LiAlH_4$, 0° 2. $LiOC(C_2H_5)_3$; [O]	$(C_6H_5)_2COHC_2H_5$ (75, –)	287
	$(CH_2{=}CHCH_2)_3B$, $C_6H_5(CH{=}CH)_2COCH_3$	–	Ether; EA	$C_6H_5(CH{=}CH)_2COH(CH_3)CH_2CH{=}CH_2$ (–, 80)	264
	 , $C_6H_5(CH_2)_2CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, ether, −78° 2. CH_3OH, H_2O_2	 (–, 72)	74
	$i\text{-}C_4H_9COCH_3$, "	"	"	$i\text{-}C_4H_9COCH_2CHOH(CH_2)_2C_6H_5$ (–, 82)	74
		BH_3-THF	1. $LiAlH(OCH_3)_3$ 2. CO, 0° 3. CH_3CO_2H or HCl; [O]	 (40, –) or (87, 85)	116
	", $(C_6H_5S)_2CH_2$	"	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), −78 to 0°; [O]	" (–, 75)	121,122
	Cyclohexene		CO, 150°, EG; [O]	 (–, 97)	274
	$CH_2{=}C(CH_3)C_3H_7\text{-}i$	"	"	 (–, 85)	274
	 (2 eq)	–	1. $LiAlH_4$, $AlCl_3$ 2. NaOH 3. CO, 70 atm, 50°, H_2O, EG; [O]	$(C_5H_9)_2COHC_4H_9\text{-}t$ (72, 60)	272
	Cyclohexene, $CH_3OCH{=}CH_2$, CH_3I	BH_3-DMS	$t\text{-}C_4H_9Li$, −78°; [O]	$(C_6H_{11})_2COHC_2H_5$ (66, –)	125
	", ", CH_3OSO_2F	"	"	" (85, –)	125
	$i\text{-}C_3H_7C(CH_3)_2B(C_4H_9\text{-}i)_2$, Cl_2CHOCH_3	–	$LiOC(C_2H_5)_3$ (2 eq), EG; [O]	$i\text{-}C_3H_7C(CH_3)_2COH(C_4H_9\text{-}i)_2$	39
	$(n\text{-}C_6H_{13})_3B$, $C_6H_5Si(CH_3)_2CH_2Cl$	–	LTMP, 0–20°; [O]	$C_6H_5Si(CH_3)_2CHOHC_6H_{13}\text{-}n$ (–, 80)	268
	$(C_6H_{11})_3B$, "	–	"	$C_6H_5Si(CH_3)_2CHOHC_6H_{11}$ (–, 42)	268
	$[n\text{-}C_3H_7CH(C_2H_5)]_3B$, "	–	"	$C_6H_5Si(CH_3)_2CHOHCH(C_2H_5)C_3H_7\text{-}n$ (–, 37)	268
16	$CH_2{=}CHCH_2B(C_2H_5)_2$, $C_6H_5COC_6H_5$	–	0°; [O]	$(C_6H_5)_2COHCH_2CH{=}CH_2$ (–, 79)	254
	 , "	–	*n*-Pentane; EA	" (100, –)	114
	$C_2H_5CH{=}CH_2$, $C_6H_5C{\equiv}CH$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$C_6H_5CH_2COH(C_4H_9\text{-}n)_2$ (73, –)	124
	$CH_3CH{=}CHCH_3$, "	"	"	$C_6H_5CH_2COH(C_4H_9\text{-}sec)_2$ (30, –)	124
	$(CH_3)_2C{=}CH_2$, "	"	"	$C_6H_5CH_2COH(C_4H_9\text{-}i)_2$ (86, –)	124
	$CH_2{=}CHCH_2B(C_2H_5)_2$, 	–	0°; [O]	 (–, 87)	254

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

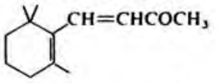
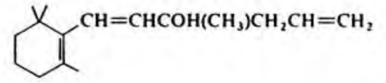
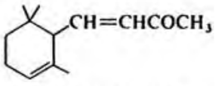
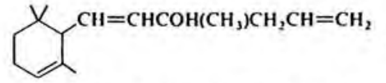
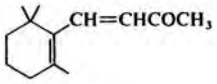
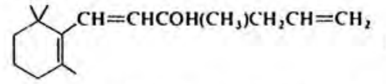
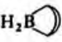
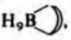
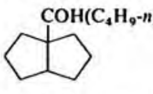
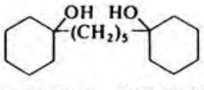
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$CH_2=CHCH_2B(C_2H_5)_2$, 	–	0°; [O]	 (. 90)	254
	$(CH_2=CHCH_2)_3B$, 	–	Ether; EA	 (–, 83)	264
	$(CH_2=CHCH_2)_3B$, 	–	Ether; EA	 (–, 78)	264
	$(i\text{-}C_4H_9)_3B$, $CH_3OCH=CH_2$, $C_6H_5CH_2Br$ or $C_6H_5CH_2Cl$	–	$t\text{-}C_4H_9Li$, −78°; [O]	$C_6H_5CH_2COH(C_4H_9\text{-}i)_2$ (75, –) or (78, –)	125
	Cyclopentene	BH_3-THF	CO, EG, DG (3 eq); [O]	$(C_5H_9)_3COH$ (–, 65)	258
	"	"	CO; [O]	" (–, 90)	281
	", KCN	"	TFAA (3 eq), DG, 0–40°; [O]	" (91, 86)	282
	$(C_5H_9)_3B$, $HCClF_2$	–	1. $LiOC(C_2H_5)_3$ (2 eq) 2. CH_3SO_3H; [O]	" (90, –)	36
	", Cl_2CHOCH_3	–	$LiOC(C_2H_5)_3$ (1.3 eq); [O]	" (97, 91)	37
	Cyclopentene, $HC\equiv CC_3H_7\text{-}n$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$(C_5H_9)_2COHC_5H_{11}\text{-}n$ (–, 84)	124
	Cyclohexene, $(C_6H_5S)_2CHC_3H_7\text{-}n$	"	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), −78 to 0°; [O]	$(C_6H_{11})_2COHC_3H_7\text{-}n$ (–, 98)	121,285
	$C_2H_5CH=CH_2$, $C_6H_{11}C\equiv CH$	"	1. $n\text{-}C_4H_9Li$ 2. HCl, −78° to reflux 3. KOH; [O]	$C_6H_{11}CH_2COH(C_4H_9\text{-}n)_2$ (74, –)	124
	$CH_3CH=CHCH_3$, "	"	"	$C_6H_{11}CH_2COH(C_4H_9\text{-}s)_2$ (78, –)	124
	$(CH_3)_2C=CH_2$, "	"	"	$C_6H_{11}CH_2CO''(C_4H_9\text{-}i)_2$ (77, –)	124
	$n\text{-}C_4H_9CH=CH_2$, $(C_6H_5S)_2CHC_3H_7\text{-}n$	"	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq), −78 to 0°; [O]	$(n\text{-}C_6H_{13})_2COH(C_3H_7\text{-}n)_2$ (–, 96)	121,285
	$(n\text{-}C_6H_{13})_2BCl$, $LiC_3H_7\text{-}i$, $t\text{-}C_4H_9NC$	–	1. $HSCH_2CO_2H$, −78° to room temp 2. NaOH, reflux, DG; [O]	$(n\text{-}C_6H_{13})_2COHC_3H_7\text{-}i$ (–, 75)	21
	$i\text{-}C_3H_7C(CH_3)_2B(C_4H_9\text{-}s)(C_5H_{11}\text{-}n)$, Cl_2CHOCH_3	–	1. $LiOC(C_2H_5)_3$, (2 eq), EG; [O]	$i\text{-}C_3H_7C(CH_3)_2COH(C_4H_9\text{-}s)(C_5H_{11}\text{-}n)$ (78, -)	39
17	$C_6H_5C(CH_3)=C=CH_2$, C_6H_5CHO	Sia_2BH	[O]	$C_6H_5C(CH_3)(CH=CH_2)CHOHC_6H_5$ (, 65)	279
	$CH_3CH=CHCH_2B$, $C_6H_5COC_6H_5$	–	n-Pentane; EA	$(C_6H_5)_2COHCH(CH_3)CH=CH_3$ (96, –)	114
	$C_6H_5COCH_3$, $C_6H_5(CH_2)_2CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, ether, −78° 2. CH_3OH, H_2O_2	$C_6H_5COCH_2CHOH(CH_2)_2C_6H_5$ (–, 75)	74
	$C_6H_5COC_3H_7\text{-}n$, C_6H_5CHO	"	"	$C_6H_5COCH(C_2H_5)CHOHC_6H_5$ (–, 80)	74
	$C_6H_5(CH_2)_2COCH_3$, "	TfOB	"	$C_6H_5CH_2CH(COCH_3)CHOHC_6H_5$ (–, 90)	278
	$n\text{-}C_4H_9B$, $LiC_4H_9\text{-}n$	–	1. n-Pentane, −78° 2. CH_3COCl, 0° 3. CO, 60 atm, 150° EG; [O]	 (–, 87)	275
	$(C_6H_{11})_2BOCH_3$, $CH_2=C(CH_3)_2$	–	1. $LiAlH_4$ 2. CO, 1000 psi, 150°, EG; [O]	$(C_6H_{11})_2COHC_4H_9\text{-}i$ (74, 63)	266
	$(C_6H_{11})_2BC_4H_9\text{-}t$	–	CO, DG; [O]	$(C_6H_{11})_2COHC_4H_9\text{-}t$ (–, –)	284
	", Cl_2CHOCH_3 (2 eq)	–	$LiOC(C_2H_5)_3$, 15°; [O]	" (94, 90)	39
	$CH_2=CHCH_2CH=CH_2$	BH_3-THF	1. 170°, neat 2. CO, EG; [O]	 (–, 40)	288
	$C_5H_9(C_5H_{11}\text{-}n)BC(CH_3)_2C_3H_7\text{-}i$, Cl_2CHOCH_3	–	$LiOC(C_2H_5)_3$, EG; [O]	$C_5H_9(C_5H_{11}\text{-}n)COHC(CH_3)_2C_3H_7\text{-}i$ (75, –)	39

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

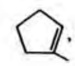
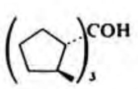
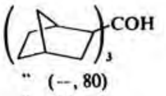
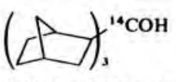
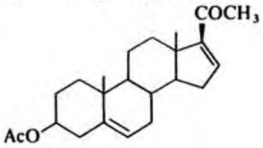
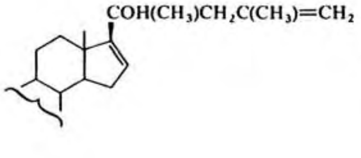
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$n\text{-}C_6H_{13}CH{=}CH_2$	BH_3-THF	1. $LiAlH(OCH_3)_3$ 2. CO, 0° 3. HCl; [O]	$(n\text{-}C_8H_{17})_2CHOH$ (78, —)	116
	$(n\text{-}C_6H_{13})_2BCl$, $LiC_4H_9\text{-}n$, $t\text{-}C_4H_9NC$	—	1. $HSCH_2CO_2H$, −78 to 20° 2. NaOH, reflux, DG; [O]	$(n\text{-}C_6H_{13})_2COHC_4H_9\text{-}n$ (87, —)	21
	$i\text{-}C_3H_7C(CH_3)_2B(C_5H_{11}\text{-}n)_2Cl_2CHOCH_3$	—	$LiOC(C_2H_5)_3$, 15°; [O]	$i\text{-}C_3H_7C(CH_3)_2COHC_5H_{11}\text{-}n$ (85, 80)	39
	$(n\text{-}C_8H_{17})_3B$, $C_6H_5Si(CH_3)_2CH_2Cl$	—	LTMP, 0–20°; [O]	$C_6H_5Si(CH_3)_2CHOHC_8H_{17}\text{-}n$ (—, 78)	268
18	$(CH_2{=}CHCH_2)_3B$, $C_6H_5COCH{=}CHC_6H_5$	—	Ether; EA	$C_6H_5CH{=}CHCOH(C_6H_5)CH_2CH{=}CH_2$ (—, 77)	264
	Cyclopentene, $C_6H_{11}C{\equiv}CH$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78°-reflux 3. KOH; [O]	$(C_5H_9)_2COHCH_2C_6H_{11}$ (75, —)	124
	Cyclohexene, $HC{\equiv}CC_4H_9\text{-}n$	"	"	$(C_6H_{11})_2COHC_5H_{11}\text{-}n$ (80, —)	124
	", $HC{\equiv}CC_4H_9\text{-}t$	"	"	$(C_6H_{11})_2COHCH_2C_4H_9\text{-}t$ (15, —)	124
19	$(C_6H_5)_3B$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$ (1.3 eq); [O]	$(C_6H_5)_3COH$ (95, —)	37
	$C_6H_5COC_3H_7\text{-}n$, $C_6H_5(CH_2)_2CHO$	$(n\text{-}C_4H_9)_2BOTf$	1. DIPEA, ether, −78° 2. CH_3OH, H_2O_2	$C_6H_5COCH(C_2H_5)CHOH(CH_2)_2C_6H_5$ (—, 83)	74
	Cyclohexene	BH_3-DG	CO, DG; [O]	$(C_6H_{11})_3COH$ (—, 80)	281
	", KCN	BH_3-THF	TFAA (3 eq), 0–40°, DG; [O]	" (—, 80)	282
	, KCN	"	TFAA (6 eq), 0–40°, DG; [O]	 (—, 85)	282
	", NaCN	"	TFAA, −78 to 45°; [O]	" (—, —)	289
	$(C_6H_{11})_3B$	—	CO, $LiAlH_4$, EG, DG; [O]	$(C_6H_{11})_3COH$ (—, 86)	280
	", $HCClF_2$	—	1. $LiOC(C_2H_5)_3$ (2 eq) 2. CH_3SO_3H; [O]	" (80, —)	36
	", Cl_2CHOCH_3	—	1. $LiOC(C_2H_5)_3$ (1.3 eq); [O]	" (92, —)	37
	$C_6H_{11}B(C_6H_{13}\text{-}n)_2$, KCN	—	TFAA (3 eq), 0–20°; [O]	$C_6H_{11}COH(C_6H_{13}\text{-}n)_2$ (62, —)	290
	$n\text{-}C_4H_9CH{=}CH_2$	BH_3-ether	CO, 900 atm, 150°, H_2O H_2O; [O]	$(n\text{-}C_6H_{13})_3COH$ (—, 41)	119
	"	BH_3-THF	CO, EG, DG (3 eq); [O]	" (—, 68)	258
	", KCN	"	TFAA (3 eq), 0–20°; [O]	" (98, —)	282,290
	$i\text{-}C_3H_7C(CH_3)_2BH_2$, KCN, $CH_2{=}CHC_4H_9\text{-}n$	—	TFAA (6 eq), 0–40°, DG; [O]	$i\text{-}C_3H_7C(CH_3)_2COH(C_6H_{13}\text{-}n)_2$ (—, 64)	282
	$i\text{-}C_3H_7C(CH_3)_2BH_2$, $CH_2{=}CHC_4H_9\text{-}n$	—	CO, 70 atm, 50°, H_2O, EG; [O]	" (88, 81)	271
20	Cyclohexene, $C_6H_{11}C{\equiv}CH$	BH_3-THF	1. $n\text{-}C_4H_9Li$ 2. HCl, −78 to 0°; [O] 3. KOH; [O]	$(C_6H_{11})_2COHCH_2C_6H_{11}$ (63, —)	124
	$(n\text{-}C_8H_{17})_2BC(CH_3)_2C_3H_7\text{-}i$, $LiC(SC_6H_5)_2C_3H_7\text{-}n$	—	$HgCl_2$, −78 to 0°; [O]	$(n\text{-}C_8H_{17})_2COHC_3H_7\text{-}n$ (—, 80)	285
	$(n\text{-}C_8H_{17})_3B$, $(C_6H_5S)_2CHC_3H_7\text{-}n$	—	1. $n\text{-}C_4H_9Li$ 2. $HgCl_2$ (3 eq); [O]	" (—, 90)	121,285
21	Cyclohexene, $CH_2{=}CHC_6H_{13}\text{-}n$, KCN	BH_3-THF	TFAA (3 eq), DG, pyridine, 0–40°; [O]	$(C_6H_{11})_2COHC_8H_{17}\text{-}n$ (—, 92)	282
22	, KCN	"	"	 (—, 79)	282
	"	BH_3-DG	CO, DG; [O]	" (—, 80)	281
	B, $HCClF_2$	—	1. $LiOC(C_2H_5)_3$ (2 eq) 2. CH_3SO_3H; [O]	" (84, —)	36
	", Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$ (1.3 eq); [O]	" (84, —)	37
		BH_3	^{14}CO, 1 atm; [O]	 (—, 72)	291
	$n\text{-}C_5H_{11}CH{=}CH_2$	BH_3-THF	CO, EG, DG (3 eq); [O]	$(n\text{-}C_7H_{15})_3COH$ (—, 67)	258

TABLE I. ALCOHOLS. A. ONE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	", NaCN	"	TFAA, −78 to 45°; [O]	" (–, 79)	283
23	i-$C_3H_7C(CH_3)_2BH_2$, KCN, $CH_2{=}CHC_6H_{13}$-n	—	TFAA (6 eq), DG, 0–40°; [O]	i-$C_3H_7C(CH_3)_2COH(C_8H_{17}$-$n)_2$ (–, 70)	282
25	n-$C_6H_{13}CH{=}CH_2$	BH_3-DG	CO, DG; [O]	$(n$-$C_8H_{17})_3COH$ (–, 90)	281
	", KCN	BH_3-THF	TFAA (3 eq), 0–20°; [O]	" (85, --)	282
	", NaCN	"	TFAA, −78° to 45°; [O]	" (–, 75)	283
27	$[CH_2{=}C(CH_3)CH_2]_3B$, 	—		 (–, 55)	292

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[a] Reagents after the semicolon are those used to decompose an intermediate organoborane; abbreviations are: TEA = triethanolamine, EA = ethanolamine, [O] = oxidation with alkaline hydrogen peroxide.

[b] M can be either Li or Na; the solvent is either DG or THF.

[c] The yield is not given in the original paper. The yield in the table is obtained by multiplication of yields supplied in intermediate steps.

[d] R = 3-Methyl-2-n-butyl

[e] R = *trans*-2-Methylcyclopentyl

[f] R = Cyclohexyl

[g] R = 3-Methyl-1-n-pentyl

[h] R = Norbornyl

TABLE I. ALCOHOLS. B. TWO-CARBON HOMOLOGATION

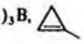
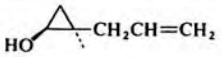
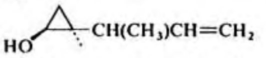
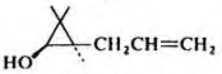
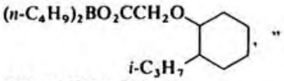
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	$(CH_2{=}CHCH_2)_3B$, 	—	CH_3OH, −60°; [O]	 (—, 48)^b	131
8	$(CH_3CH{=}CHCH_2)_3B$, "	—	CH_3OH, −70°; [O]	 (—, 88)	132,132
	$(C_2H_5)_3B$, cyclohexene (3 eq)	—	$h\nu$, C_6H_6; [O]	2-Ethylcyclohexanol (86,)	129
9	$(CH_2{=}CHCH_2)_3B$, benzoquinone	—	—	2-Allylhydroquinone (—, 61)	140
	$CH_2{=}CHCH_2B(OC_4H_9\text{-}n)_2$, "	—	—	" (—, —)	140
	$(CH_2{=}CHCH_2)_3B$, 	—	CH_3OH, reflux; [O]	 (—, 38)^b	133
	$(C_2H_5)_3B$, cycloheptene (3 eq)	—	$h\nu$, C_6H_6; [O]	(*E*)-2-Ethylcycloheptanol (10, —)	130
10	$NCCH_2CH{=}CH_2$, benzoquinone	BH_3-THF	1. H_2O 2. Air	2-(3-Cyanopropyl)hydroquinone (55, —)^c 2-(2-Cyanoisopropyl)hydroquinone (35, —)^c	137
	$CH_3CH_2CH{=}CH_2$, "	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-*n*-Butylhydroquinone (—, 86)	139
	$CH_3CH{=}CHCH_3$, "	"	"	2-*s*-Butylhydroquinone (—, 94)	139
	$(CH_3)_2C{=}CH_2$, "	"	"	2-*i*-Butylhydroquinone (—, 91)	139
	$(C_2H_5)_3B$, 1-ethylcyclohexene	—	$h\nu$, C_6H_6; [O]	2,2-Diethylcyclohexanol (70, —)	129
	$(n\text{-}C_4H_9)_3B$, cyclohexene	—	"	2-*n*-Butylcyclohexanol (80, —)	129
	, "	—	"	" (12, —)^d	130
	$[CH_3O(CH_2)_3]_3B$, "	—	"	2-(3-Methoxypropyl)cyclohexanol (55, —)	130

TABLE I. ALCOHOLS. B. TWO-CARBON HOMOLOGATION (*Continued*)

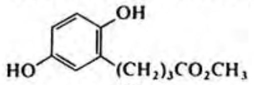
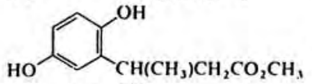
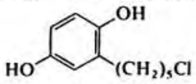
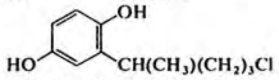
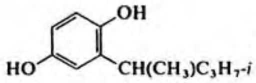
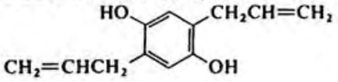
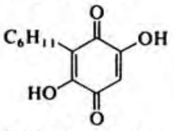
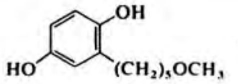
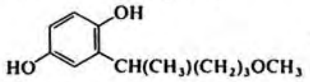
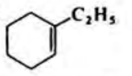
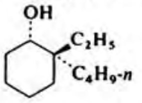
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
11	$N_2CHCO_2C_2H_5$, C_6H_5CHO	9-BBN	—	$C_6H_5CHOHCH_2CO_2C_2H_5$ (—, 43)	135
	$CH_2{=}CHCH_2CO_2CH_3$, benzoquinone	BH_3-THF	1. H_2O 2. Air	 (61, —)[c],  (35, —)[c]	137
	$CH_2{=}CH(CH_2)_3Cl$, ″	″	″	 (76, —)[c],  (14, —)	137
	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, $CH_2{=}CHCHO$	—	1. n-C_4H_9Li, −78 to 20° 2. −78°; [O]	$C_5H_9C({=}C{=}CH_2)CHOHCH{=}CH_2$ (—, 84)	134
	$[i$-$C_3H_7CH(CH_3)]_2BCH{=}CHC_4H_9$-$n$, benzoquinone	—	1. DG 2. Ether, reflux	 (—, 95)	139
	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, C_2H_5CHO	—	1. n-C_4H_9Li, −78 to 20° 2. −78°; [O]	$C_5H_9C({=}C{=}CH_2)CHOHC_2H_5$ (—, 80)	134
	$(n$-$C_4H_9)_3B$, cycloheptene	—	$h\nu$, C_6H_6; [O]	(*E*)-2-*n*-Butylcycloheptanol (18, —)	130
	″, $N_2CHCO_2C_2H_5$, CH_3COCH_3	—	—	n-$C_4H_9CH[COH(CH_3)_2]CO_2C_2H_5$ (—, 73)	73
12	$CH_2{=}CH_2$, 1,4-naphthoquinone	BH_3-THF	H_2O; air	2-Ethyl-1,4-dihydroxynaphthalene (95, —)	136
	$(CH_2{=}CHCH_2)_3B$, benzoquinone	—		 (—, 58)	140
	$(C_6H_{11})_3B$, 2,5-dihydroxybenzoquinone	—	0°, DMF	 (—, 172)	141
	Cyclohexene, benzoquinone	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-Cyclohexylhydroquinone (—, 99)	139
	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, (*E*)-$CH_3CH{=}CHCHO$	—	1. n-C_4H_9Li, −78 to 20 2. −78°; [O]	$C_5H_9C({=}C{=}CH_2)CHOHCH{=}CHCH_3$ (*E*)-(—, 84)	134
	n-$C_4H_9CH{=}CH_2$, benzoquinone	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-*n*-Hexylhydroquinone (—, 99)	139
	$CH_3O(CH_2)_3CH{=}CH_2$, ″	BH_3-THF	H_2O; air	 (77, —)[c]  (18, —)[c]	137
	$(C_6H_{11})_3B$, $HC{\equiv}CCH_2Cl$, C_2H_5CHO	—	1. n-C_4H_9Li, −78 to 20° 2. −78°; [O]	$C_6H_{11}C({=}C{=}CH_2)CHOHC_2H_5$ (—, 77)	134
	$(n$-$C_6H_{13})_3B$, ″, ″	—	″	n-$C_6H_{13}C({=}C{=}CH_2)CHOHC_2H_5$ (—, 73)	134
	$(n$-$C_4H_9)_3B$, 	—	$h\nu$, C_6H_6; [O]	 (70, —)	129
	$(n$-$C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, n-C_3H_7CHO	—	—	n-$C_4H_9CH(CO_2C_2H_5)CHOHC_3H_7$-$n$ (—, 87)	73

TABLE I. ALCOHOLS. B. TWO-CARBON HOMOLOGATION (*Continued*)

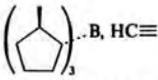
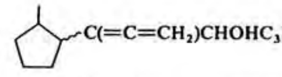
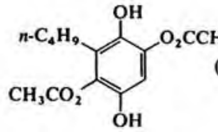
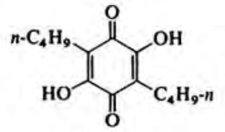
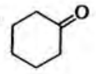
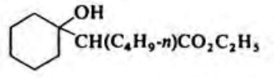
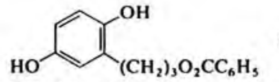
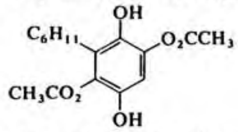
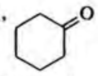
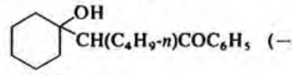
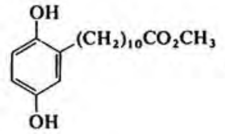
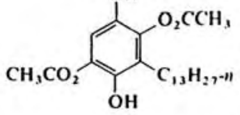
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
13	$(C_6H_5CH_2)_3B$, benzoquinone	—	1. DG 2. Ether, reflux	2-Benzylhydroquinone (—, 90)	139
	$(n\text{-}C_3H_7)_3B$, 1,4-naphthoquinone	—	C_6H_6	2-*n*-Propyl-1,4-dihydroxynaphthalene (—, 68)	138
	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, $t\text{-}C_4H_9CHO$	—	1. $n\text{-}C_4H_9Li$, −78 to 20° 2. −78°; [O]	$C_5H_9C(=C=CH_2)CHOHC_4H_9\text{-}t$ (—, 79)	134
	 B, $HC{\equiv}CCH_2Cl$, $i\text{-}C_3H_7CHO$	—	"	 $C(=C=CH_2)CHOHC_3H_7\text{-}i$ (—, 78)	134
14	$C_2H_5CH{=}CH_2$, 1,4-naphthoquinone	BH_3-THF	H_2O; air	2-*n*-Butyl-1,4-dihydroxynaphthalene (85, —)	136
	$(n\text{-}C_4H_9)_3B$, "	—	C_6H_6	" (—, 54)	138
	Cyclooctene, benzoquinone	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-Cyclooctylhydroquinone (—, 91)	139
	$(n\text{-}C_4H_9)_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, 25)	141
	$(n\text{-}C_4H_9)_3B$, 2,5-dihydroxybenzoquinone	—	Air, DMF, 0°	 (—, 16)	141
	", $N_2CHCO_2C_2H_5$, 	—	—	 $CH(C_4H_9\text{-}n)CO_2C_2H_5$ (—, 96)	73
15	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, C_6H_5CHO	—	1. $n\text{-}C_4H_9Li$, −78 to 20° 2. −78°; [O]	$C_6H_5CHOHC(=C=CH_2)C_5H_9$ (—, 85)	134
	$(n\text{-}C_4H_9)_3B$, $N_2CHCOC_6H_5$, CH_3COCH_3	—	—	$C_6H_5COCH(C_4H_9\text{-}n)COH(CH_3)_2$ (—, 42)	73
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, C_6H_5CHO	—	—	$C_6H_5CHOHCH(C_4H_9\text{-}n)CO_2C_2H_5$ (—, 81)	72,73
	$(C_5H_9)_3B$, $HC{\equiv}CCH_2Cl$, $C_6H_{11}CHO$	—	1. $n\text{-}C_4H_9Li$, −78 to 20° 2. −78°; [O]	$C_6H_{11}CHOHC(=C=CH_2)C_5H_9$ (—, 86)	134
16	$C_6H_5CO_2CH_2CH{=}CH_2$, benzoquinone	BH_3-THF	H_2O; air	 (66, —)[c]	137
	Cyclohexene, 1,4-naphthoquinone	"	"	2-Cyclohexyl-1,4-dihydroxynaphthalene (90, —)	136
	$(C_6H_{11})_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, —)	141
	$(n\text{-}C_4H_9)_3B$, $N_2CHCOC_6H_5$, $n\text{-}C_3H_7CHO$	—	—	$C_6H_5COCH(C_4H_9\text{-}n)CHOHC_3H_7\text{-}n$ (—, 88)	73
17	$(C_6H_5CH_2)_3B$, 1,4-naphthoquinone	—	C_6H_6	2-Benzyl-1,4-dihydroxynaphthalene (—, 27)	138
	$(C_6H_{11})_3B$, $N_2CHCO_2C_2H_5$, C_6H_5CHO	—	—	$C_6H_5CHOHCH(C_6H_{11})CO_2C_2H_5$ (—, 87)	73
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, $C_6H_5COC_2H_5$	—	—	$C_6H_5COH(C_2H_5)CH(C_4H_9\text{-}n)CO_2C_2H_5$ (—, 68)	73
18	$(n\text{-}C_4H_9)_3B$, $N_2CHCOC_6H_5$, 	—	—	 $CH(C_4H_9\text{-}n)COC_6H_5$ (—, 69)	73
	$CH_2{=}CH(CH_2)_8CO_2CH_3$, benzoquinone	BH_3-THF	H_2O; air	 (74, —)	137

TABLE I. ALCOHOLS. B. TWO-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
19	$(n\text{-}C_4H_9)_3B$, $N_2CHCOC_6H_5$, C_6H_5CHO	—	—	$C_6H_5CHOHCH(C_4H_9\text{-}n)COC_6H_5$ (—, 98)	73
20	", $N_2CHCOSCH_2C_6H_6$, "	—	—	$C_6H_5CHOHCH(C_4H_9\text{-}n)COSCH_2C_6H_5$ (—, 51)	135
22	$(n\text{-}C_4H_9)_3B$, $C_6H_5C(N_2)CO_2C_2H_5$, C_6H_5CHO	—	—	$C_6H_5CHOHC(C_4H_9\text{-}n)(CO_2C_2H_5)CH_2C_6H_5$ (—, 70)	73
23	$(n\text{-}C_{13}H_{27})_3B$, 2,5-diacetoxybenzoquinone	—	Reflux	 (—, —)	141

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[a] Reagents after the semicolon are those used to decompose an intermediate borate or boronate; [O] = oxidation with alkaline hydrogen peroxide.

[b] The yield is not given in the original paper. The yield in the table is determined by multiplication of yields supplied in intermediate steps.

[c] The yield is based on ^1H NMR analysis.

[d] The product is optically active: 15% e.e.

TABLE I. ALCOHOLS. C. THREE-CARBON HOMOLOGATION

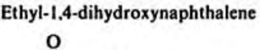
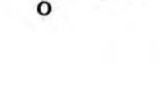
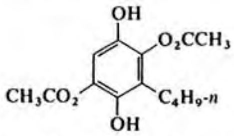
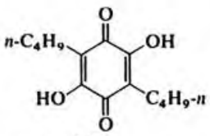
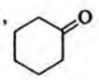
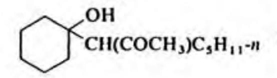
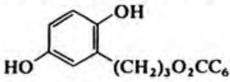
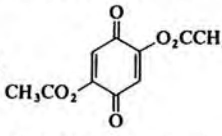
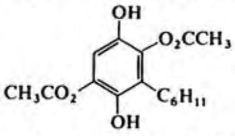
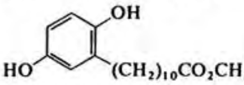
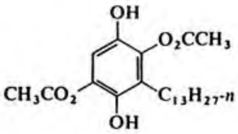
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$(i\text{-}C_3H_7)_3B$, $LiCH{=}CH_2$, CH_2O	—	Ether, 0–45°; [O]	$i\text{-}C_3H_7CHOH(CH_2)_2OH$ (--, 74)	68
7	", ", CH_3CHO	—	"	$i\text{-}C_3H_7CHOHCH_2CHOHCH_3$ (—, 52)	68
	$(n\text{-}C_4H_9)_3B$, ", CH_2O	--	"	$n\text{-}C_4H_9CHOH(CH_2)_2OH$ (--, 80)	68
9	$(CH_2{=}CHCH_2)_3B$, benzoquinone	—	—	2-Allylhydroquinone (—, 61)	140
	$CH_2{=}CHCH_2B(OC_4H_9\text{-}n)_2$, "	--	—	" (- , —)	140
	$(i\text{-}C_3H_7)_3B$, $LiCH{=}CH_2$, $CH_3CH{=}CHCHO$	—	Ether, 0–45°; [O]	$i\text{-}C_3H_7CHOHCH_2CHOHCH{=}CHCH_3$ (--, 28)	68
	$(i\text{-}C_3H_7)_3B$, $LiCH{=}CH_2$, $i\text{-}C_3H_7CHO$	—	"	$i\text{-}C_3H_7CHOHCH_2CHOHC_3H_7\text{-}i$ (—, 73)	68
10	$CH_2{=}CHCH_2CN$, benzoquinone	BH_3-THF	H_2O; air	2-(3-Cyanopropyl)hydroquinone (55, —)[b]	137
	$C_2H_5CH{=}CH_2$, "	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-*n*-Butylhydroquinone (—, 86)	139
	$CH_3CH{=}CHCH_3$, "	"	"	2-*s*-Butylhydroquinone (—, 94)	139
	$(CH_3)_2C{=}CH_2$, "	"	"	2-Isobutylhydroquinone (—, 91)	139
	$(n\text{-}C_4H_9)_3B$, $LiCH{=}CH_2$, $CH_3CH{=}CHCHO$	—	Ether, 0–45°; [O]	$n\text{-}C_4H_9CHOHCH_2CHOHCH{=}CHCH_3$ (—, 48)	68
	$(n\text{-}C_4H_9)_3B$, $LiCH{=}CH_2$, $i\text{-}C_3H_7CHO$	—	"	$n\text{-}C_4H_9CHOHCH_2CHOHC_3H_7\text{-}i$ (--, 74)	68
11	$CH_2{=}CHCH_2CO_2CH_3$, benzoquinone	BH_3-THF	H_2O; air	2-(3-Carbomethoxypropyl)hydroquinone (61, —)	137
	$n\text{-}C_5H_{11}Cl$, "	"	"	2-(5-Chloropentyl)hydroquinone (76, —)[b]	137
	$(C_2H_5)_3B$, $LiCH{=}CH_2$, C_6H_5CHO	—	Ether, 0–45°; [O]	$C_6H_5CHOHCH_2CHOHC_2H_5$ (—, 78)	68
	$[i\text{-}C_3H_7CH(CH_3)]_2BCH{=}CHC_4H_9\text{-}n$, benzoquinone	—	1. DG 2. Ether, reflux	 (—, 95)	139
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, CH_3COCH_3	—	—	$n\text{-}C_5H_{11}CH(COCH_3)COH(CH_3)_2$ (—, 15)	135
12	$CH_2{=}CH_2$, 1,4-naphthoquinone	BH_3-THF	H_2O; air	2-Ethyl-1,4-dihydroxynaphthalene (95, —)	136
	$(C_6H_{11})_3B$, 2,5-dihydroxybenzoquinone	—	DMF, 0°	 (—, 172)	141

TABLE I. ALCOHOLS. C. THREE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	Cyclohexene, benzoquinone	$NaBH_4$, BF_3-etherate	1. DG 2. Ether, reflux	2-Cyclohexylhydroquinone (–, 99)	139
	n-$C_4H_9CH{=}CH_2$, "	"	"	2-n-Hexylhydroquinone (–, 99)	139
	$CH_3O(CH_2)_3CH{=}CH_2$, "	BH_3-THF	H_2O; air	2-(5-Methoxypentyl)hydroquinone (78, –)[b]	137
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, n-C_3H_7CHO	—	—	n-$C_5H_{11}CH(COCH_3)CHOHC_3H_7$-$n$ (–, 71)	135
13	$(C_6H_5CH_2)_3B$, benzoquinone	—	1. DG 2. Ether, reflux	2-Benzylhydroquinone (–, 90)	139
	$(n\text{-}C_3H_7)_3B$, 1,4-naphthoquinone	—	C_6H_6	2-n-Propyl-1,4-dihydroxynaphthalene (–, 68)	130
14	$C_2H_5CH{=}CH_2$, "	BH_3-THF	H_2O; air	2-n-Butyl-1,4-dihydroxynaphthalene (–, 35)	136
	$(n\text{-}C_4H_9)_3B$, "	"	C_6H_6	" (–, 54)	138
	", 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (–, 25)	141
	Cyclooctene, benzoquinone	$NaBH_4$, BF_3-etherate	1. DG	2-Cyclooctylhydroquinone (–, 91)	139
	$(n\text{-}C_4H_9)_3B$, 2,5-dihydroxybenzoquinone	—	DMF, 0°; air	 (–, 16)	141
	", $CH_2{=}CHCOCH_3$, 	—	—	 (–, 38)	135
15	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, C_6H_5CHO	—	—	$C_6H_5CHOHCH(COCH_3)C_5H_{11}$-$n$ (–, 91)	135
16	$C_6H_5CO_2CH_2CH{=}CH_2$, benzoquinone	BH_3-THF	H_2O; air	 (66, –)[b]	137
	Cyclohexene, 1,4-naphthoquinone	"	"	2-Cyclohexyl-1,4-dihydroxynaphthalene (90, –)	136
	$C_6H_{11}B$, 	—	DMF, 0°	 (–, –)	141
17	$(C_6H_5CH_2)_3B$, 1,4-naphthoquinone	—	C_6H_6	2-Benzyl-1,4-dihydroxynaphthalene (–, 27)	138
18	$CH_2{=}CH(CH_2)_8CO_2CH_3$, benzoquinone	BH_3-THF	H_2O; air	 (74, –)[b]	137
19	Cyclohexene, $BrC{\equiv}CCH(OTHP)C_5H_{11}$-$n$	$ThexylBH_2$	1. $NaOCH_3$, CH_3OH 2. $Ag(NH_3)_2NO_3$ (5 eq), 75–80°	$C_6H_{11}CH{=}CHCH(OTHP)C_5H_{11}$-$n$ (E)-(–, 65)	30
23	$(n\text{-}C_{13}H_{27})_3B$, 2,5-diacetoxybenzoquinone	—	Reflux	 (–, –)	141

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[a] Reagents after the semicolon are those used in decomposing an intermediate borate or boronate; [O] = oxidation with alkaline hydrogen peroxide.

[b] The yield is determined by ^1H NMR analysis.

TABLE I. ALCOHOLS. D. FOUR-OR-MORE-CARBON HOMOLOGATION

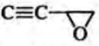
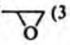
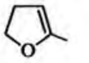
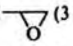
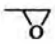
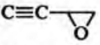
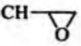
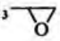
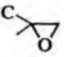
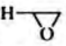
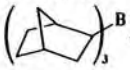
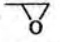
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$(C_2H_5)_3B$, $HC\equiv C$ (3 eq)	—	C_6H_6 then air; [O]	$C_2H_5CH=C=CHCH_2OH$ (53, —)	143
	", $HC\equiv C(CH_2)_2OTs$	—	*n*-C_4H_9Li, −78 to 20°; [O]	$C_2H_5C\equiv C(CH_2)_2OH$ (—, 55–74)	95
	", $CH_2=CH$ (3 eq)	—	C_6H_6 then air; [O]	*n*-$C_3H_7CH=CHCH_2OH$ (*E*)-(67, 61), (*Z*)-(8, 7)	142
7	", $HC\equiv C$ (3 eq)	—	Air; [O]	$C_2H_5CH=C=C(CH_3)CH_2OH$ (52, —)	143
	", $HC\equiv CCH_2CH(OTs)CH_3$	—	*n*-C_4H_9Li, −78 to 20°; [O]	$C_2H_5C\equiv CCH(CH_3)CH_2OH$ (70, —)	95
8	$(CH_2=CHCH_2)_3B$, 	—	110–140°	$CH_2=CHCH_2C(CH_3)=CH(CH_2)_2OH$ (—, 76)	294
	", "	—	110–140°; [O]	" (—, 75–80)	295
	$(n\text{-}C_4H_9)_3B$, $HC\equiv C(CH_2)_2OTs$	—	*n*-C_4H_9Li, −78 to 20°; [O]	*n*-$C_4H_9C\equiv C(CH_2)_2OH$ (—, 55–74)	95
	", $CH_2=CH$ (3 eq)	—	C_6H_6 then air; [O]	*n*-$C_5H_{11}CH=CHCH_2OH$ (73, —)	142
	$(i\text{-}C_4H_9)_3B$, " (3 eq)	—	Ether then air; [O]	*i*-$C_4H_9CH_2CH=CHCH_2OH$ (53, —)	142
	$(C_2H_5)_3B$, furan	—	1. *n*-C_4H_9Li, ether 2. CH_3CO_2H; [O]	$(C_2H_5)_2COHCH=CHCH_2OH$ (*E*)-(80, —)	23
	$(i\text{-}C_3H_7)_3B$, $LiCH=CH_2$, 	—	Ether, 0°; [O]	*i*-$C_3H_7CHOH(CH_2)_2CHOHCH_3$ (—, 100)	69
	$(n\text{-}C_4H_9)_3B$, ", 	—	"	*n*-$C_4H_9CHOH(CH_2)_3OH$ (—, 100)	69
9	$(C_5H_9)_3B$, $HC\equiv C$	—	C_6H_6 then air; [O]	$C_5H_9CH=C=CHCH_2OH$ (62, —)	143
	", $CH_2=CH$	—	Ether then air; [O]	$C_5H_9CH_2CH=CHCH_2OH$ (56, —)	142
	$(n\text{-}C_4H_9)_3B$, $HC\equiv CCH_3$, 	—	1. *n*-C_4H_9Li, −78° to 20° 2. CH_3CO_2H	*n*-$C_4H_9CH=C(CH_3)(CH_2)_2OH$ (*E*)-(, 43) (*Z*)-(–, 29)	296
	", ", "	—	1. *n*-C_4H_9Li, CH_2Cl_2, −78 to 20° 2. CH_3CO_2H	" (*Z*)-(—, 62)	296
	", $LiCH=CH_2$, CH_3	—	Ether, 0°; [O]	*n*-$C_4H_9CHOH(CH_2)_2CHOHCH_3$ (–, 93)	69
10	$(C_5H_9)_3B$, $HC\equiv C$	—	Air; [O]	$C_5H_9CH=C=C(CH_3)CH_2OH$ (55,)	143
	$(C_6H_{11})_3B$, $CH_2=CH$	--	Ether then air; [O]	$C_6H_{11}CH_2CH=CHCH_2OH$ (61,)	142
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv C(CH_2)_2OTs$	—	*n*-C_4H_9Li, −78 to 20°; [O]	*n*-$C_6H_{13}C\equiv C(CH_2)_2OH$ (—, 55–74)	95
	$(n\text{-}C_4H_9)_3B$, $HC\equiv CC_2H_5$, 	—	1. *n*-C_4H_9Li, −78° to 20° 2. CH_3CO_2H	*n*-$C_4H_9CH=C(C_2H_5)(CH_2)_2OH$ (*E*)-(, 28) (*Z*)-(–, 53)	296
	", ", "	—	1. *n*-C_4H_9Li, CH_2Cl_2, −78 to 20° 2. CH_3CO_2H	" (*E*)-(—, 25), (*Z*)-(—, 65)	296
	$(n\text{-}C_3H_7)_3B$, furan	—	1. *n*-C_4H_9Li, ether 2. CH_3CO_2H; [O]	$(n\text{-}C_3H_7)_2COHCH=CHCH_2OH$ (*E*)-(98, —)	23
	$(n\text{-}C_6H_{13})_3B$, $LiCH=CH_2$, 	—	Ether, 0°; [O]	*n*-$C_6H_{13}CHOH(CH_2)_3OH$ (—, 89)	128
11	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, $CH_2=CHCHO$	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHCH=CH_2$ (—, 75)	134
	, $HC\equiv C(CH_2)_2OTs$	—	*n*-C_4H_9Li, −78 to 20°; [O]	$C\equiv C(CH_2)_2OH$ (—, 55–74)	95
	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, C_2H_5CHO	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHC_2H_5$ (—, 89)	134
	$(C_6H_{11})_2BH$, $HC\equiv CC(CH_3)=CH_2$	—	*hν*; [O]	$C_6H_{11}CHOHCH=C(CH_3)CH_2OH$ (—, 58)	276
	$(n\text{-}C_6H_{13})_3B$, $LiC\equiv CH$-EDA, 	—	Reflux; [O]	*n*-$C_6H_{13}CO(CH_2)_2CHOHCH_3$ (—, 65)	66
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CSi(CH_3)_3$, 	—	*n*-C_4H_9Li, reflux; [O]	" (—, 21)	162
	", $LiCH=CH_2$, "	—	Ether, 0°; [O]	*n*-$C_6H_{13}CHOH(CH_2)_2CHOHCH_3$ (—, 85)	69

TABLE I. Alcohols. D. Four-or-More-Carbon Homologation (*Continued*)

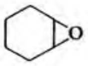
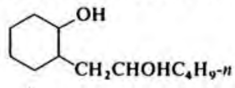
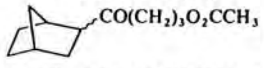
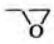
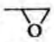
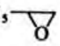
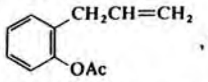
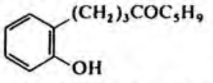
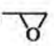
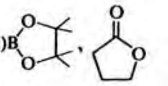
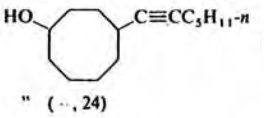
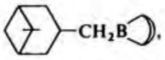
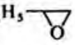
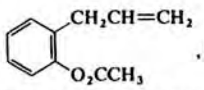
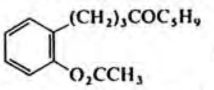
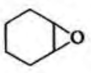
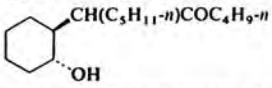
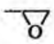
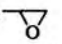
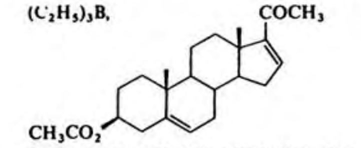
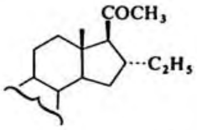
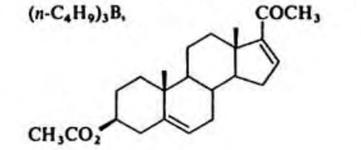
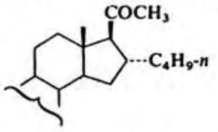
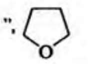
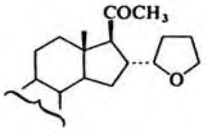
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
12	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, (*E*)-$CH_3CH{=}CHCHO$	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHCH{=}CHCH_3$ (–, 84)	134
	(*n*-$C_6H_{13})_3B$, $HC\equiv CCH_2Cl$, C_2H_5CHO	—	"	*n*-$C_6H_{13}C\equiv CCH_2CHOHC_2H_5$ (–, 85)	134
	$CH_3CH{=}CHCH_3$, $CH_2{=}CH(CH_2)_3O_2CCH_3$	ThexylBH_2	1. CO, 70 atm, 50°, H_2O 2. NaO_2CCH_3, H_2O_2	*s*-$C_4H_9CO(CH_2)_5O_2CCH_3$ (72, 63)	155
	(*i*-$C_3H_7)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	1. *n*-C_4H_9Li, reflux 2. CH_3CO_2H, reflux 3. NaOH	*i*-$C_3H_7CH{=}C(C_5H_{11}\text{-}n)(CH_2)_2OH$ (*E*)-(–, 80)	162
	", ", "	—	*n*-C_4H_9Li, reflux; [O]	*i*-$C_3H_7COCH(C_5H_{11}\text{-}n)(CH_2)_2OH$ (–, 82)	162
	(*n*-$C_4H_9)_3B$, $LiCH{=}CH_2$, 	—	Ether, 0°; [O]	 (–, 77)	69
13	, $CH_2{=}CHCH_2O_2CCH_3$	ThexylBH_2	CO, 70 atm, 50°, H_2O; [O]	 (–, 66)	155
	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, *t*-C_4H_9CHO	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHC_4H_9$-*t* (–, 86)	134
	n-$C_3H_7C(CH_3){=}CH_2$, $CH_2{=}CH(CH_2)_2O_2CCH_3$	ThexylBH_2	CO, 70 atm, 50°, H_2O; [O]	*n*-$C_3H_7CH(CH_3)CH_2CO(CH_2)_4O_2CCH_3$ (67, 61)	155
	(*i*-$C_3H_7)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	1. *n*-C_4H_9Li, reflux 2. CH_3CO_2H, reflux 3. NaOH	*i*-$C_3H_7CH{=}C(C_5H_{11}\text{-}n)CH_2CHOHCH_3$ (*E*)-(–, 70)	162
	(*n*-$C_4H_9)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	"	*n*-$C_4H_9CH{=}C(C_5H_{11}\text{-}n)(CH_2)_2OH$ (*E*)-(–, 74)	162
	(*i*-$C_3H_7)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	*n*-C_4H_9Li, reflux; [O]	*i*-$C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHCH_3$ (–, 72)	162
	(*n*-$C_4H_9)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	"	*n*-$C_4H_9COCH(C_5H_{11}\text{-}n)(CH_2)_2OH$ (–, 74)	162
14	Cyclopentene, $CH_2{=}CH(CH_2)_4O_2CCH_3$	ThexylBH_2	CO, 70 atm, 50°, H_2O; [O]	$C_5H_9CO(CH_2)_6O_2CCH_3$ (79, 73)	155
	n-$C_6H_{13}CH{=}CH_2$, $HC\equiv CCH_2Cl$, C_2H_5CHO (2 eq)	Thexyl$BHCl$	*n*-C_4H_9Li (2 eq), −78°; [O]	*n*-$C_8H_{17}C\equiv CCH_2CHOHC_2H_5$ (–, 76)	134
	(*i*-$C_3H_7)_3B$, $HC\equiv CCH_2Cl$, C_2H_5	—	1. *n*-C_4H_9Li, reflux 2. CH_3CO_2H, reflux 3. NaOH	*i*-$C_3H_7CH{=}C(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (*E*)-(–, 98)	66
	", ", "	—	*n*-C_4H_9Li, reflux; [O]	*i*-$C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (–, 72)	162
	(*n*-$C_5H_{11})_3B$, furan	—	1. *n*-C_4H_9Li, ether 2. CH_3CO_2H; [O]	$(n\text{-}C_5H_{11})_2COHCH{=}CHCH_2OH$ (*E*)-(100, –)	23
15	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, C_6H_5CHO	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHC_6H_5$ (–, 86)	134
	Cyclopentene, , NaCN	ThexylBH_2	TFAA, −78 to 20°; [O]	 (–, 80)	297
	(*i*-$C_3H_7)_3B$, $C_6H_5C\equiv CH$, C_2H_5	—	1. *n*-C_4H_9Li, reflux 2. CH_3CO_2H, reflux 3. NaOH	*i*-$C_3H_7CH{=}C(C_6H_5)CH_2CHOHC_2H_5$ (–, 51)	162
	", ", "	—	*n*-C_4H_9Li, reflux; [O]	*i*-$C_3H_7COCH(C_6H_5)CH_2CHOHC_2H_5$ (–, 59)	162
	$C_6H_5SCH(C_4H_9\text{-}n)B$	—	LDA, then H^+	$C_6H_5SCH(C_4H_9\text{-}n)CO(CH_2)_3OH$ (50, –)	298
	$(C_5H_9)_3B$, $HC\equiv CCH_2Cl$, $C_6H_{11}CHO$	—	*n*-C_4H_9Li, −78°; [O]	$C_5H_9C\equiv CCH_2CHOHC_6H_{11}$ (–, 88)	134
	n-$C_6H_{13}B$, $HC\equiv CC_5H_{11}$-*n*	—	1. *n*-C_6H_{14}, 0° 2. CH_3SOCl; [O]	 (–, 23)	299
	,	—	"	" (–, 24)	299
	(*n*-$C_4H_9)_3B$, ", C_2H_5	—	1. *n*-C_4H_9Li, reflux 2. CH_3CO_2H, reflux 3. NaOH	*n*-$C_4H_9CH{=}C(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (*E*)-(–, 75)	162
	", ", "	—	*n*-C_4H_9Li, reflux; [O]	*n*-$C_4H_9COCH(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (–, 53)	162
17	Cyclopentene, , NaCN	ThexylBH_2	1. TFAA, −78 to 20° 2. MCPBA, 0°	 (–, 80)	297
	$(C_6H_{11})_2BH$, $C_6H_5CO_2CH_2CH{=}CH_2$	—	CO, 45°, H_2O; [O]	$C_6H_5CO_2(CH_2)_3COC_6H_{11}$ (–, 43)	153
	(*n*-$C_4H_9)_3B$, $HC\equiv CC_5H_{11}$-*n*, 	—	*n*-C_4H_9Li, reflux; [O]	 (–, 19)	162
	(*n*-$C_6H_{13})_3B$, $HC\equiv CC_6H_{13}$-*n*, 	—	*n*-C_4H_9Li, reflux; [O]	*n*-$C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CHOHCH_3$ (–, 66)	162

TABLE I. ALCOHOLS. D. FOUR-OR-MORE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
18	$(i\text{-}C_3H_7)_3B$, $HC{\equiv}CC_5H_{11}\text{-}n$, C_6H_5	—	"	$i\text{-}C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHC_6H_5$ (−, 65)	162
19	$n\text{-}C_3H_7CH{=}CH_2$, $CH_2{=}CH(CH_2)_9O_2CCH_3$	$\text{Thexyl}BH_2$	CO, 70 atm, 50°, H_2O; [O]	$n\text{-}C_5H_{11}CO(CH_2)_{11}O_2CCH_3$ (42, —)	155
	$(n\text{-}C_4H_9)_3B$, $HC{\equiv}CC_5H_{11}\text{-}n$, C_2H_5	—	1. $n\text{-}C_4H_9Li$, reflux 2. NaOH, I_2	$(n\text{-}C_4H_9)_2C{=}C(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (−, 34)	162
25	$(C_2H_5)_3B$, 	—	NaOH, H_2O_2	 (−, 32)	300
	$(C_6H_{11})_2BH$, $C_6H_5CO_2(CH_2)_9CH{=}CH_2$	—	CO, 45°, H_2O; [O]	$C_6H_5CO_2(CH_2)_{11}COC_6H_{11}$ (−, 61)	153
27	$(n\text{-}C_4H_9)_3B$, 	—	$i\text{-}C_3H_7OH$; [O]	 (−, 40)	300
	", ", 	—	NaOH, H_2O_2	 (−, 34)	300
	$(i\text{-}C_4H_9)_3B$, ", "	—	NaOH, H_2O_2	" (−, 32)	300

[a] The abbreviation [O] after the semicolon indicates oxidation of an intermediate organoborane with alkaline hydrogen peroxide.

TABLE I. ALCOHOLS. E. MISCELLANEOUS PREPARATIONS

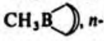
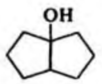
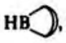
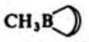
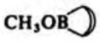
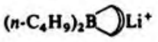
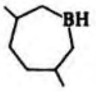
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
3	$BrCH_2C{\equiv}CH$	9-BBN, 2 eq	NaOH; [O]	Cyclopropanol (—, 65)	94
4	$TsO(CH_2)_2C{\equiv}CH$	"	CH_3Li; [O]	Cyclobutanol (—, 65)	94
	$CH_2{=}CH_2$, CH_3OCHCl_2	BH_3-THF	CH_3Li (3 eq); [O]	$CH_3CHOHC_2H_5$ (50, —)	120
5	, n-C_4H_9Br	—	LTMP, C_6H_6; [O]	n-$C_5H_{11}OH$ (—, 42)	97
6	$CH_3CH{=}CH_2$, CH_3OCHCl_2	BH_3-THF	CH_3Li (10 eq); [O]	$C_2H_5CHOHC_3H_7$-n (45, —)	120
	$(C_2H_5)_3B$	—	Br_2, $h\nu$, CH_2Cl_2, H_2O; [O]	$C_2H_5COH(CH_3)C_2H_5$ (88, —)	24
	"	—	1. $NaBrO_3$ (0.7 eq), CH_2Cl_2, H_2O 2. HBr (0.5 eq); [O]	" (92, —)	146
	"	—	NBS (2.2 eq), CH_2Cl_2, H_2O; [O]	" (97, —)	146
8		—	Br_2, H_2O; [O]	 (—, —)	147
	, $CH_2{=}CH_2$	—	1. CH_3Li, C_5H_{12}, −78° 2. CH_3COCl, 0°; [O]	" (—, 75)	275
		—	Br_2, H_2O; [O]	" (88–94, —)	147
		—	Br_2, CH_2Cl_2, H_2O; [O]	" (65, 55)	28
		—	H_2O_2, C_2H_5OH, C_5H_{12}	" (66, —)	301
	n-$C_3H_7C{\equiv}CH$, $CH_2{=}CHCH_2Br$		CH_3Li, 0° to reflux; [O]	n-$C_4H_9CHOHCH_2CH{=}CH_2$ (—, 84)	302

TABLE I. ALCOHOLS. E. MISCELLANEOUS PREPARATIONS (*Continued*)

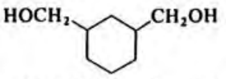
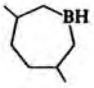
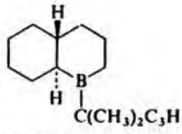
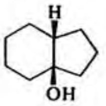
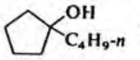
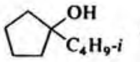
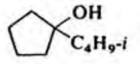
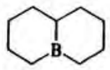
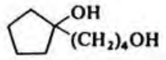
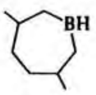
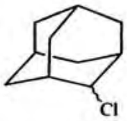
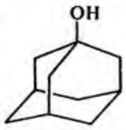
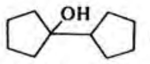
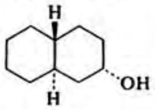
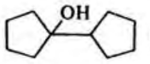
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CH$	—	H_2, Pt, 130°; [O]	 (—, 53)[b]	303
	$C_2H_5CH{=}CH_2$	BH_2Cl-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	n-$C_4H_9CHOHC_3H_7$-n (43, —)	25
	n-$C_3H_7C{\equiv}CH$, i-C_3H_7Br		CH_3Li, 0° to reflux; [O]	n-$C_4H_9CHOHC_3H_7$-i (—, 70)	302
	$(n\text{-}C_4H_9)_3B$	—	1. $CBrCl_3$ (0.5 eq), $h\nu$, CH_2Cl_2 2. H_2O; [O]	n-$C_4H_9CHOHC_3H_7$-n (60, —)	144
	$(s\text{-}C_4H_9)_3B$	—	1. $NaBrO_3$ (0.35 eq), CH_2Cl_2, H_2O 2. HBr (0.5 eq); [O]	s-$C_4H_9COH(CH_3)C_2H_5$ (83, —)	146
	"	—	NBS (1.1 eq), CH_2Cl_2, H_2O; [O]	" (85, —)	146
	"	—	Br_2, $h\nu$, CH_2Cl_2, H_2O; [O]	" (86, —)	24
9		—	Br_2, CH_2Cl_2, H_2O; [O]	 (60, —)	27
	Cyclopentene, $CH_2{=}CHC_2H_5$	ThexylBH_2	1. Br_2, CH_2Cl_2, H_2O 2. NaOH, C_2H_5OH 3. H_2O_2, reflux	 (85, —)	26
	", $CH_2{=}C(CH_3)_2$	"	"	 (82, 70)	26
	n-$C_6H_{13}C{\equiv}CH$, CH_3I	Sia_2BH	LTMP; [O]	n-$C_5H_{11}CH{=}CHCHOHCH_3$ (70, —)	277
	$C_5H_9(C_4H_9\text{-}i)BC(CH_3)_2C_3H_7$-$i$	—	1. $NaBrO_3$ (0.35 eq), CH_2Cl_2, H_2O 2. HBr (0.5 eq); [O]	 (80, —)	146
	"	—	NBS (1.1 eq), CH_2Cl_2, H_2O; [O]	" (82, —)	146
		—	Br_2, CH_2Cl_2, H_2O; [O]	 (50, —)	28
	i-$C_3H_7C{\equiv}CH$, n-C_4H_9Br		CH_3Li, 0° to reflux; [O]	i-$C_4H_9CHOHC_4H_9$-n (—, 69)	302
	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CCH_2OSi(CH_3)_3$	—	1. H_2, heat, CH_3OH 2. H_2; [O]	$CH_3CH(CH_2OH)CH_2CH(CH_2OH)C_3H_7$-$n$ (—, 36)[b]	304
10	", $HC{\equiv}CCH_2Cl$	—	1. 130°, CH_3OH, B_2H_6 2. CO, 70 atm, 150°, EG; [O]	 (—, —)	305
	", ", KCN	—	1. 130°, CH_3OH, B_2H_6, ether 2. TFAA; [O]	 (—, —)	305
	Cyclopentene	BH_2Cl-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	 (97, 75)	25
		BH_3-THF	[O]	 (—, 42)	306
	$(C_5H_9)_3B$, CH_3OCHCl_2	—	CH_3Li (3 eq), ether; [O]	 (51, —)	120

TABLE I. ALCOHOLS. E. MISCELLANEOUS PREPARATIONS (*Continued*)

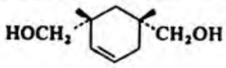
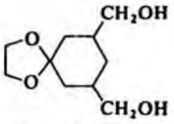
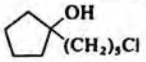
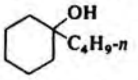
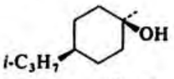
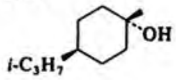
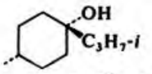
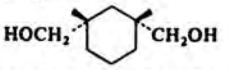
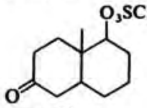
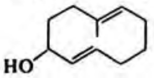
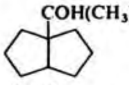
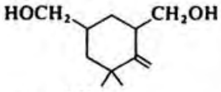
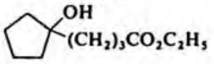
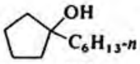
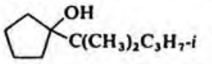
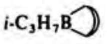
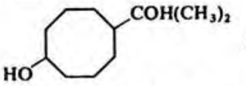
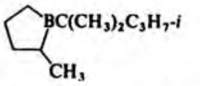
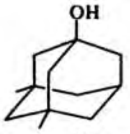
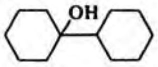
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(CH_2{=}C(CH_3)CH_2)_3B$, $HC{\equiv}CH$	—	CH_3OH, 140–150°; [O]	 (−, 62)^b	307
	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}COCH_3$	—	1. CH_3OH, 170–180° 2. EG, 100°; [O]	 (−, 29)^b	308
	Cyclopentene, $CH_2{=}CH(CH_2)_3Cl$	ThexylBH$_2$	1. Br_2, CH_2Cl_2, H_2O 2. C_2H_5OH; [O]	 (89, —)	26
	Cyclohexene, $CH_2{=}CHC_2H_5$	"	"	 (51, —)	26
	$(CH_3)_2C{=}CH(CH_2)_2COH(CH_3)CH{=}CH_2$	BH$_3$-THF	1. KOH, CH_3OH 2. $AgNO_3$	 (36, —),  (36, —)	234
	$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OAc$	"	1. Br_2, *hv*, CH_2Cl_2, H_2O, 0° 2. CH_3OH; [O]	 (—, 93)	309
	$(CH_2{=}C(CH_3)CH_2)_3B$, $HC{\equiv}CH$	—	1. CH_3OH, 140–150° 2. H_2, Ni, 100°; [O]	 (—, 37)^e	307
	$(CH_3)_2C{=}CHCH_3$	BH$_3$-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	$i\text{-}C_3H_7CH(CH_3)COH(CH_3)C_3H_7\text{-}i$ (87, 82)	25
	$n\text{-}C_3H_7CH{=}CH_2$, CH_3OCHCl_2	"	CH_3Li (10 eq); [O]	$n\text{-}C_4H_9CHOHC_5H_{11}\text{-}n$ (54, —)	120
11	$(CH_2{=}CHCH_2)_3B$, $(CH_3)_2C{=}C{=}CHCl$	—	CH_3OH; [O]	$CH_2{=}CH(CH_2)_2CHOHCH_2C(CH_3)_2C{\equiv}CH$ (—, 64)^b	310
		BH$_3$-THF	CH_3ONa, CH_3OH	 (—, 60)	311
		—	1. CH_3Li, 2. [O], EG 3. [O]	 (—, 62)	275
	$(CH_2{=}CHCH_2)_3B$, $CH_2{=}C{=}C(CH_3)_2$	—	CH_3OH, heat; [O]	 (—, 41)^b	312
	Cyclopentene, $CH_2{=}CHCH_2CO_2C_2H_5$	ThexylBH$_2$	1. Br_2, CH_2Cl_2, H_2O 2. NaOH, C_2H_5OH; [O]	 (90, 72)	26
	", $CH_2{=}CHC_4H_9\text{-}n$	"	"	 (94, 82)	26
	", $(CH_3)_2C{=}C(CH_3)_2$	BH$_3$-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	 (34, —)	25
		—	Br_2, CH_2Cl_2, H_2O; [O]	 (—, —)	313
		—	"	$i\text{-}C_3H_7C(CH_3)_2COH(CH_3)(CH_2)_3OH$ (55, —)	27
12	$[CH_2{=}C(CH_3)CH_2]_3B$, $CH_2{=}C{=}CH_2$	—	1. CH_3OH, 160–170° 2. $(C_2H_5)_2B_2H_4$, ether 3. CO, 65 atm, 100° 4. 140°; [O]	 (29, —)^b	269
	Cyclohexene	BH$_3$-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	 (94, 88)	25

TABLE I. ALCOHOLS. E. MISCELLANEOUS PREPARATIONS (*Continued*)

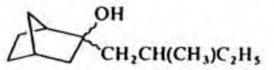
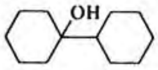
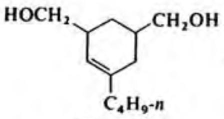
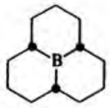
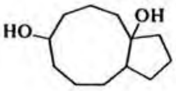
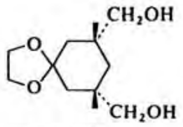
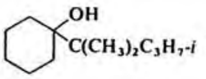
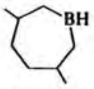
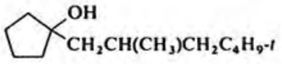
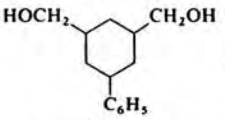
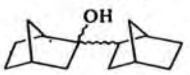
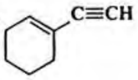
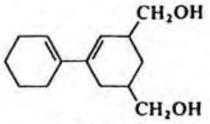
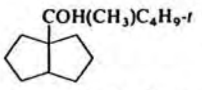
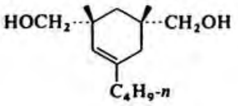
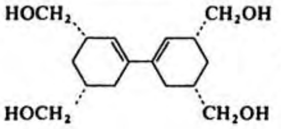
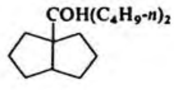
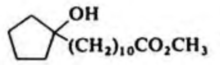
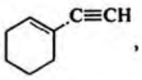
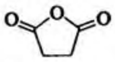
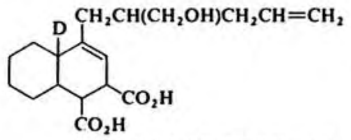
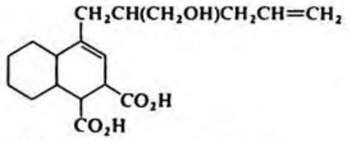
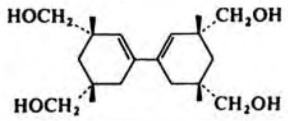
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	, $CH_2=C(CH_3)C_2H_5$	ThexylBH$_2$	Br_2, *hv*, H_2O; [O]	 (78, 62)	145
	$(C_6H_{11})_2BOH$	—	1. $NaBrO_3$ (0.35 eq), CH_2Cl_2, H_2O 2. HBr (0.5 eq); [O]	 (95, —)	146
	"	—	NBS (1.1 eq), CH_2Cl_2, H_2O; [O]	" (98, —)	146
	$(C_6H_{11})_3B$	—	Br_2, *hv*, CH_2Cl_2, H_2O; [O]	" (89, —)	24
	$(CH_2=CHCH_2)_3B$, $HC\equiv CC_4H_9$-*n*	—	CH_3OH, 130–140°; [O]	 (—, 53)^b	314
		—	Br_2, CH_2Cl_2, H_2O; [O]	 (70, —)	28
	$[CH_2\equiv C(CH_3)CH_2]_3B$, $HC\equiv COCH_3$	—	EG; [O]	 (—, —)	315
	Cyclohexene, $(CH_3)_2C=C(CH_3)_2$	BH_3-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	 (57, 39)	25
	$(n\text{-}C_4H_9)_3B$	—	1. $NaBrO_3$ (0.35 eq), Br_2, CH_2Cl_2, H_2O 2. HBr (0.5 eq); [O]	*n*-$C_4H_9COH(C_3H_7$-*n*$)C_4H_9$-*n* (76, —)	146
	"	—	Br_2, CH_2Cl_2, H_2O; [O]	" (76, —)	24
	"	—	NBS (2.2 eq), CH_2Cl_2, H_2O; [O]	" (78, —)	146
	$(s\text{-}C_4H_9)_3B$	—	Br_2 (2 eq), CH_2Cl_2, H_2O; [O]	$C_2H_5COH(CH_3)C(CH_3)(C_2H_5)C_4H_9$-*s* (46, —)	24
	"	—	NBS (2.2 eq), CH_2Cl_2, H_2O; [O]	" (62, —)	146
13	*t*-$C_4H_9C\equiv CH$, $C_6H_5CH_2Cl$		CH_3Li, 0° to reflux; [O]	$C_6H_5CH_2CHOHCH_2C_4H_9$-*t* (—, 69)	302
	Cyclopentene, $CH_2=C(CH_3)CH_2C_4H_9$-*t*	ThexylBH$_2$	Br_2, *hv*, H_2O; [O]	 (88, 75)	145
14	$(CH_2=CHCH_2)_3B$, $C_6H_5C\equiv CH$	—	CH_3OH, H_2, Pd-$SrCO_3$; [O]	 (—, 67)^b	316
		BH_2Cl-THF	CH_3OH, Br_2, CH_2Cl_2, H_2O; [O]	 (—, 68)	25
	$(CH_2=CHCH_2)_3B$, 	—	CH_3OH, heat; [O]	 (—, 56)^b	317
	CH_3B, LiC_4H_9-*t*	—	—	 (—, 41)	275
	$[CH_2=C(CH_3)CH_2]_3B$, $HC\equiv CC_4H_9$-*n*	—	1. 140–150° 2. CH_3OH; [O]	 (—, 64)^e	307

TABLE I. ALCOHOLS. E. MISCELLANEOUS PREPARATIONS (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
16	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CC{\equiv}CH$	—	1. 120–150° 2. CH_3OH; [O]	 (—, —)	318
17	$n\text{-}C_4H_9B$, $LiC_4H_9\text{-}n$	—	1. Pentane, −78° 2. CH_3COCl, 0° 3. CO, 60 atm, 150°; [O]	 (—, 87)	275
	Cyclopentene, $CH_2{=}CH(CH_2)_8CO_2CH_3$	ThexylBH_2	1. Br_2, CH_2Cl_2, H_2O 2. NaOH, C_2H_5OH; [O]	 (—, 75)	26
18	$(CH_2{=}CHCH_2)_3B$, , 	—	1. CH_3OH, 0° 2. H_2, Pt black 3. CH_3OD, CD_3CO_2D CD_3CO_2D; [O]	 (—, —)	319
	", ", "	—	1. CH_3OH, 0° 2. CH_3OH, CH_3CO_2H; [O]	 (—, 8)[b]	319
20	$[CH_2{=}C(CH_3)CH_2]_3B$, $HC{\equiv}CC{\equiv}CH$	—	1. 120–150° 2. CH_3OH; [O]	 (—, —)	318

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The yield is not given in the original paper. The yield in the table is determined by multiplication of the yields in intermediate steps.

TABLE II. ETHERS. A. DIRECT FUNCTIONALIZATION

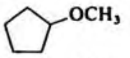
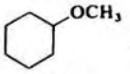
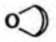
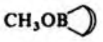
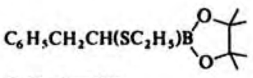
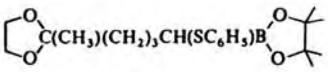
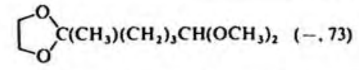
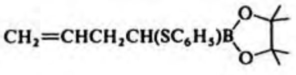
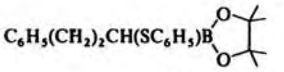
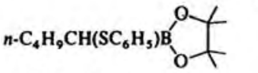
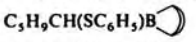
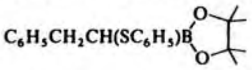
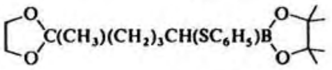
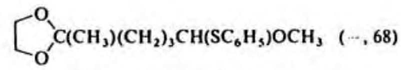
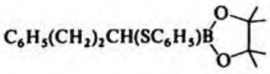
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	Cyclopentene	BH_3-THF	1. $NaOCH_3$, $NaClO_4$, CH_3OH 2. Electrolysis; [O]	 (95, –)	102
	n-$C_3H_7CH{=}CH_2$	"	"	n-$C_5H_{11}OCH_3$ (83, –)	102
	$C_2H_5C(CH_3){=}CH_2$	"	"	$C_2H_5CH(CH_3)CH_2OCH_3$ (102, –)	102
7	Cyclohexene	"	"	 (92, –)	102
	$C_2H_5CHClC{\equiv}CH$	CATBH	1. H_2O 2. $NaOCH_3$, CH_3OH 3. Br_2 (2 eq), –78°	$C_2H_5CHClCHBrCH(OCH_3)_2$ (82, –)	148
	n-$C_4H_9CH{=}CH_2$	BH_3-THF	1. $NaOCH_3$, $NaClO_4$, CH_3OH 2. Electrolysis; [O]	n-$C_6H_{13}OCH_3$ (104, –)	102
8		–	Br_2, H_2O; [O]	 (–, –)	147
		–	1. I_2 2. $NaOCH_3$, CH_3OH; [O]	" (60–85, –)	220
	n-$C_4H_9C{\equiv}CH$	CATBH	1. H_2O 2. $NaOCH_3$, CH_3OH 3. Br_2 (2 eq), –78°	n-$C_4H_9CHBrCH(OCH_3)_2$ (82, –)	148
	t-$C_4H_9C{\equiv}CH$	CATBH	"	t-$C_4H_9CHBrCH(OCH_3)_2$ (49, –)	148
9	n-$C_6H_{13}CH{=}CH_2$	BH_3-THF	1. $NaOCH_3$, $NaClO_4$, CH_3OH 2. Electrolysis; [O]	n-$C_8H_{17}OCH_3$ (84, –)	102
10		–	1. $(C_2H_5)_3N$, CH_3OH 2. NCS (2 eq)	$C_6H_5CH_2CH(OCH_3)_2$ (–, 83)	320
	$C_6H_{11}C{\equiv}CH$	CATBH	1. H_2O 2. $NaOCH_3$, CH_3OH 3. Br_2 (2 eq), –78°	$C_6H_{11}CHBrCH(OCH_3)_2$ (81, –)	148

TABLE II. ETHERS. A. DIRECT FUNCTIONALIZATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
		—	1. $(C_2H_5)_3N$, CH_3OH 2. NCS (2 eq)	 (—, 73)	320
	n-$C_6H_{13}CH{=}CH_2$	CATBH	1. H_2O 2. $NaOCH_3$, CH_3OH 3. Br_2 (2 eq), −78°	n-$C_6H_{13}CHBrCH(OCH_3)_2$ (82, 65)	148
11		—	1. $(C_2H_5)_3N$, CH_3OH 2. NCS	$CH_2{=}CHCH_2CH(SC_6H_5)OCH_3$ (—, 65)	320
		—	1. $(C_2H_5)_3N$, CH_3OH 2. NCS (2 eq)	$C_6H_5(CH_2)_2CH(OCH_3)_2$ (—, 79)	320
12		—	1. $(C_2H_5)_3N$, CH_3OH 2. NCS	n-$C_4H_9CH(SC_6H_5)OCH_3$ (—, 69)	320
	n-$C_4H_9CH(SC_6H_5)B(C_4H_9$-n$)_2$	—	"	" (—, 71)	320
13		—	"	$C_5H_9CH(SC_6H_5)OCH_3$ (—, 60)	320
	$C_5H_9CH(SC_6H_5)B(C_5H_9)_2$	—	"	" (—, 74)	320
15		—	"	$C_6H_5CH_2CH(SC_6H_5)OCH_3$ (—, 72)	320
		—	"	 (—, 68)	320
16		—	"	$C_6H_5(CH_2)_2CH(SC_6H_5)OCH_3$ (—, 66)	320

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE II. ETHERS. B. ONE-CARBON HOMOLOGATION

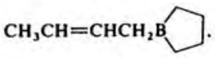
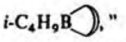
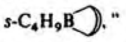
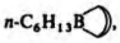
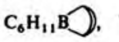
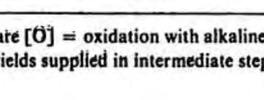
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}COCH_3$	—	$C_9H_{19}OH$	$CH_2{=}CHCH_2C(OCH_3){=}CH_2$ (—, 74)[b]	321
7	", $HC{\equiv}COC_2H_5$	—	"	$CH_2{=}CHCH_2C(OC_2H_5){=}CH_2$ (—, 70)[b]	321
	$(n\text{-}C_3H_7)_3B$, furan	—	1. $n\text{-}C_4H_9Li$, ether, −20° 2. I_2, −78°; [O]	2-*n*-Propylfuran (64, —)	322
8	, $HC{\equiv}COC_2H_5$	—	$C_9H_{19}OH$, −20°	$CH_2{=}CHCH(CH_3)C(OC_2H_5){=}CH_2$ (—, 77)	323
	$(CH_3CH{=}CHCH_2)_3B$, "	—	$C_9H_{19}OH$	" (—, —)	321
	$[CH_2{=}C(CH_3)CH_2]_3B$, "	—	1. −70°	$CH_2{=}C(CH_3)CH_2C(OC_2H_5){=}CH_2$ (—, 98)	324
	", "	—	2. CH_3OH	$CH_2{=}C(CH_3)CH_2C(OCH_3)_2CH_3$ (—, 60)	324
	$(i\text{-}C_4H_9)_3B$, furan	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	2-Isobutylfuran (76, —)	325
	, "	—	"	" (82, —)	325
	$(s\text{-}C_4H_9)_3B$, "	—	"	2-*s*-Butylfuran (70, —)	325
	, "	—	"	" (67, —)	325
	$(n\text{-}C_4H_9)_3B$, "	—	1. $n\text{-}C_4H_9Li$, ether, −20° 2. I_2, −78°; [O]	2-*n*-Butylfuran (76, —)	322
	$(i\text{-}C_4H_9)_3B$, "	—	"	2-Isobutylfuran (92, —)	322
	$(s\text{-}C_4H_9)_3B$, "	—	"	2-*s*-Butylfuran (84, 65)	322
9	$(C_5H_9)_3B$, "	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	2-Cyclopentylfuran (73, —)	325
	, "	—	"	" (73, —)	325
	$(C_5H_9)_3B$, "	—	1. $n\text{-}C_4H_9Li$, ether, −20° 2. I_2, −78°; [O]	" (95, —)	322
	$(n\text{-}C_4H_9)_3B$, 2-methylfuran	—	"	2-Methyl-5-*n*-butylfuran (21, —)	322
	$(i\text{-}C_4H_9)_3B$, "	—	"	2-Methyl-5-isobutylfuran (83, —)	322
	$(s\text{-}C_4H_9)_3B$, "	—	"	2-Methyl-5-*s*-butylfuran (97, 71)	322

TABLE II. ETHERS. B. ONE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	(n-$C_6H_{13})_3B$, furan	—	1. n-C_4H_9Li, −25° 2. NCS; EA	2-n-Hexylfuran (82, —)	325
	, "	—	"	" (72, 51)	325
	$(C_6H_{11})_3B$, "	—	"	2-Cyclohexylfuran (74, —)	325
	, "	—	"	" (74, —)	325
	(n-$C_6H_{13})_3B$, "	—	1. n-C_4H_9Li, ether, −20° 2. I_2, −78°; [O]	2-n-Hexylfuran (66, —)	322
	$(C_5H_9)_3B$, 2-methylfuran	—	"	2-Methyl-5-cyclopentylfuran (93, —)	322
11	$(C_6H_5CH_2)_3B$, $HC{\equiv}COC_2H_5$	—	$C_9H_{19}OH$	o-$CH_3C_6H_4C(OC_2H_5){=}CH_2$ (—, 79)	321,323
	(n-$C_6H_{13})_3B$, 2-methylfuran	—	1. n-C_4H_9Li, ether, −20° 2. I_2, −78°; [O]	2-Methyl-5-n-hexylfuran (26, —)	322
25	(n-$C_4H_9)_3B$, p-$O_2NC_6H_4CHO$ (2 eq), C_6H_5NC	—	Ether	 (—, 66)	326
	(n-$C_4H_9)_3B$, p-ClC_6H_4CHO (2 eq), C_6H_5NC	—	Ether	(—, 72)	326
	(n-$C_4H_9)_3B$, C_6H_5CHO (2 eq), C_6H_5NC	—	Ether	(—, 72)	326

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[a] Reagents after the semicolon are those used to decompose an intermediate organoborane; abbreviations are [O] = oxidation with alkaline hydrogen peroxide, EA = ethanolamine.

[b] The yield is not given in the original paper. The yield in the table is determined by multiplication of the yields supplied in intermediate steps.

TABLE II. ETHERS. C. THREE-CARBON HOMOLOGATION

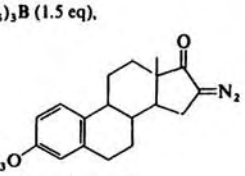
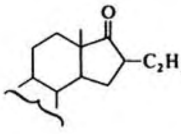
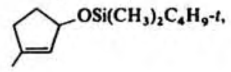
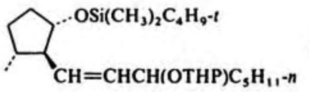
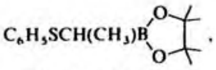
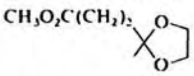
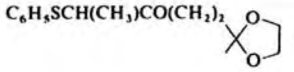
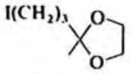
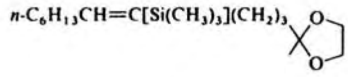
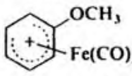
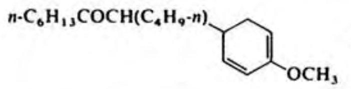
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	$(C_2H_5)_3\bar{B}H\ Na^+$, $HC{\equiv}CCH_3$, CH_3OCH_2Cl	—	1. Ether 2. H_2O	$C_2H_5CH{=}C(CH_3)CH_2OCH_3$ (*Z*)-(—, 83)	149
	", ", "	—	1. Ether 2. AcOH	" (*E*)-(—, 95)	149
21	$(C_2H_5)_3B$ (1.5 eq), 	—	H_2O	 (82, —)	327
	 $BrC{\equiv}CCH(OTHP)C_5H_{11}$-*n*	ThexylBH$_2$	1. $NaOCH_3$, CH_3OH, 0° 2. $Ag(NH_3)_2NO_3$, (5 eq), 75–80°	 (—, —)	30

TABLE II. ETHERS. D. FOUR-OR-MORE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
15	 	–	1. LDA 2. H^+	 (66, --)	298
18	n-$C_6H_{13}C{\equiv}CSi(CH_3)_3$, 	DCHB	1. CH_3Li, ether 2. CuI, –30° 3. $P(OC_2H_5)_3$, HMPT; [O]	 (*Z*)-(–, 41) (*E*)-(–, 5)	328
19	$(n\text{-}C_6H_{13})_3B$, $LiC{\equiv}CC_4H_9$-n, 	--	1. $(CH_3)_3NO$ (excess) 2. Ce^{4+}	 (—, 46)	166
20	p-$CH_3OC_6H_4CH{=}CHCH_3$	BH_3-DG	1. KOH, H_2O 2. $AgNO_3$	p-$CH_3OC_6H_4CH(C_2H_5)CH(C_2H_5)C_6H_4OCH_3$-$p$ (–, 35–50)	232
24	$(n\text{-}C_3H_7)_3B$, $HC{\equiv}CSi(CH_3)_3$, $TsO(CH_2)_2C{\equiv}C(CH_2)_4OTHP$	--	1. n-C_4H_9Li, –78° 2. I_2, NaOH, 0°	$(n\text{-}C_3H_7)_2C{=}C[Si(CH_3)_3](CH_2)_2C{\equiv}C(CH_2)_4OTHP$ (–, 71)	329

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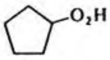
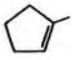
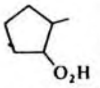
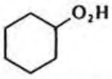
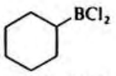
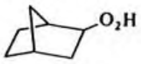
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE III. ORGANIC PEROXIDES

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	$C_2H_5CH{=}CH_2$	BH_3-THF	1. O_2, −78° 2. H_2O_2, C_6H_{14}, 0°	n-$C_4H_9O_2H$ (92, —)[a]	112
	$CH_3CH{=}CHCH_3$	"	"	$C_2H_5CH(CH_3)O_2H$ (91, —)[a]	112
5	Cyclopentene	"	"	 (95, —)[a]	112
6		"	"	 (91, —)[a]	112
	Cyclohexene	"	"	 (95, —)[a]	112
		—	1. O_2, ether, −18° 2. H_2O	" (93, —)[a]	150
	n-$C_3H_7C(CH_3){=}CH_2$	BH_3-THF	1. O_2, −78° 2. H_2O_2, C_6H_{14}, 0°	n-$C_3H_7CH(CH_3)CH_2O_2H$	112
	n-$C_6H_{13}BCl_2$	—	1. O_2, ether, −18° 2. H_2O	n-$C_6H_{13}O_2H$ (94, —)[a]	150
	n-$C_3H_7CH(CH_3)CH_2BCl_2$	—	"	n-$C_3H_7CH(CH_3)CH_2O_2H$ (84, —)[a]	150
	n-$C_3H_7CH(C_2H_5)BCl_2$	—	"	n-$C_3H_7CH(C_2H_5)O_2H$ (93, —)[a]	150
7		BH_3-THF	1. O_2, −78° 2. H_2O_2, C_6H_{14}, 0°	 (84, —)[a]	112
		—	1. O_2, ether, −18° 2. H_2O	" (91, —)[a]	150
8	n-$C_6H_{13}CH{=}CH_2$	BH_3-THF	1. O_2, −78° 2. H_2O_2, C_6H_{14}, 0°	n-$C_8H_{17}O_2H$ (81, —)[a]	112

[a] The yield was determined by iodimetric titration.

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION

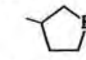
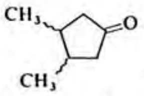
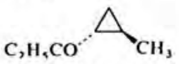
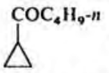
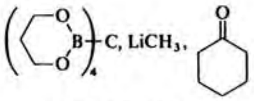
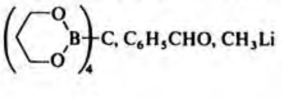
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	$(C_2H_5)_2BC_6H_{11}$, NaCN	—	TFAA; [O]	Diethyl ketone (—, —)	289
	", "	—	1. DG 2. TFAA 3. MCPBA	" (55, 55)	290
6	$CH_2{=}CHCH_2CH{=}CH_2$, CH_3OCHCl_2	BH_2Cl	CH_3OH, $LiOC(C_2H_5)_3$; [O]	Cyclohexanone (57, —)	160
	", "	ThexylBH_2	CO, H_2O (high pressure), 50°; [O]	2-Methylcyclopentanone (61, —)	157
	$CH_2{=}C(CH_3)CH{=}CH_2$	"	"	3-Methylcyclopentanone (46, —)	157
	$HC{\equiv}C(CH_2)_2OTs$, $(C_2H_5)_3B$,	—	n-C_4H_9Li, −78°; [O]	Ethyl cyclopropyl ketone (—, 55-74)	95
	$BC(CH_3)_2C_3H_7$-*i*	—	CO, H_2O (high pressure), 50°; [O]	3-Methylcyclopentanone (86, —)	157
	$CH_3CH{=}CHCH_3$, $CH_2{=}CHOCH_3$	BH_3-DMS	t-C_4H_9Li, −78° to room temp; [O]	*s*-Butyl methyl ketone (75, —)	125
	$CH_3CH{=}CHCH_2B$, $HC{\equiv}COC_2H_5$	—	1. −20° 2. H_2, Pt 3. H_2O	" (—, —)	323
	$(n$-$C_4H_9)_3B$, $LiC{\equiv}CH$	—	HCl, −78°; [O]	*n*-Butyl methyl ketone (78, —)	42
	$(i$-$C_4H_9)_3B$, "	—	"	Isobutyl methyl ketone (90, —)	42
	", $CH_2{=}CHOCH_3$	—	t-C_4H_9Li, −78° to room temp; [O]	" (91, —)	125
7	Cyclopentene, "	BH_3-DMS	"	$C_5H_9COCH_3$ (83, —)	125
	$CH_2{=}CH(CH_2)_2CH{=}CH_2$	ThexylBH_2	CO, H_2O (high pressure), 50°; [O]	Cycloheptanone (62, —)	157
	", CH_3OCHCl_2	BH_2Cl	CH_3OH, $LiOC(C_2H_5)_3$, [O]	" (—, 67)	160
	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	ThexylBH_2	CO, H_2O (high pressure), 50°; [O]	 *cis*-(48, —) *trans*-(21, —)	157
	$(C_2H_5)_3B$, $LiC{\equiv}CCH_2CHOTsCH_3$	—	n-C_4H_9Li, −78°; [O]	 (71, —)	95
	$(C_5H_9)_3B$, $LiC{\equiv}CH$	—	HCl, −78°; [O]	$C_5H_9COCH_3$ (70, —)	42
	$CH_3SOCH_2\bar{B}(C_4H_9$-$n)_3Li^+$, $ClCO(CH_2)_2CO_2CH_3$	—	C_6H_{14}, THF	$CH_3SOCH_2CO(CH_2)_2CO_2CH_3$ (—, 61)	56
8	C_6H_5Br, CH_3COCl	BR_3[b]	n-C_4H_9Li, C_6H_6; [O]	Acetophenone (—, 75)	57
	Cyclohexene, $CH_2{=}CHOCH_3$	BH_3-DMS	t-C_4H_9Li, −78° to room temp; [O]	$C_6H_{11}COCH_3$ (97, —)	125
	$(C_2H_5)_3B$, $HC{\equiv}CC_4H_9$-n	—	1. n-C_4H_9Li 2. C_6H_5SeCl, −116°, ether 3. $(CH_3)_3NO$, H_2O 4. H_2O_2	$C_2H_5COCH{=}CHC_3H_7$-n (*E*)-(—, 71)	168
	$CH_2{=}CH(CH_2)_3CH{=}CH_2$, Cl_2CHOCH_3	BH_2Cl	CH_3OH, $LiOC(C_2H_5)_3$; [O]	Cyclooctanone (—, 49)	160
	$(n$-$C_4H_9)_3B$, $HC{\equiv}C(CH_2)_2OTs$	—	n-C_4H_9Li, −78°; [O]	 (—, 55-74)	95
		—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	$C_6H_{11}COCH_3$ (41, —)	330
	$(C_6H_{11})_3B$, $LiC{\equiv}CH$	—	HCl, −78°; [O]	" (77, —)	42
	n-$C_4H_9CH{=}CH_2$, $CH_2{=}CHOCH_3$	BH_3-DMS	t-C_4H_9Li, −78° to room temp; [O]	n-$C_6H_{13}COCH_3$ (82, —)	125
	$(C_2H_5)_3B$, $HC{\equiv}CC_4H_9$-n	—	1. n-C_4H_9Li, 0° 2. $(n$-$C_4H_9)_3SnCl$; [O]	Ethyl *n*-pentyl ketone (88, —)	167
9	p-$CF_3C_6H_4Br$, CH_3COCl	BR_3[b]	n-C_4H_9Li, C_6H_6; [O]	p-$CF_3C_6H_4COCH_3$ (—, 62)	57
	$CH_3SOCH_2B(C_4H_9$-$n)_3Li^+$, p-$O_2NC_6H_4COCl$	—	C_6H_{14}, THF	p-$O_2NC_6H_4COCH_2SOCH_3$ (—, 55)	56
		—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	Benzyl methyl ketone (75, —)	330

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

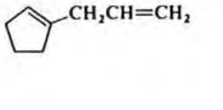
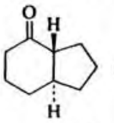
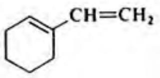
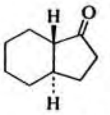
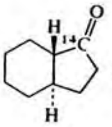
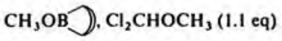
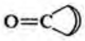
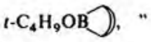
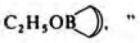
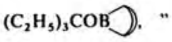
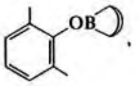
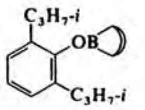
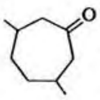
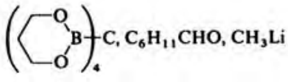
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$CH_3SOCH_2\bar{B}(C_4H_9\text{-}n)_3Li^+$, C_6H_5COCl	—	C_6H_{14}, THF	$C_6H_5COCH_2SOCH_3$ (—, 51)	56
	 $CH_2CH{=}CH_2$	ThexylBH_2	CO, 70 atm, 50°, H_2O; [O]	 (54, 40)	158
	 $CH{=}CH_2$	"	"	 (66, 60)	158 157
	"	"	^{14}CO, "	 (—, 50)	291
	 CH_3OB, Cl_2CHOCH_3 (1.1 eq)	—	$LiOC(C_2H_5)_3$ (2 eq); [O]	 $O{=}C$ (13, —)	40
	 $t\text{-}C_4H_9OB$, "	—	"	" (24, —)	40
	 C_2H_5OB, "	"	"	" (55, —)	40
	 $(C_2H_5)_3COB$, "	—	"	" (47, —)	40
		—	"	" (90, 87)	40
		—	$LiOC(C_2H_5)_3$; [O]	" (96, 70)	40
	Cyclopentene, $t\text{-}C_4H_9NC$, $LiC_3H_7\text{-}i$	BH_2Cl	TFAA, 0°; [O]	$C_5H_9COC_3H_7\text{-}i$ (44, —)	20
	Cyclohexene, $CH_2{=}CH_2$, NaCN	BH_3-THF	1. DG 2. TFAA 3. MCPBA	$C_6H_{11}COC_2H_5$ (76, —)	290
	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	BH_2Cl	CH_3OH, $LiOC(C_2H_5)_3$; [O]	2-*n*-Propylcyclohexanone (—, 41)	160
	$CH_2{=}C(CH_3)(CH_2)_2C(CH_3){=}CH_2$	"	"	 (—, 86)	160
	 C, $C_6H_{11}CHO$, CH_3Li	—	1. CH_3Li, −70° 2. CH_3I (2 eq) 3. $NaBO_3$, CH_2Cl_2	$C_6H_{11}CH_2COCH_3$ (76, —)	330
	$(C_6H_{11})_2BC_2H_5$, NaCN	—	TFAA; [O]	$C_6H_{11}COC_2H_5$ (—, —)	289
	$n\text{-}C_4H_9\bar{B}(C_5H_9)_3Li^+$, $ClCO(CH_2)_2CO_2CH_3$	—	C_6H_{14}, THF	$n\text{-}C_4H_9CO(CH_2)_2CO_2CH_3$ (76, —)	56
	$C_2H_5CH{=}CH_2$	BH_3-THF	CO, DG, H_2O; [O]	$(n\text{-}C_4H_9)_2CO$ (—, 85)	152
	$CH_3CH{=}CHCH_3$	"	"	$(s\text{-}C_4H_9)_2CO$ (—, 81)	152
	$C_2H_5CH{=}CH_2$, KCN	"	DG, $C_6H_5N{=}CClC_6H_5$; [O]	$(n\text{-}C_4H_9)_2CO$ (—, 86)	250
	", NaCN	"	1. CH_3SO_3H, DG 2. HCN; [O]	" (—, 65)	331
	", "	BH_3-DG	DG, HCN, −78°; [O]	" (, 65)	332
	", "	"	DG, C_6H_5COCl, 45°; [O]	" (—, 74)	332
	", "	"	DG, TFAA; [O]	" (—, 94)	332
	$n\text{-}C_4H_9CH{=}CH_2$, $t\text{-}C_4H_9NC$, C_2H_5Li	BH_2Cl	TFAA, 0°; [O]	$n\text{-}C_6H_{13}COC_2H_5$ (86, —)	20
	$(n\text{-}C_4H_9)_2BOCH_3$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$, (2 eq); [O]	$(n\text{-}C_4H_9)_2CO$ (96, —)	38
	$(s\text{-}C_4H_9)_2BOCH_3$, "	—	"	$(s\text{-}C_4H_9)_2CO$ (80, —)	38
	$(i\text{-}C_4H_9)_2BOCH_3$, "	—	"	$(i\text{-}C_4H_9)_2CO$ (86, —)	38
	$(n\text{-}C_4H_9)_3B$, $(C_6H_5S)_2CHC_4H_9\text{-}n$	—	$n\text{-}C_4H_9Li$, −30°; [O]	$(n\text{-}C_4H_9)_2CO$ (—, 76)	169
	$(n\text{-}C_4H_9)_2BOC_4H_9\text{-}n$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$; [O]	" (44, —)	38
	$(n\text{-}C_4H_9)_2BOC_4H_9\text{-}t$, "	—	"	" (57, —)	38

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

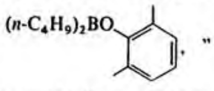
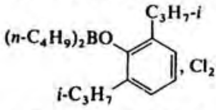
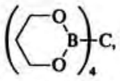
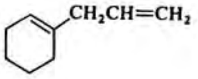
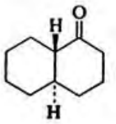
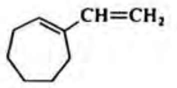
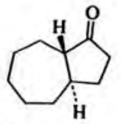
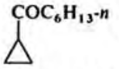
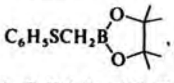
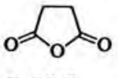
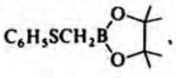
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_4H_9)_2BOC_6H_5$, "	—	"	" (31, —)	38
	$(n\text{-}C_4H_9)_2BC_6H_{11}$, NaCN	—	TFAA; [O]	" (—, —)	289
	$(n\text{-}C_4H_9)_2BOC(C_2H_5)_3$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$; [O]	" (64, —)	38
	, "	—	"	" (87, —)	38
	$(n\text{-}C_4H_9)_4\bar{B}Li^+$, $n\text{-}C_4H_9COCl$	—	C_6H_{14}, THF	" (53, —)	56
	, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$; [O]	" (80, —)	38
10	$(n\text{-}C_3H_7)_3B$, $p\text{-}ClC_6H_4COCl$	—	CH_3Li, CuCl, COD; [O]	$p\text{-}ClC_6H_4COC_3H_7\text{-}n$ (90, —)	151
	", $o\text{-}ClC_6H_4COCl$	—	"	$o\text{-}ClC_6H_4COC_3H_7\text{-}n$ (80, —)	151
	", C_6H_5COCl	—	CH_3Li, CuCN; [O]	$C_6H_5COC_3H_7\text{-}n$ (53, —)	151
	", "	—	CH_3Li, CuCl; [O]	" (62, —)	151
	", "	—	CH_3Li, CuCl, COD; [O]	" (83, —)	151
	", "	—	CH_3Li, CuBr; [O]	" (62, —)	151
	", "	—	CH_3Li, CuI; [O]	" (62, —)	151
	", "	—	CH_3Li, CuI; [O]	" (36, —)	151
	, C_6H_5CHO, C_2H_5Li	—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	Benzyl ethyl ketone (38, —)	330
	Cyclopentene, $CH_2{=}CHCH_2CN$	ThexylBH$_2$	CO, 70 atm, 50°, H_2O; [O]	$C_5H_9CO(CH_2)_3CN$ (50, 45)	154
		"	"	 (73, 66)	158
		ThexylBH$_2$	"	 (71,67)	158
	Cyclopentene, $t\text{-}C_4H_9NC$, $n\text{-}C_4H_9Li$	BH$_2$Cl	TFAA, 0°	$C_5H_9COC_4H_9\text{-}n$ (63, —)	20
	$(n\text{-}C_4H_9)_3B$, $HC{\equiv}CC_4H_9\text{-}n$	—	1. $n\text{-}C_4H_9Li$ 2. C_6H_5SeCl, −116°, ether 3. $(CH_3)_3NO$, H_2O 4. H_2O_2	$n\text{-}C_4H_9COCH{=}CHC_3H_7\text{-}n$ (*E*)-(—, 64)	168
	$(C_5H_9)_3B$, $(C_6H_5S)_2CHC_4H_9\text{-}n$	—	$NaOC_2H_5$, −30°; [O]	$C_5H_9COC_4H_9\text{-}n$ (—, 77)	169
	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_3H_7\text{-}n$	—	1. $n\text{-}C_4H_9Li$ 2. C_6H_5SeCl, ether, −116° 3. $(CH_3)_3NO$, H_2O 4. H_2O_2	$n\text{-}C_5H_{11}COCH{=}CHC_2H_5$ (*E*)-(—, 60)	168
	", $HC{\equiv}C(CH_2)_2OTs$	—	$n\text{-}C_4H_9Li$, −78°; [O]	 (—, 55–74)	95
	$CH_2{=}CH(CH_2)_3Br$, $t\text{-}C_4H_9NC$, $n\text{-}C_4H_9Li$	BH$_2$Cl	TFAA, 0°; [O]	$n\text{-}C_4H_9CO(CH_2)_5Br$ (61, —)	20
	$n\text{-}C_4H_9CH{=}CH_2$, $t\text{-}C_4H_9NC$, $i\text{-}C_3H_7Li$	"	"	$n\text{-}C_6H_{13}COC_3H_7\text{-}i$ (71, —)	20
11	, 	—	1. LDA 2. H$^+$	$C_6H_5SCH_2CO(CH_2)_2CO_2H$ (74, —)	298
	$(n\text{-}C_3H_7)_3B$, $p\text{-}CH_3C_6H_4COCl$	—	CH_3Li, CuCl, COD; [O]	$p\text{-}CH_3C_6H_4COC_3H_7\text{-}n$ (81, —)	151
	$(n\text{-}C_4H_9)_3B$, C_6H_5COCl	—	"	$C_6H_5COC_4H_9\text{-}n$ (85, —)	151
	$(i\text{-}C_4H_9)_3B$, "	—	"	$C_6H_5COC_4H_9\text{-}i$ (92, —)	151
	$(n\text{-}C_4H_9)_4\bar{B}Li^+$, C_6H_5COF	—	C_6H_{14}, THF	$C_6H_5COC_4H_9\text{-}n$ (4, —)	56
	", C_6H_5COCl	—	"	" (80, —)	56
	$(n\text{-}C_4H_9)_3\bar{B}(C_4H_9\text{-}s)Li^+$, C_6H_5COCl	—	"	" (57, —)	56
	$(n\text{-}C_4H_9)_4\bar{B}Li^+$, C_6H_5COBr	—	"	" (65, —)	56
	$(C_5H_9)_3\bar{B}(C_4H_9\text{-}n)Li^+$, C_6H_5COF	—	"	" (89, —)	56
	, $n\text{-}C_3H_7CO_2CH_3$	—	1. LDA 2. H$^+$	$C_6H_5SCH_2COC_3H_7\text{-}n$ (82, —)	298

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

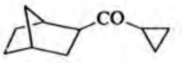
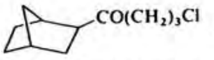
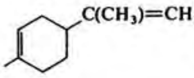
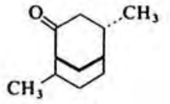
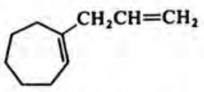
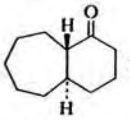
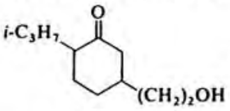
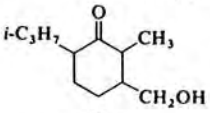
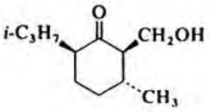
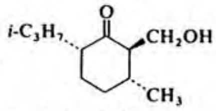
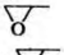
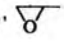
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	, $HC\equiv C(CH_2)_2OTs$	—	n-C_4H_9Li, −78°; [O]	 (—, 55 74)	95
	, $CH_2=CHCH_2Cl$	$ThexylBH_2$	CO, 70 atm, 50°, H_2O; [O]	 (75, 63)	154
	$(C_6H_{11})_2BH$, $CH_2=CHCH_2CN$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_3CN$ (—, 45)	153
	Cyclopentene	BH_3-THF	CO, DG, H_2O; [O]	$(C_5H_9)_2CO$ (—, 90)	152
	", KCN	"	1. DG 2. $C_6H_5N=CClC_6H_5$; [O]	" (—, 88)	250
	", NaCN	"	1. CH_3SO_3H, DG 2. HCN; [O]	" (—, 69)	331
	", "	BH_3-DG	DG, HCN, −78°; [O]	" (—, 69)	332
	", "	"	DG, TFAA; [O]	" (—, 84)	332
	", "	"	DG, C_6H_5COCl, 45°; [O]	" (—, 87)	332
	", "	$ThexylBH_2$	TFAA, −78° to room temp; [O]	" (—, 80)	297
	, NaCN	"	"	 (—, 95)	297
		"	CO, 70 atm, 50°, H_2O; [O]	 (68, 62)	158
	$(C_5H_9)_2BOCH_3$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$, (2 eq); [O]	$(C_5H_9)_2CO$ (86, —)	38
	$(C_5H_9)_3B$, $HC\equiv CC_4H_9$-n	—	1. n-C_4H_9Li 2. C_6H_5SeCl, ether, −116° 3. $(CH_3)_3NO$ 4. H_2O_2	$C_5H_9COCH=CHC_3H_7$-n (*E*)-(—, 69)	168
	$(C_6H_{11})_2BH$, $CH_2=CHC_2H_5$	—	CO, DG, H_2O, 100°; [O]	$C_6H_{11}COC_4H_9$-n (72, —)	333
	$(C_6H_{11})_2BH$, $CH_3CH=CHCH_3$	—	"	$C_6H_{11}COC_4H_9$-s (66, —)	333
	$(C_5H_9)_3B$, $HC\equiv CC_4H_9$-n	—	1. n-C_4H_9Li, DG 2. CH_3SO_3H, −78 −78° to room temp; [O]	$C_5H_9COC_5H_{11}$-n (—, 78)	161
	$(C_6H_{11})_3B$, $(C_6H_5S)_2CHC_4H_9$-n	—	$NaOC_2H_5$, −30°; [O]	$C_6H_{11}COC_4H_9$-n (—, 84)	169
	$(CH_3)_2C=CH(CH_2)_2C(=CH_2)CH=CH_2$, NaCN	BH_3-THF	TFAA; [O]	 (—, 34)	334
	", "	$ThexylBH_2$	"	 (—, 60)	
	$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2OTHP$	$ThexylBH_2$	CO, 1000 psi, 50°, H_2O; [O]	 (—, 44)[c] + 	309
	", NaCN	"	TFAA, −78° to room temp; [O]	" + " (—, 79)[c]	309
	$(CH_3)_2C=CH_2$, $CH_2=CHCH_2CO_2C_2H_5$	"	CO, 70 atm, 50°, H_2O; [O]	i-$C_4H_9CO(CH_2)_3CO_2C_2H_5$ (98, 84)	154
	n-$C_4H_9CH=CH_2$, t-C_4H_9NC, n-C_4H_9Li	BH_2Cl	TFAA, 0°; [O]	n-$C_6H_{13}COC_4H_9$-n (95, —)	20
	$(i$-$C_3H_7CHCH_3)_2BOCH_3$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$ (2 eq); [O]	$(i$-$C_3H_7CHCH_3)_2CO$ (54, 42)	38
	$(n$-$C_6H_{13})_3B$, $(C_6H_5S)_2CHC_4H_9$-n	—	n-C_4H_9Li, −30°; [O]	n-$C_6H_{13}COC_4H_9$-n (—, 95)	169
	$(n$-$C_6H_{13})_3B$, $LiC\equiv CH$-EDA, 	—	Reflux; [O]	n-$C_6H_{13}CO(CH_2)_2CHOHCH_3$ (—, 65)	66
	$(n$-$C_6H_{13})_3B$, $HC\equiv CSi(CH_3)_3$, 	—	n-C_4H_9Li, reflux; [O]	" (—, 21)	162

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

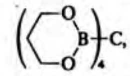
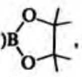
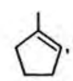
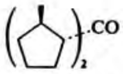
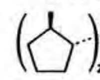
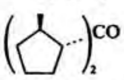
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
12	C, C_6H_5CHO, LiC_4H_9-*n*	—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	$C_6H_5CH_2COC_4H_9$-*n* (17, —)	330
	$(C_6H_5)_3B$, $HC{\equiv}CC_4H_9$-*n*	—	1. *n*-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	$C_6H_5COC_5H_{11}$-*n* (—, 83)	161
	", $(C_6H_5S)_2CHC_4H_9$-*n*	—	*n*-C_4H_9Li, −30°; [O]	$C_6H_5CH_2COC_4H_9$-*n* (—, 74)	169
	$C_6H_5SCH(CH_3)B$, $CH_3O_2CC_3H_7$-*n*	—	1. LDA 2. H^+	$C_6H_5SCH(CH_3)COC_3H_7$-*n* (81, —)	298
	$(C_5H_{11})_2BH$, cyclopentene	—	CO, H_2O, 45°; [O]	$C_6H_{11}COC_5H_9$ (53, —)	333
	$(C_6H_{11})_3B$, $HC{\equiv}CC_4H_9$-*n*	—	1. *n*-C_4H_9Li 2. C_6H_5SeCl, ether, −116° 3. $(CH_3)_3NO$, H_2O 4. H_2O_2	$C_6H_{11}COCH{=}CHC_3H_7$-*n* (*E*)-(—, 75)	168
	Cyclohexene, $BrC{\equiv}CC_4H_9$-*n*	BH_3–THF	0°; [O]	$C_6H_{11}COC_5H_{11}$-*n* (85, —)	29
	", $IC{\equiv}CC_4H_9$-*n*	"	"	" (87, —)	29
	$(C_6H_{11})_3B$, $HC{\equiv}CC_4H_9$-*n*	—	1. *n*-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	" (—, 86)	161
	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_4H_9$-*n*	—	1. *n*-C_4H_9Li 2. C_6H_5SeCl, ether, −116° 3. $(CH_3)_3NO$, H_2O 4. H_2O_2	*n*-$C_6H_{13}COCH{=}CHC_3H_7$-*n* (*E*)-(—, 61)	168
	$CH_3CH{=}CHCH_3$, $CH_2{=}CH(CH_2)_3OAc$	$ThexylBH_2$	CO, 70 atm, 50°, H_2O; [O]	*s*-$C_4H_9CO(CH_2)_5OAc$ (72, 63)	155
	n-$C_4H_9CH{=}CH_2$, *t*-C_4H_9NC, *i*-C_4H_9Li	BH_2Cl	TFAA, 0°; [O]	*n*-$C_6H_{13}CO(CH_2)_2C_3H_7$-*i* (92, —)	20
	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_4H_9$-*n*	—	1. *n*-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	*n*-$C_6H_{13}COC_5H_{11}$-*n* (—, 78)	161
	$(i\text{-}C_3H_7)_3B$, $HC{\equiv}CC_5H_{11}$-*n*, 	—	*n*-C_4H_9Li, reflux; [O]	*i*-$C_3H_7COCH(C_5H_{11}\text{-}n)(CH_2)_2OH$ (—, 82)	162
13	*p*-ClC_6H_4Br, *p*-FC_6H_4COCl	BR_3[b]	*n*-C_4H_9Li, C_6H_6; [O]	*p*-$ClC_6H_4COC_6H_4F$-*p* (—, 68)	57
	p-BrC_6H_4Br, C_6H_5COCl	"	"	*p*-$BrC_6H_4COC_6H_5$ (64, 54)	57
	C_6H_5Br, C_6H_5COCl	"	"	$(C_6H_5)_2CO$ (85, 80)	57
	$(C_6H_5)_3B$, $HC{\equiv}CC_4H_9$-*n*	—	*n*-C_4H_9Li, DG, 0°; [O]	$C_6H_5COCH(CH_3)C_4H_9$-*n* (—, 79)	163
	$(n\text{-}C_6H_{13})_3B$, C_6H_5COCl	—	CH_3Li, CuBr; [O]	$C_6H_5COC_6H_{13}$-*n* (75, —)	151
	", "	—	CH_3Li, CuCl, COD; [O]	" (45, —)	151
	, $CH_2{=}CHCH_2OAc$	$ThexylBH_2$	CO, 70 atm, 50°, H_2O; [O]	$CO(CH_2)_3OAc$ (—, 66)	155
	Cyclohexene	BH_3–THF	CO, DG, H_2O; [O]	$(C_6H_{11})_2CO$ (—, 80)	152
	", KCN	"	DG, $C_6H_5N{=}CClC_6H_5$; [O]	" (—, 80)	250
	, NaCN	"	DG, TFAA; [O]	 (—, 82)	290
	Cyclohexene, NaCN	"	1. CH_3SO_3H, DG 2. HCN; [O]	$(C_6H_{11})_2CO$ (—, 50)	331
	", "	BH_3–DG	DG, HCN, −78°; [O]	" (—, 50)	332
	", "	"	DG, C_6H_5COCl, 45°; [O]	" (—, 65)	332
	", "	"	DG, TFAA; [O]	" (—, 100)	332
	$(C_6H_{11})_2BH$, 	—	CO, 100°, DG, H_2O; [O]	" (51, —)	333
	", $CH_2{=}C(CH_3)_2$	—	"	" (42, —)	333
	$BOCH_3$, Cl_2CHOCH_3	—	$LiOC(C_2H_5)_3$; [O]	 (83, 80)	38
	$(C_6H_{11})_2BOCH_3$, Cl_2CHOCH_3	—	"	$(C_6H_{11})_2CO$ (95, 85)	38
	$(C_6H_{11})_2BH$, $CH_2{=}CHCH_2CO_2C_2H_5$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_3CO_2C_2H_5$ (—, 44)	153

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

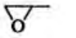
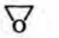
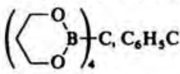
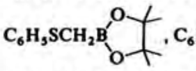
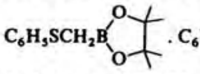
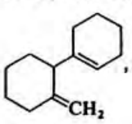
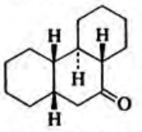
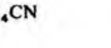
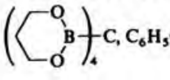
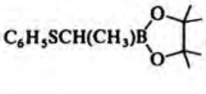
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(C_5H_9)_3B$, $HC\equiv CC_6H_{13}$-n	—	1. n-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	$C_5H_9COC_7H_{15}$-n (—, 85)	161
	n-$C_4H_9CH{=}CH_2$, KCN	BH_3-THF	DG, $C_6H_5N{=}CClC_6H_5$; [O]	$(n\text{-}C_6H_{13})_2CO$ (- , 80)	250
	", "	ThexylBH_2	TFAA (3 eq), 0° to room temp	" (35, —)	290
	$(i\text{-}C_3H_7)_3B$, $HC\equiv CC_5H_{11}$-n, 	—	n-C_4H_9Li, reflux; [O]	i-$C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHCH_3$ (—, 72)	162
	$(n\text{-}C_4H_9)_3B$, $HC\equiv CC_5H_{11}$-n, 	—	"	n-$C_4H_9COCH(C_5H_{11}\text{-}n)(CH_2)_2OH$ (—, 74)	162
14	C_6H_5Br, p-$ClCOC_6H_4CN$	BR_3^b	n-C_4H_9Li, C_6H_6; [O]	$C_6H_5COC_6H_4CN$-p (—, 70)	57
	$C_6H_5CH_2\bar{B}(C_4H_9\text{-}n)_3Li^+$, p-$ClCOC_6H_4I$	—	C_6H_{14}, THF	$C_6H_5CH_2COC_6H_4I$-p (—, 72)	56
	, C_6H_5CHO, C_6H_5Li	—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	$C_6H_5CH_2COC_6H_5$ (53, —)	330
	$C_6H_5CH_2\bar{B}(C_4H_9\text{-}n)_3Li^+$, C_6H_5COCl	—		" (88, —)	56
	, $C_6H_5CO_2CH_3$	—	1. LDA 2. H^+	$C_6H_5SCH_2COC_6H_5$ (75, —)	298
	p-$CH_3OC_6H_4Br$, C_6H_5COCl	BR_3^b	n-C_4H_9Li, C_6H_6; [O]	p-$CH_3OC_6H_4COC_6H_5$ (- , 75)	56
	. $C_6H_{11}CO_2CH_3$	—	1. LDA 2. H^+	$C_6H_5SCH_2COC_6H_{11}$ (80, —)	298
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CC_6H_5$	—	1. n-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	n-$C_6H_{13}COCH_2C_6H_5$ (—, 79)	161
	$[C_6H_5CH(CH_3)CH_2]_3B$, $(C_6H_5S)_2CHC_4H_9$-n	—	n-C_4H_9Li, −30°; [O]	$C_6H_5CH(CH_3)CH_2COC_4H_9$-$n$ (—, 86)	169
	, NaCN	ThexylBH_2	TFAA, −78° to room temp; [O]	 (—, 80)	250
	$(C_5H_9)_3B$, $HC\equiv CC_4H_9$-n, $HC\equiv CCH_2Br$	—	n-C_4H_9Li, DG, 0°; [O]	$C_5H_9COCH(C_4H_9\text{-}n)CH_2C\equiv CH$ (—, 75)	67
	", ", $CH_2{=}CHCH_2Br$	—	"	$C_5H_9COCH(C_4H_9\text{-}n)CH_2CH{=}CH_2$ (—, 86)	163
	", ", CH_3COCH_2Br	—	"	$C_5H_9COCH(C_4H_9\text{-}n)CH_2COCH_3$ (—, 74)	164
	Cyclopentene, $CH_2{=}CH(CH_2)_4OAc$	ThexylBH_2	CO, 70 atm, 50°, H_2O; [O]	$C_5H_9CO(CH_2)_8OAc$ (79, 73)	155
	", $CH_2{=}CH(CH_2)_6Cl$, NaCN	"	TFAA, −78° to room temp; [O]	$C_5H_9CO(CH_2)_8Cl$ (—, 76)	297
	", $CH_2{=}CH(CH_2)_6I$, NaCN	"	"	$C_5H_9CO(CH_2)_8I$ (—, 76)	297
	", $CH_2{=}CHC_6H_{13}$-n, NaCN	"	"	$C_5H_9COC_8H_{17}$-n (—, 83)	297
	$(C_5H_9)_3B$, $HC\equiv CC_6H_{13}$-n, $(CH_3)_2SO_4$	—	n-C_4H_9Li, DG, 0°; [O]	$C_5H_9COCH(CH_3)C_6H_{13}$-$n$ (—, 81)	163
	", ", CH_3OTs	—	"	" (—, 88)	163
	$(C_6H_{11})_3B$, $HC\equiv CC_4H_9$-n, $(C_2H_5)_3\overset{+}{O}\overset{-}{B}F_4$	—	"	$C_6H_{11}COCH(C_2H_5)C_4H_9$-$n$ (- , 83)	163, 64
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CC_6H_{13}$-n	—	1. n-C_4H_9Li, DG 2. CH_3SO_3H, −78° to room temp; [O]	n-$C_6H_{13}COC_7H_{15}$-n (—, 82)	161
	$(i\text{-}C_3H_7)_3B$. $HC\equiv CC_5H_{11}$-n, 	—	n-C_4H_9Li, reflux; [O]	i-$C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHC_2H_5$ (—, 82)	163,64
15	m-$CH_3C_6H_4Br$, p-$ClCOC_6H_4CN$	BR_3^b	n-C_4H_9Li, C_6H_6; [O]	m-$CH_3C_6H_4COC_6H_4CN$-p (78, 68)	56
	", o-$ClCOC_6H_4CH_3$	"	"	m-$CH_3C_6H_4COC_6H_4CH_3$-o (65, 50)	56
	, C_6H_5CHO, C_6H_5Li	—	1. CH_3Li, −70° 2. $NaBO_3$, CH_2Cl_2	$(C_6H_5CH_2)_2CO$ (25, —)	330
	", $(C_6H_5)_2CO$, CH_3Li	—	1. CH_3Li (2 eq), −70° 2. $NaBO_3$, CH_2Cl_2	$(C_6H_5)_2CHCOCH_3$ (1, —)	330
	, $C_6H_5CO_2CH_3$	—	1. LDA 2. H^+	$C_6H_5SCH(CH_3)COC_6H_5$ (86, —)	298

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

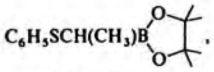
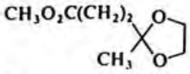
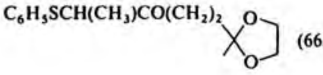
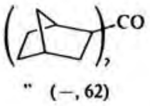
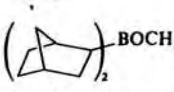
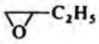
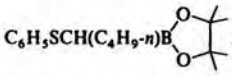
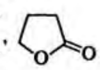
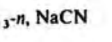
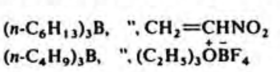
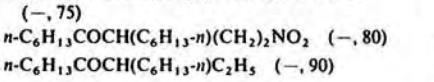
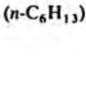
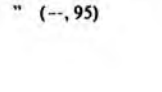
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	Cyclopentene, o-$\mathrm{AcOC_6H_4CH_2CH{=}CH_2}$, NaCN	Thexyl$\mathrm{BH_2}$	TFAA, −78° to room temp; [O]	$\mathrm{C_5H_9CO(CH_2)_3C_6H_4OH}$-$o$ (—, 80)	297
	, 	—	1. LDA 2. $\mathrm{H^+}$	 (66, —)	298
		$\mathrm{BH_3}$-THF	CO, DG, $\mathrm{H_2O}$; [O]	 (82, —)	152
	", NaCN	"	1. $\mathrm{CH_3SO_3H}$, DG 2. HCN; [O]	" (—, 62)	331
	", "	$\mathrm{BH_3}$-DG	DG, HCN, −78°; [O]	" (—, 62)	332
	", "	"	DG, $\mathrm{C_6H_5COCl}$, 45°; [O]	" (—, 85)	332
	", "	"	DG, TFAA; [O]	" (—, 99)	332
	, $\mathrm{Cl_2CHOCH_3}$	—	$\mathrm{LiOC(C_2H_5)_3}$; [O]	" (62, 53)	38
	$(i\text{-}\mathrm{C_3H_7})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_6H_5}$, 	—	n-$\mathrm{C_4H_9Li}$, reflux; [O]	i-$\mathrm{C_3H_7COCH(C_6H_5)CH_2CHOHC_2H_5}$ (—, 59)	162
	, 	—	1. LDA 2. $\mathrm{H^+}$	$\mathrm{C_6H_5SCH(C_4H_9}$-$n\mathrm{)CO(CH_2)_3OH}$ (50, —)	298
	$\mathrm{(C_5H_9)_3B}$, $\mathrm{HC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{ICH_2CN}$	—	1. n-$\mathrm{C_4H_9Li}$, DG, 0° 2. $\mathrm{(CH_3)_3NO}$	$\mathrm{C_5H_9COCH(C_6H_{13}}$-$n\mathrm{)CH_2CN}$ (—, 62)	67
	", $\mathrm{HC{\equiv}CC_4H_9}$-$n$, $\mathrm{BrCH_2CO_2C_2H_5}$	—	n-$\mathrm{C_4H_9Li}$, DG, 0°; [O]	$\mathrm{C_5H_9COCH(C_4H_9}$-$n\mathrm{)CH_2CO_2C_2H_5}$ (—, 74)	164
	Cyclohexene, $\mathrm{CH_2{=}CHC_6H_{13}}$-$n$, KCN	Thexyl$\mathrm{BH_2}$–$\mathrm{C_6H_5N(C_2H_5)_2}$	1. 0° 2. TFAA, −78°; [O]	$\mathrm{C_6H_{11}COC_8H_{17}}$-$n$ (—, 78)	335
	$\mathrm{(C_6H_{11})_2BH}$, $\mathrm{CH_2{=}CHC_6H_{13}}$-$n$	—	CO, DG, $\mathrm{H_2O}$, 100°; [O]	" (71, —)	333
	", "	—	CO, $\mathrm{H_2O}$, 45°; [O]	" (79, —)	153
	$\mathrm{CH_2{=}CH(CH_2)_{10}CH{=}CH_2}$, $\mathrm{Cl_2CHOCH_3}$	$\mathrm{BH_2Cl}$	$\mathrm{CH_3OH}$, $\mathrm{LiOC(C_2H_5)_3}$; [O]	$\mathrm{\underparen{(CH_2)_{14}C}O}$ (—, 7)	160
	$(n\text{-}\mathrm{C_4H_9})_4\bar{\mathrm{B}}\mathrm{Li^+}$, $\mathrm{ClCO(CH_2)_8CH{=}CH_2}$	—	$\mathrm{C_6H_{14}}$, THF	n-$\mathrm{C_4H_9CO(CH_2)_8CH{=}CH_2}$ (69, —)	56
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{(CH_3)_2SO_4}$	—	n-$\mathrm{C_4H_9Li}$, DG, 0°; [O]	n-$\mathrm{C_6H_{13}COCH(CH_3)C_6H_{13}}$-$n$ (—, 84)	163
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{CH_3OTs}$	—	"	" (—, 98)	163
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{LiC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{(CH_3)_2SO_4}$	—	1. DG, $\mathrm{C_6H_{14}}$, 0° 2. −78° to room temp; [O]	" (—, 84)	64
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{LiC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{CH_3OTs}$	—	"	" (—, 93)	64
	$(n\text{-}\mathrm{C_8H_{17}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_4H_9}$-$n$, $\mathrm{(CH_3)_2SO_4}$	—	n-$\mathrm{C_4H_9Li}$, DG, 0°; [O]	n-$\mathrm{C_8H_{17}COCH(CH_3)C_4H_9}$-$n$ (—, 85)	163
	$(n\text{-}\mathrm{C_8H_{17}})_3\mathrm{B}$, $\mathrm{LiC{\equiv}CC_4H_9}$-$n$, $\mathrm{(CH_3)_2SO_4}$	—	1. DG, $\mathrm{C_6H_{14}}$, 0° 2. −78° to room temp; [O]	" (—, 85)	163
	$(n\text{-}\mathrm{C_4H_9})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_5H_{11}}$-$n$, 	—	n-$\mathrm{C_4H_9Li}$, reflux; [O]	n-$\mathrm{C_4H_9COCH(C_5H_{11}}$-$n\mathrm{)CH_2CHOHC_2H_5}$ (—, 53)	162
16	$\mathrm{(C_5H_9)_3B}$, $\mathrm{LiC{\equiv}CC_4H_9}$-$n$, $\mathrm{C_5H_5N}$	—	$\mathrm{CH_3COCl}$, −78° to room temp; [O]	$\mathrm{C_5H_9COCH(C_4H_9}$-$n\mathrm{)C_5H_4N}$-4 (—, 74)	165
		Thexyl$\mathrm{BH_2}$	CO, $\mathrm{H_2O}$; [O]	 (—, 78)	156
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{ICH_2CN}$	—	1. n-$\mathrm{C_4H_9Li}$, DG, 0° 2. $\mathrm{(CH_3)_3NO}$	n-$\mathrm{C_6H_{13}COCH(C_6H_{13}}$-$n\mathrm{)CH_2CN}$ (—, 71)	67
	$(n\text{-}\mathrm{C_8H_{17}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_4H_9}$-$n$, $\mathrm{ICH_2CN}$	—	"	n-$\mathrm{C_8H_{17}COCH(C_4H_9}$-$n\mathrm{)CH_2CN}$ (—, 70)	67
	$\mathrm{(C_5H_9)_3B}$, $\mathrm{LiC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{CH_3CH{=}CHNO_2}$	—	0°; [O]	$\mathrm{C_5H_9COCH(C_6H_{13}}$-$n\mathrm{)CH(CH_3)CH_2NO_2}$ (—, 75)	90
	 , $\mathrm{CH_2{=}CHC_6H_{13}}$-$n$, NaCN	$\mathrm{BH_3}$-THF	DG, TFAA, MCPBA	 (—, 84)	290
	$(n\text{-}\mathrm{C_5H_{11}})_3\mathrm{B}$, $\mathrm{LiC{\equiv}CC_6H_{13}}$-$n$, $\mathrm{CH_3CH{=}CHNO_2}$	—	0°; [O]	n-$\mathrm{C_5H_{11}COCH(C_6H_{13}}$-$n\mathrm{)CH(CH_3)CH_2NO_2}$ (—, 75)	90
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, ", $\mathrm{CH_2{=}CHNO_2}$	—	"	n-$\mathrm{C_6H_{13}COCH(C_6H_{13}}$-$n\mathrm{)(CH_2)_2NO_2}$ (—, 80)	90
	$(n\text{-}\mathrm{C_4H_9})_3\mathrm{B}$, ", $\mathrm{(C_2H_5)_3\overset{+}{O}\overset{-}{B}F_4}$	—	1. 0°, DG, $\mathrm{C_6H_{14}}$ 2. −78° to room temp; [O]	n-$\mathrm{C_6H_{13}COCH(C_6H_{13}}$-$n\mathrm{)C_2H_5}$ (—, 90)	64
	$(n\text{-}\mathrm{C_6H_{13}})_3\mathrm{B}$, $\mathrm{HC{\equiv}CC_6H_{13}}$-$n$, "	—	n-$\mathrm{C_4H_9Li}$, DG, 0°; [O]	" (—, 95)	163

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

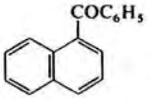
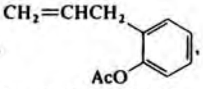
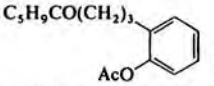
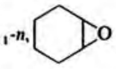
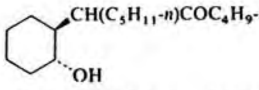
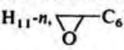
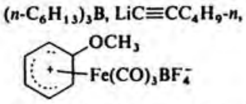
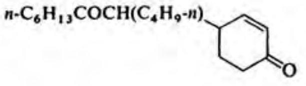
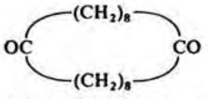
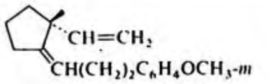
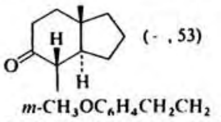
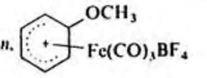
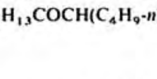
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_8H_{17})_3B$, "	—	1. $n\text{-}C_4H_9Li$, DG 2. CH_3SO_3H, −78° to room temp; [O]	$n\text{-}C_8H_{17}COC_7H_{15}\text{-}n$ (–, 78)	161
	", $HC\equiv CC_4H_9\text{-}n$, $(C_2H_5)_3\overset{+}{O}\overset{-}{B}F_4$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_8H_{17}COCH(C_4H_9\text{-}n)C_2H_5$ (–, 93)	163
	", $LiC\equiv CC_4H_9\text{-}n$, "	—	1. 0°, DG 2. −78° to room temp; [O]	" (–, 88)	64
	", $LiC\equiv CC_6H_{13}\text{-}n$, CH_3SO_3H	—	"	$n\text{-}C_8H_{17}COC_7H_{15}\text{-}n$ (–, 78)	64
17	, C_6H_5COCl	BR_3[b]	$n\text{-}C_4H_9Li$, C_6H_6; [O]	 (80, –)	56
	Cyclopentene, , NaCN	ThexylBH$_2$	1. TFAA, −78° to room temp 2. MCPBA, 0°	 (–, 80)	297
	$(C_6H_{11})_3B$, $CH_2{=}CHCH_2O_2CC_6H_5$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_3O_2CC_6H_5$ (–, 43)	153
	$(n\text{-}C_6H_{13})_3B$, $LiC\equiv CC_4H_9\text{-}n$, C_5H_5N	—	CH_3COCl, −78° to room temp; [O]	$n\text{-}C_6H_{13}COCH(C_4H_9\text{-}n)C_5H_4N\text{-}4$ (–, 76)	165
	", $HC\equiv CC_6H_{13}\text{-}n$, $BrCH_2C\equiv CH$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2C\equiv CH$ (–, 80)	67
	$(n\text{-}C_8H_{17})_3B$, $HC\equiv CC_4H_9\text{-}n$, "	—	"	$n\text{-}C_8H_{17}COCH(C_4H_9\text{-}n)CH_2C\equiv CH$ (–, 76)	67
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CC_6H_{13}\text{-}n$, $BrCH_2CH{=}CH_2$	—	"	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CH{=}CH_2$ (–, 88)	163
	", $LiC\equiv CC_6H_{13}\text{-}n$, "	"	1. DG, C_6H_{14}, 0° 2. −78° to room temp; [O]	" (–, 88)	64
	$(n\text{-}C_8H_{17})_3B$, $HC\equiv CC_4H_9\text{-}n$, $BrCH_2CH{=}CH_2$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_8H_{17}COCH(C_4H_9\text{-}n)CH_2CH{=}CH_2$ (–, 80)	163
	", $LiC\equiv CC_4H_9\text{-}n$, "	—	1. DG, C_6H_{14}, 0° 2. −78° to room temp; [O]	" (–, 80)	64
	$(n\text{-}C_4H_9)_3B$, $HC\equiv CC_5H_{11}\text{-}n$, 	—	$n\text{-}C_4H_9Li$, reflux; [O]	 (–, 19)	162
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CC_6H_{13}\text{-}n$, $BrCH_2COCH_3$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2COCH_3$ (–, 75)	164
	", $LiC\equiv CC_6H_{13}\text{-}n$, $CH_3CH{=}CHNO_2$	—	0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH(CH_3)CH_2NO_2$ (–, 93)	90
	", ", $CH_2{=}C(CH_3)NO_2$	—	"	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CH(CH_3)NO_2$ (–, 57)	90
	$n\text{-}C_6H_{13}CH{=}CH_2$	BH_3-THF	CO, DG; [O]	$(n\text{-}C_8H_{17})_2CO$ (–, 80)	152
	", KCN	"	DG, $C_6H_5N{=}CClC_6H_5$; [O]	" (–, 86)	250
	", NaCN	"	DG, HCN, −78°; [O]	" (–, 68)	332
	", "	"	1. CH_3SO_3H, DG 2. HCN; [O]	" (–, 68)	331
	", "	ThexylBH$_2$	TFAA, −78° to room temp; [O]	" (–, 78)	297
	", "	BH_3-DG	DG, C_6H_5COCl, 45°; [O]	" (–, 89)	332
	", "	"	DG, TFAA; [O]	" (–, 95)	283
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CH$, 	—	$n\text{-}C_4H_9Li$, reflux; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CHOHCH_3$ (–, 66)	162
18	$(C_5H_9)_3B$, $HC\equiv CC_4H_9\text{-}n$, $C_6H_5CH_2Br$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$C_5H_9COCH(C_4H_9\text{-}n)CH_2C_6H_5$ (–, 81)	163
	$(i\text{-}C_3H_7)_3B$, $HC\equiv CC_5H_{11}\text{-}n$, 	—	$n\text{-}C_4H_9Li$, reflux; [O]	$i\text{-}C_3H_7COCH(C_5H_{11}\text{-}n)CH_2CHOHC_6H_5$ (–, 65)	162
	$(n\text{-}C_6H_{13})_3B$, $LiC\equiv CC_4H_9\text{-}n$, 	—	1. $(CH_3)_3NO$ 2. Ce^{4+}	 (–, 46)	166
	$CH_2{=}CH(CH_2)_4CH{=}CH_2$, Cl_2CHOCH_3	BH_2Cl	CH_3OH, $LiOC(C_2H_5)_3$; [O]	 (–, 6)	160
	$(n\text{-}C_6H_{13})_3B$, $HC\equiv CC_6H_{13}\text{-}n$, $BrCH_2CO_2C_2H_5$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CO_2C_2H_5$ (–, 78)	164

TABLE IV. KETONES. A. ONE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
19		ThexylBH$_2$	CO, 1200 psi, 50°; [O]	 (–, 53)	159
	$(C_6H_{11})_3B$, $LiC{\equiv}CC_6H_{13}$-*n*, C_5H_5N	–	CH_3COCl, –78° to room temp; [O]	$C_6H_{11}COCH(C_6H_{13}$-*n*$)C_5H_4N$-4 (–, 68)	165
	(*n*-$C_6H_{13})_3B$, ", "	"	"	*n*-$C_6H_{13}COCH(C_6H_{13}$-*n*$)C_5H_4N$-4 (–, 72)	165
	", $LiC{\equiv}CC_4H_9$-*n*, 	–	1. $(CH_3)_3NO$ 2. Ce^{4+}	*n*-$C_6H_{13}COCH(C_4H_9$-*n*$)$  (–, 46)	166
	$(C_6H_{11})_2BH$, $CH_2{=}CH(CH_2)_8CO_2CH_3$	–	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_{10}CO_2CH_3$ (–, 53)	153
	", $CH_2{=}CHC_{10}H_{21}$-*n*	–	"	$C_6H_{11}COC_{12}H_{25}$-*n* (84, –)	153
	n-$C_3H_7CH{=}CH_2$, $CH_2{=}CH(CH_2)_9OAc$	ThexylBH$_2$	CO, H_2O, 70 atm, 50°; [O]	*n*-$C_5H_{11}CO(CH_2)_{11}OAc$ (42, –)	155
20	$(C_6H_5)_3B$, $ClCH{=}C(C_6H_4Cl$-*p*$)_2$	–	*n*-C_4H_9Li; [O]	$C_6H_5COCH(C_6H_4Cl$-*p*$)_2$ (–, 22)	336
	", $ClCH{=}C(C_6H_5)_2$	–	"	$C_6H_5COCH(C_6H_5)_2$ (–, 20)	337
21	$C_6H_5CH{=}CH_2$, $CH_2{=}CH(CH_2)_8CO_2CH_3$	ThexylBH$_2$	CO, H_2O, 70 atm, 50°; [O]	$C_6H_5(CH_2)_2CO(CH_2)_{10}CO_2CH_3$ (–, 73)	154
	(*n*-$C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}$-*n*,	–	*n*-C_4H_9Li, DG, 0°; [O]	*n*-$C_6H_{13}COCH(C_6H_{13}$-*n*$)CH_2C_6H_5$ (–, 78)	163
	(*n*-$C_8H_{17})_3B$, $HC{\equiv}CC_4H_9$-*n*, $C_6H_5CH_2Br$	–	"	*n*-$C_8H_{17}COCH(C_4H_9$-*n*$)CH_2C_6H_5$ (–, 79)	163
	n-$C_8H_{17}CH{=}CH_2$, (Z)-$ClMg(CH_2)_3CH{=}CHC_5H_{11}$-*n*, NaCN	ThexylBH$_2$	1. HCl, ether, –78 to 0° 2. C_6H_5COCl, 45°; [O]	*n*-$C_{10}H_{21}CO(CH_2)_3CH{=}CHC_5H_{11}$-*n* (Z)-(–, 74)	336
22	(*n*-$C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}$-*n*, $C_6H_5COCH_2Br$	–	"	*n*-$C_6H_{13}COCH(C_6H_{13}$-*n*$)CH_2COC_6H_5$ (–, 74)	90
	(*n*-$C_6H_{13})_3B$, $LiC{\equiv}CC_6H_{13}$-*n*, $C_6H_5SOCH{=}CH_2$	–	0°; [O]	*n*-$C_6H_{13}COCH(C_6H_{13}$-*n*$)(CH_2)_2SOC_6H_5$ (–, 10)	90
25	$(C_6H_{11})_3B$, $C_6H_5CO_2(CH_2)_9CH{=}CH_2$	–	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_{11}O_2CC_6H_5$ (–, 61)	153

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The alkyl groups (R) in the organoborane can be either cyclopentyl or norbornyl.

[c] The yield given is the total for the combined products.

TABLE IV. KETONES. B. TWO-CARBON HOMOLOGATION

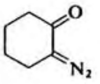
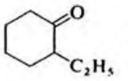
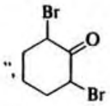
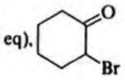
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	$(C_2H_5)_3B$, $N_2CHCOCH_3$	—	1. NBS, 0° 2. NaOH	$C_2H_5CHBrCOCH_3$ (83, —)	176
	", "	—	1. NCS, 0° 2. NaOH	$C_2H_5CHClCOCH_3$ (86, —)	176
	", $BrCH_2COCH_3$	—	0°[b]	n-$C_3H_7COCH_3$ (88, 70)	174
7	", $N_2CHCOC_3H_7$-i	—	1. NCS, 0° 2. NaOH	$C_2H_5CHClCOC_3H_7$-i (93, —)	176
	$CH_3CH{=}CHCH_3$, $N_2CHCOCH_3$	BH_3-THF	1. Reflux 2. KOH	s-$C_4H_9CH_2COCH_3$ (36, —)	17
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH_2COCH_3$ (56, —)	17
	n-C_4H_9B , $BrCH_2COCH_3$	—	0 [b]	n-$C_5H_{11}COCH_3$ (80, —)	174
	s-C_4H_9B , "	—	"	s-$C_4H_9CH_2COCH_3$ (71, —)	174
	i-C_4H_9B , "	—	"	i-$C_4H_9CH_2COCH_3$ (62, —)	174
	$(n$-$C_4H_9)_3B$, "	—	"	n-$C_5H_{11}COCH_3$ (84, —)	174
8	Cyclopentene, $N_2CHCOCH_3$	BH_3-THF	1. Reflux 2. KOH	$C_5H_9CH_2COCH_3$ (67, —)	17
	$(C_2H_5)_3B$ (1.5 eq), 	—	THF, H_2O	 (98, —)	327
	", 	—	t-C_4H_9OK	" (—, 76)	338
	" (2 eq), 	—	t-C_4H_9OK, 0°	" (68, —)	170

TABLE IV. KETONES. B. TWO-CARBON HOMOLOGATION (*Continued*)

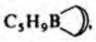
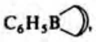
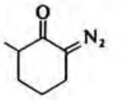
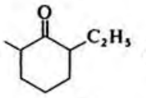
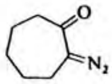
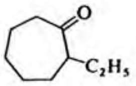
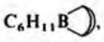
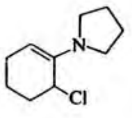
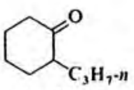
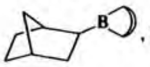
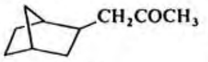
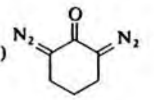
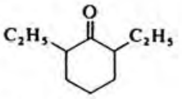
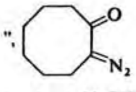
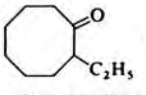
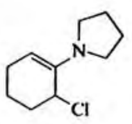
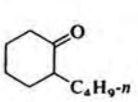
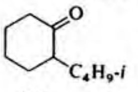
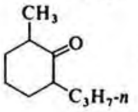
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	, $BrCH_2COCH_3$	—	0°[b]	$C_5H_9CH_2COCH_3$ (73, —)	174
	$(C_5H_9)_3B$, "	—	"	" (43, —)	174
	$n\text{-}C_3H_7CH{=}CH_2$, $N_2CHCOCH_3$	BH_3-THF	1. Reflux 2. KOH	$n\text{-}C_6H_{13}COCH_3$ (85, —)	17
9	CH_3Li, $C_6H_5COCH_2Br$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_6H_5COC_2H_5$ (40, —)	173
	, $BrCH_2COCH_3$	—	0°[b]	$C_6H_5CH_2COCH_3$ (76, —)	174
	$(C_2H_5)_3B$ (1.5 eq), 	—	THF, H_2O	 (93, —)	327
	", 	—	"	 (92, —)	327
	, $BrCH_2COCH_3$	—	0°[c,b]	$C_6H_{11}CH_2COCH_3$ (72, —)	174
	$n\text{-}C_4H_9CH{=}CH_2$, $N_2CDCOCH_3$	BH_3-THF	THF, D_2O	$n\text{-}C_6H_{13}CD_2COCH_3$ (100, —)	18
	", $N_2CHCOCH_3$	"	"	$n\text{-}C_6H_{13}CHDCOCH_3$ (99, —)	18
	", "	"	1. Reflux 2. KOH	$n\text{-}C_7H_{15}COCH_3$ (89, 65)	17
	$(n\text{-}C_3H_7)_3B$, 	—	CH_3Li, CuI; [O]	 (31, —)	339
	", "	—	CH_3Li, CuBr; [O]	" (32, —)	339
	", "	—	CH_3Li, CuCl; [O]	" (29, —)	339
	", "	—	CH_3Li, CuCN; [O]	" (53, —)	339
	", "	—	CH_3Li, CuCN, DME; [O]	" (60, —)	339
10	$(C_2H_5)_3B$, $N_2CHCOC_6H_5$	—	1. NBS, 0° 2. NaOH	$C_2H_5CHBrCOC_6H_5$ (76, —)	176
	$CH_2{=}CH_2$ (2 eq), $BrCH_2COC_6H_5$	9-BBN (2 eq)	$t\text{-}C_4H_9OK$, 0°	$n\text{-}C_3H_7COC_6H_5$ (91, —)	172
	$(C_2H_5)_3B$ (2 eq), "	—	"	" (100, —)	170
	", $CH_2{=}CN_3C_6H_5$	—	H_2SO_4, 70°; [O]	" (95, —)	178
	, $BrCH_2COCH_3$	—	0°[c,b]	 (25, —)	174
	$(C_2H_5)_3B$ (1.5 eq) 	—	THF, H_2O	 (95, —)	327
	", 	—	"	 (82, —)	327
	" (2 eq), $N_2CHCO(CH_2)_2COCHN_2$	—	—	$n\text{-}C_3H_7CO(CH_2)_2COC_3H_7\text{-}n$ (92, —)	340
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, CH_3CN	—	—	$n\text{-}C_4H_9CH(CO_2C_2H_5)COCH_3$ (—, 57)	135
	$C_2H_5CH{=}CH_2$, $BrCH_2COC_4H_9\text{-}t$	9-BBN	$t\text{-}C_4H_9OK$, 0°	$n\text{-}C_5H_{11}COC_4H_9\text{-}t$ (78, —)	172
	$CH_3CH{=}CHCH_3$, "	"	"	$s\text{-}C_4H_9CH_2COC_4H_9\text{-}t$ (79, —)	172
	$(CH_3)_2C{=}CH_2$, "	"	"	$i\text{-}C_4H_9CH_2COC_4H_9\text{-}t$ (61, —)	172
	$(C_2H_5)_3B$, $N_2CHCOC_3H_7\text{-}i$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	—	1. $(CH_3)_2SO$ 2. NaOH	$C_2H_5CH(COC_3H_7\text{-}i)CH_2N(CH_3)_2$ (94, —)	180
	$(n\text{-}C_4H_9)_3B$, 	—	CH_3Li, CuCN, DME; [O]	 (81, —)	339
	$(i\text{-}C_4H_9)_3B$, "	—	"	 (83, —)	339
	$(n\text{-}C_3H_7)_3B$, ", $(CH_3)_2SO_4$	—	"	 (37, —)	339

TABLE IV. KETONES. B. TWO-CARBON HOMOLOGATION (*Continued*)

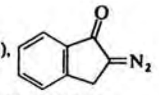
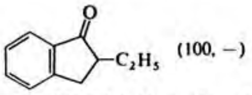
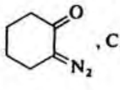
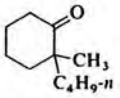
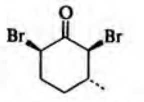
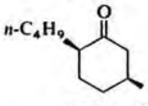
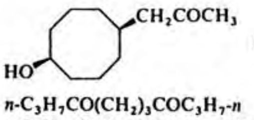
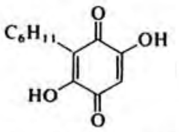
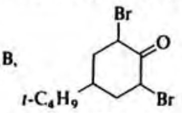
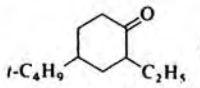
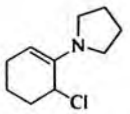
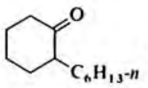
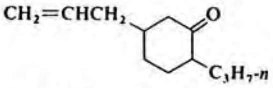
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
11	$(C_2H_5)_3B$ (1.5 eq), 	—	THF, H_2O	 (100, —)	327
	Cyclopentene, $BrCH_2COC_4H_9$-t	9-BBN	t-C_4H_9OK, 0°	$C_5H_9CH_2COC_4H_9$-t (77, —)	172
	$(n$-$C_4H_9)_3B$,  , CH_3I	—	n-C_4H_9Li (2 eq)	 (61, —)	177
	", 	—	t-C_4H_9OK	 (—, 65)	338
	n-$C_6H_{13}B$, $N_2CHCOCH_3$	—	[O]	 (80, —)	175
	$(C_2H_5)_3B$ (2 eq), $N_2CHCO(CH_2)_3COCHN_2$	—	—	n-$C_3H_7CO(CH_2)_3COC_3H_7$-n (87, —)	340
	n-$C_4H_9CH{=}CH_2$, $N_2CHCOC_3H_7$-i	BH_3–THF	1. NBS, 0° 2. NaOH	n-$C_6H_{13}CHBrCOC_3H_7$-i (80, 63)	176
12	$(C_6H_{11})_3B$, 2,5-dihydroxybenzoquinone	—	DMF, 0°	 (—, 172)	141
	$C_2H_5CH{=}CH_2$ (2 eq), $C_6H_5COCH_2Br$	9-BBN (2 eq)	t-C_4H_9OK, 0°	$C_6H_5COC_5H_{11}$-n (83, —)	172
	$CH_3CH{=}CHCH_3$ (2 eq), "	"[c]	"	$C_6H_5COCH_2C_4H_9$-s (65, 50)	172
	$(CH_3)_2C{=}CH_2$ (2 eq)	"[c]	"	$C_6H_5COCH_2C_4H_9$-i (65, —)	172
	n-C_4H_9Li, "	"	1. CH_3SO_3H, 0° 2. t-C_4H_9OK, 0°	$C_6H_5COC_5H_{11}$-n (80, —)	173
	C_6H_5Li, $BrCH_2COC_4H_9$-t	"	"	$C_6H_5CH_2COC_4H_9$-t (92, —)	173
	$(n$-$C_4H_9)_3B$ (2 eq), $C_6H_5COCH_2Br$	—	t-C_4H_9OK, 0°	$C_6H_5COC_5H_{11}$-n (93, —)	170
	", $C_6H_5CN_3{=}CH_2$	—	H_2SO_4, 70°; [O]	" (82, —)	178
	$(s$-$C_4H_9)_3B$, "	—	"	$C_6H_5COCH_2C_4H_9$-s (79, —)	178
	$(i$-$C_4H_9)_3B$, "	—	"	$C_6H_5COCH_2C_4H_9$-i (83, —)	178
	Cyclohexene, $BrCH_2COC_4H_9$-t	9-BBN	t-C_4H_9OK, 0°	$C_6H_{11}CH_2COC_4H_9$-t (60, —)	172
	$(C_2H_5)_3B$, 	—	t-C_4H_9OK	 (—, 95)	338
	$(n$-$C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, n-C_3H_7CN	—	—	n-$C_4H_9CH(CO_2C_2H_5)COC_3H_7$-$n$ (—, 54)	135
	n-$C_5H_{11}CH{=}CH_2$, $N_2CHCOC_3H_7$-i	BH_3–THF	1. NBS, 0° 2. NaOH	n-$C_7H_{15}CHBrCOC_3H_7$-i (84, —)	176
	" "	"	1. NCS, 0° 2. NaOH	n-$C_7H_{15}CHClCOC_3H_7$-i (88, —)	176
	$(n$-$C_6H_{13})_3B$, 	—	CH_3Li, CuCN, DME; [O]	 (70, —)	339
	$(n$-$C_3H_7)_3B$, ", $BrCH_2CH{=}CH_2$	—	"	 (59, —)	339
13	Cyclopentene, $C_6H_5COCH_2Br$	9-BBN	t-C_4H_9OK	$C_6H_5COCH_2C_5H_9$ (20, —)	172
	$(C_5H_9)_3B$, $C_6H_5CN_3{=}CH_2$	—	H_2SO_4, 70°; [O]	" (80, —)	178
	n-$C_3H_7CH{=}CH_2$, $C_6H_5COCHN_2$	BH_3–THF	1. Reflux 2. KOH	$C_6H_5COC_6H_{13}$-n (91, 78)	17
	$(n$-$C_4H_9)_3B$, ", CH_3Li	—	n-C_4H_9Li[c]	$C_6H_5COCH(CH_3)C_4H_9$-n (72, —)	177
	$(C_2H_5)_3B$, ", $CH_2{=}N(CH_3)_2I^-$	—	1. $(CH_3)_2SO$ 2. NaOH	$C_6H_5COCH(C_2H_5)CH_2N(CH_3)_2$ (92, 70)	180
14	C_6H_5Li, $C_6H_5COCH_2Br$	9-BBN	1. CH_3SO_3H, 0° 2. t-C_4H_9OK, 0°	$C_6H_5CH_2COC_6H_5$ (93, —)	173
	Cyclohexene, "	"	t-C_4H_9OK, 0°	$C_6H_5COCH_2C_6H_{11}$ (30, —)	172

TABLE IV. KETONES. B. TWO-CARBON HOMOLOGATION (*Continued*)

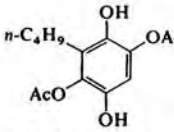
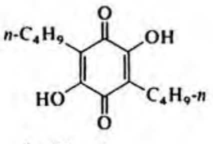
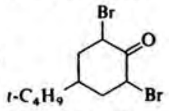
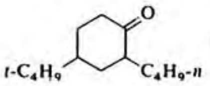
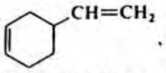
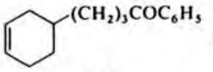
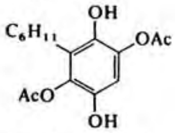
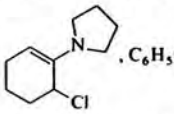
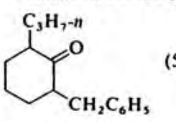
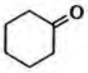
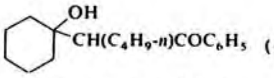
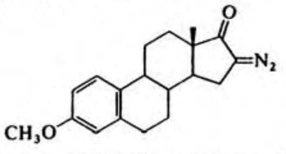
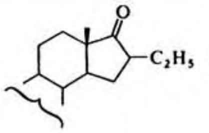
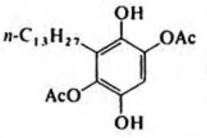
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_4H_9)_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, 25)	141
	$n\text{-}C_4H_9CH{=}CH_2$, $C_6H_5COCHN_2$	BH_3-THF	1. NBS, 0° 2. NaOH	$C_6H_5COCHBrC_6H_{13}\text{-}n$ (79, —)	176
	", "	"	THF, D_2O	$C_6H_5COCHDC_6H_{13}\text{-}n$ (100, —)	18
	", "	"	1. Reflux 2. KOH	$C_6H_5COC_7H_{15}\text{-}n$ (91, 78)	17
	$(n\text{-}C_4H_9)_3B$, 2,5-dihydroxybenzoquinone	—	DMF, air, 0°	 (—, 16)	141
	$(n\text{-}C_6H_{13})_3B$, $C_6H_5CN_3{=}CH_2$	—	H_2SO_4, 70°; [O]	" (60, —)	178
	$(n\text{-}C_4H_9)_3B$, 	—	Footnote *c*	 (—, 100)	338
	", $N_2CHCO(CH_2)_2COCHN_2$	—	—	$n\text{-}C_5H_{11}CO(CH_2)_2COC_5H_{11}\text{-}n$ (84, —)	340
	$n\text{-}C_4H_9CH{=}CH_2$, $i\text{-}C_3H_7COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	BH_3-THF	1. $(CH_3)_2SO$ 2. NaOH	$n\text{-}C_6H_{13}CH(COC_3H_7\text{-}i)CH_2N(CH_3)_2$ (84, —)	180
15	$p\text{-}CH_3C_6H_4Li$, $C_6H_5COCH_2Br$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK$, 0°	$p\text{-}CH_3C_6H_4CH_2COC_6H_5$ (95, —)	173
	$n\text{-}C_5H_{11}CH{=}CH_2$, $C_6H_5COCHN_2$	BH_3-THF	1. NBS, 0° 2. NaOH	$C_6H_5COCHBrC_7H_{15}\text{-}n$ (83, —)	176
	$n\text{-}C_5H_{11}CH{=}CH_2$, $N_2CHCOC_3H_7\text{-}n$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	BH_3-THF	1. $(CH_3)_2SO$ 2. NaOH	$n\text{-}C_7H_{15}CH(COC_3H_7\text{-}i)CH_2N(CH_3)_2$ (100, —)	180
	$(n\text{-}C_4H_9)_3B$, $C_6H_5COCHN_2$, $(CH_3)_2CO$	—	—	$C_6H_5COCH(C_4H_9\text{-}n)COH(CH_3)_2$ (—, 42)	73
	", $N_2CHCO_2C_2H_5$, C_6H_5CN	—	—	$C_6H_5COCH(CO_2C_2H_5)C_4H_9\text{-}n$ (—, 71)	135
	", $N_2CHCO(CH_2)_3COCHN_2$	—	—	$n\text{-}C_5H_{11}CO(CH_2)_3COC_5H_{11}\text{-}n$ (83, —)	340
16	 , $C_6H_5COCH_2Br$	9-BBN	$t\text{-}C_4H_9OK$, 0°	 (60, —)	172
	$(C_6H_{11})_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, —)	141
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, C_6H_5CN	—	—	$C_6H_5CH_2COCH(C_4H_9\text{-}n)CO_2C_2H_5$ (—, 61)	135
	", $C_6H_5COCHN_2$, $n\text{-}C_3H_7CHO$	—	—	$n\text{-}C_4H_9CH(COC_6H_5)CHOHC_3H_7\text{-}n$ (—, 88)	73
	$(n\text{-}C_3H_7)_3B$,  , $C_6H_5CH_2Br$	—	CH_3Li, CuCN, DME; [O]	 (59, —)	339
17	$n\text{-}C_4H_9CH{=}CH_2$, $C_6H_5COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	BH_3-THF	1. $(CH_3)_2SO$ 2. NaOH	$C_6H_5COCH(C_6H_{13}\text{-}n)CH_2N(CH_3)_2$ (86, —)	180
18	$(n\text{-}C_4H_9)_3B$, $C_6H_5COCHN_2$, 	—	—	 (—, 69)	73
	$(n\text{-}C_{10}H_{21})_3B$, $C_6H_5COCH_2Br$	—	$t\text{-}C_4H_9OK$, 0°	$C_6H_5COC_{11}H_{23}\text{-}n$ (90, —)	170
19	$(n\text{-}C_4H_9)_3B$, $C_6H_5COCHN_2$, $C_6H_5CH_2Cl$	—	$t\text{-}C_4H_9OK$	$C_6H_5COCH(C_4H_9\text{-}n)CH_2C_6H_5$ (31, —)	177
	", ", "	—	$n\text{-}C_4H_9Li$[c]	" (47, —)	177
	", ", C_6H_5CHO	—	—	$C_6H_5COCH(C_4H_9\text{-}n)CHOHC_6H_5$ (—, 98)	73
	$n\text{-}C_5H_{11}CH{=}CH_2$, ", $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	BH_3-THF	1. $(CH_3)_2SO$ 2. NaOH	$C_6H_5COCH(C_8H_{17}\text{-}n)CH_2N(CH_3)_2$ (80, —)	180
	$(n\text{-}C_6H_{13})_3B$, $N_2CHCO(CH_2)_3COCHN_2$	—	—	$n\text{-}C_7H_{15}CO(CH_2)_3COC_7H_{15}\text{-}n$ (52, —)	340

TABLE IV. KETONES. B. TWO-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
21	$(C_2H_5)_3B$ (1.5 eq), 	—	THF, H_2O	 (82, —)	327
23	$(n\text{-}C_{13}H_{27})_3B$, 2,5-diacetoxybenzoquinone	—	Reflux	 (—, —)	141

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] Potassium 2,6-di-*tert*-butylphenoxide is used as a base.

[c] Potassium *tert*-heptoxide is used as a base.

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION

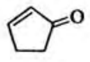
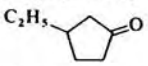
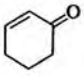
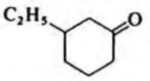
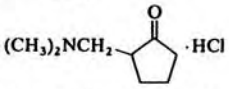
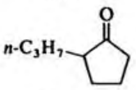
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$CH_2{=}CH_2$, $HC{\equiv}CCOCH_3$	BH_3-THF	Air, H_2O	$C_2H_5CH{=}CHCOCH_3$ (77, –)	341
	", $CH_2{=}CHCOCH_3$	"	40°	n-$C_4H_9COCH_3$ (99, –)	79
7	", 	"	Air, H_2O	 (68, –)	84
	(n-$C_3H_7)_3B$, $CH_2{=}CHCOCH_3$	–	1. Air 2. Br_2, CCl_4, dark, 0° 3. CH_3OH	n-$C_4H_9CHBrCOCH_3$ (78, –)[b]	179
	$CH_3CH{=}CH_2$, $CH_2{=}CHCOCH_3$	BH_3-THF	40°	n-$C_5H_{11}COCH_3$ (100, –)	79
	$(C_2H_5)_3B$, (E)-$CH_3CH{=}CHCOCH_3$	–	Air, H_2O	$C_2H_5CH(CH_3)CH_2COCH_3$ (70, –)	84
	", " (2 eq)	–	DG, hv, i-C_3H_7OH	" (85, –)	83
	", " (3 eq)	–	DG, $(CH_3CO_2)_2$, H_2O	" (88, –)	83
8	$C_2H_5CH{=}CH_2$, $HC{\equiv}CCOCH_3$	BH_3-THF	Air, H_2O	n-$C_4H_9CH{=}CHCOCH_3$ (72, –)	341
	$CH_3CH{=}CHCH_3$, "	"	"	$C_2H_5CH(CH_3)CH{=}CHCOCH_3$ (47, –)	341
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH{=}CHCOCH_3$ (34, –)	341
	$(C_2H_5)_3B$ (1.5 eq), 	–	"	 (50, –)	84
	", " (3 eq)	–	DG, $(CH_3CO_2)_2$, H_2O	" (56, –)	83
	", " (2 eq)	–	DG, hv, i-C_3H_7OH	" (95, –)	83
	", 	–	H_2O, CH_3I	 (90, 72)	342
	(n-$C_4H_9)_3B$, $CH_2{=}CHCOCH_3$	–	1. Air 2. Br_2, CCl_4, dark, 0° 3. CH_3OH	n-$C_5H_{11}CHBrCOCH_3$ (74, –)[b]	179
	(s-$C_4H_9)_3B$, "	–	"	s-$C_4H_9CH_2CHBrCOCH_3$ (85, –)[b]	179
	(i-$C_4H_9)_3B$, "	–	"	i-$C_4H_9CH_2CHBrCOCH_3$ (56, –)[b]	179

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

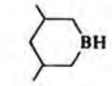
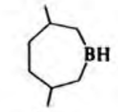
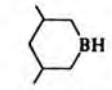
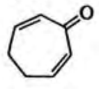
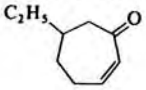
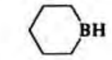
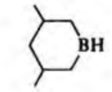
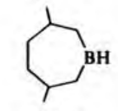
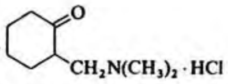
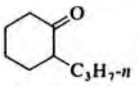
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^{a}	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$C_2H_5CH=CH_2$, "	BH_3-THF	—	n-$C_6H_{13}COCH_3$ (84, 73)	79
	$CH_3CH=CHCH_3$, "	"	—	s-$C_4H_9(CH_2)_2COCH_3$ (80, 70)	79
	$(CH_3)_2C=CH_2$, "	"	—	i-$C_4H_9(CH_2)_2COCH_3$ (65, 50)	79
	$CH_3CH=CHCH_3$, "		[O]	s-$C_4H_9(CH_2)_2COCH_3$ (74, 67)	343
	", "		[O]	" (83, 74)	343
	", "		[O]	" (80, –)	343
	t-C_4H_9Li, "		CH_3OH, –78°; [O]	t-$C_4H_9(CH_2)_2COCH_3$ (90, 76)	343
	$CH_2=CHCH=CH_2$, " (4 eq)	BH_3-THF	1. 170° 2. i-C_3H_7OH; [O]	$HO(CH_2)_6COCH_3$ (70, –)	344
9	", (E)-$CH_3OCH=CHCOCH_3$	9-BBN	C_6H_{14}; [O]	$CH_2=C(CH_3)C\equiv CCH=CHCOCH_3$ (E)-(–, 90)	88
	$Cl(CH_2)_3C\equiv CH$, "	"	"	$Cl(CH_2)_3C\equiv CCH=CHCOCH_3$ (E)-(–, 74)	88
	$CH_2=C(CH_3)C\equiv CH$, $CH_2=CHCOCH_3$	B-CH_3O-9-BBN	C_5H_{12}; EA, 0°	$CH_2=C(CH_3)C\equiv C(CH_2)_2COCH_3$ (81, –)	87
	$Cl(CH_2)_3C\equiv CH$, "	"	"	$Cl(CH_2)_3C\equiv C(CH_2)_2COCH_3$	
	Cyclopentene, $HC\equiv CCOCH_3$	BH_3-THF	Air, H_2O	$C_5H_9CH=CHCOCH_3$ (63, –)	341
	$(C_2H_5)_3B$, 	—	1. $h\nu$, ether 2. $(CH_3)_3NO$	 (90, –)	129
	$Cl(CH_2)_3C\equiv CH$, $CH_2=CHCOCH_3$	9-BBN	Reflux	$Cl(CH_2)_3CH=CH(CH_2)_2COCH_3$ (66, –)	86
	Cyclopentene, "	BH_3-THF	—	$C_5H_9(CH_2)_2COCH_3$ (99, 86)	79
	", "		H_2O; [O]	" (66, –)	343
	", "		H_2O; [O]	" (78, –)	343
	", "		H_2O; [O]	" (65, –)	343
	", "	9-BBN	H_2O; [O]	" (24, –)	343
	", "	$(C_6H_5)_2BOCH_3$	1. $LiAlH_4$ 2. CH_3SO_3H, 0° 3. Air	" (100, –)	287
	$(C_2H_5)_3B$, 	—	H_2O, CH_3I	 (85, –)	342
	$(n$-$C_4H_9)_3B$, $CH_3COCH_2COCH_3$	–	$h\nu$, C_6H_6; [O]	n-$C_4H_9C(CH_3)=CHCOCH_3$ (–, 45), n-$C_4H_9COH(CH_3)CH_2COCH_3$ (–, 45)	265
	", $CH_2=C(CH_3)COCH_3$	–	1. Air 2. Br_2, CCl_4, dark, 0° 3. CH_3OH	n-$C_5H_{11}CBr(CH_3)COCH_3$ (98, –)^{b}	179
	$(s$-$C_4H_9)_3B$, "	–	"	s-$C_4H_9CH_2CBr(CH_3)COCH_3$ (94, –)^{b}	179
	$C_2H_5CH=CH_2$ (1.5 eq), (E)-$CH_3CH=CHCOCH_3$	BH_3-THF	Air, H_2O	n-$C_4H_9CH(CH_3)CH_2COCH_3$ (65, –)	84
	$C_2H_5C(CH_3)=CH_2$, $CH_2=CHCOCH_3$	$(C_6H_5)_2BOCH_3$	1. $LiAlH_4$ 2. CH_3SO_3H, 0° 3. Air	s-$C_4H_9(CH_2)_3COCH_3$ (97, –)	287
	$(n$-$C_4H_9)_3B$, ", CH_3I	–	n-C_4H_9Li (2 eq)	n-$C_5H_{11}CH(CH_3)COCH_3$ (59, –)	177
	$CH_2=CHCH_2CH=CH_2$, " (4 eq)	BH_3-THF	1. i-C_3H_7OH (2.5 eq) 2. 170°; [O]	$HO(CH_2)_7COCH_3$ (61, –)	84
	", " (4 eq)	"	i-C_3H_7OH; [O]	$HO(CH_2)_3CH(CH_3)(CH_2)_2COCH_3$ (60, –)	84

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

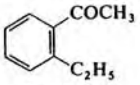
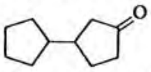
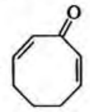
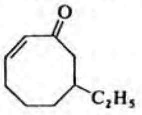
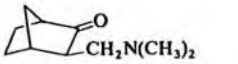
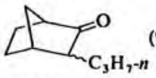
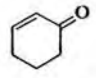
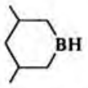
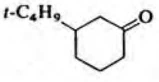
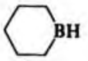
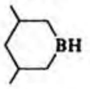
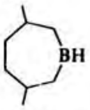
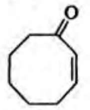
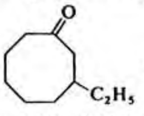
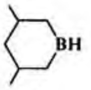
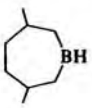
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	$(C_2H_5)_3B$, C_6H_5MgBr, CH_3COBr	—	Ether, −78°; [O]	 (71, —)	345
	", ", CH_3COCl	—	"	" (69, —)	345
	n-$C_4H_9C{\equiv}CH$, (E)-$CH_3OCH{=}CHCOCH_3$	9-BBN	C_6H_{14}; [O]	n-$C_4H_9C{\equiv}CCH{=}CHCOCH_3$ (E)-(—, 85)	88
	t-$C_4H_9C{\equiv}CH$, "	"	"	t-$C_4H_9C{\equiv}CCH{=}CHCOCH_3$ (E)-(100, 98)	88
	Cyclopentene, 	BH_3-THF	Air, H_2O	 (85, —)	84
	Cyclohexene, $HC{\equiv}CCOCH_3$	"	"	$C_6H_{11}CH{=}CHCOCH_3$ (65, —)	84
	n-$C_4H_9C{\equiv}CH$, $CH_2{=}CHCOCH_3$ (1.2 eq)	B-CH_3O-9-BBN	C_5H_{12}; EA	n-$C_4H_9C{\equiv}C(CH_2)_2COCH_3$ (96, —)	87
	t-$C_4H_9C{\equiv}CH$, " (1.2 eq)	"	"	t-$C_4H_9C{\equiv}C(CH_2)_2COCH_3$ (100, 83)	87
	$(C_2H_5)_3B$, 	—	1. $h\nu$, −78° 2. $(CH_3)_3NO$	 (15, —)	130
	", 	—	H_2O, CH_3I	 (94, 90)	342
	t-C_4H_9Li, 		1. CH_3OH, −78° 2. H_2O; [O]	 (73, 0)	343
	Cyclopentene, (E)-$CH_3CH{=}CHCOCH_3$	BH_3-THF	Air, H_2O	$C_5H_9CH(CH_3)CH_2COCH_3$ (98, —)	84
	", $CH_2{=}C(CH_3)COCH_3$	"	—	$C_5H_9CH_2CH(CH_3)COCH_3$ (88, —)	84
	Cyclohexene, $CH_2{=}CHCOCH_3$	"	H_2O	$C_6H_{11}(CH_2)_2COCH_3$ (95, 80)	79
	", "	"	40°	" (100, —)	79
	", "		H_2O; [O]	" (80, —)	343
	", "		"	" (81, —)	343
	", "		"	" (74, —)	343
	n-$C_4H_9C{\equiv}CH$, "	9-BBN	Reflux	n-$C_4H_9CH{=}CH(CH_2)_2COCH_3$ (E)-(87, —)	86
	$C_2H_5C{\equiv}CC_2H_5$, "	9-BBN	Reflux	$C_2H_5CH{=}C(C_2H_5)(CH_2)_2COCH_3$ (E)-(35, —)	86
	t-$C_4H_9C{\equiv}CH$, "	"	Reflux	t-$C_4H_9CH{=}CH(CH_2)_2COCH_3$ (E)-(—, 85)	86
	$(C_2H_5)_3B$, 	—	1. $h\nu$, −78° 2. $(CH_3)_3NO$	 (70, —)	130
	n-$C_3H_7CH{=}CH_2$, $CH_2{=}C(CH_3)COCH_3$	BH_3-THF	—	n-$C_6H_{13}CH(CH_3)COCH_3$ (70, —)	84
	$(CH_3)_2C{=}C(CH_3)_2$, $CH_2{=}CHCOCH_3$		H_2O; [O]	i-$C_3H_7C(CH_3)_2(CH_2)_2COCH_3$ (75, 71)	343
	n-$C_4H_9CH{=}CH_2$, "		H_2O; [O]	n-$C_8H_{17}COCH_3$ (32, —)	343
	$(CH_3)_2C{=}C(CH_3)_2$, "	"	H_2O; [O]	i-$C_3H_7C(CH_3)_2(CH_2)_2COCH_3$ (88, 81)	343
	n-$C_4H_9CH{=}CH_2$, "		H_2O; [O]	n-$C_8H_{17}COCH_3$ (51, —)	343
	$(CH_3)_2C{=}C(CH_3)_2$, "	"	"	i-$C_3H_7C(CH_3)_2(CH_2)_2COCH_3$ (51, —)	343
	$(C_2H_5)_3B$, $CH_2{=}C(CH_3)COCH_3$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$		1. $(CH_3)_2SO$ 2. NaOH	n-$C_3H_7C(CH_3)(COCH_3)CH_2N(CH_3)_2$ (87, —)	180

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

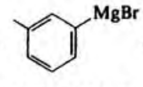
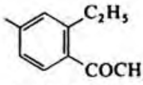
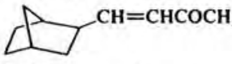
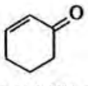
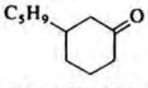
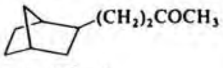
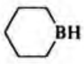
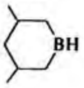
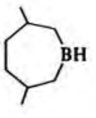
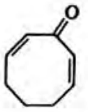
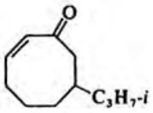
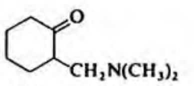
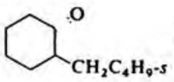
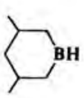
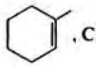
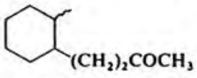
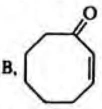
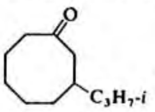
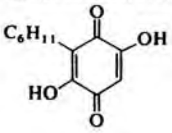
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
11	$(C_2H_5)_3B$, , CH_3COCl	—	1. Ether, −78° 2. NaOH	 (—, 33)	345
	$(n\text{-}C_3H_7)_3B$, C_6H_5MgBr, CH_3COBr	—	"	$o\text{-}(n\text{-}C_3H_7)C_6H_4COCH_3$ (25, —)	345
	", ", CH_3COCl	—	"	" (23, —)	345
	$(i\text{-}C_3H_7)_3B$, ", "	—	"	$o\text{-}(i\text{-}C_3H_7)C_6H_4COCH_3$	345
	$t\text{-}C_4H_9C{\equiv}CH$, $(E)\text{-}CH_3OC(CH_3){=}CHCOCH_3$	9-BBN	C_6H_{14}; [O]	$t\text{-}C_4H_9C{\equiv}CC(CH_3){=}CHCOCH_3$ (E)-(12, —) $o\text{-}(i\text{-}C_3H_7)C_6H_4COCH_3$ (2, —) (Z)-(5, —)	88
	", "[c]	"	"	" (E)-(20, —) (Z)-(9, —)	88
	, $HC{\equiv}CCOCH_3$	BH_3-THF	Air, H_2O	 (67, —)	341
	Cyclopentene, 	"	"	 (96, —)	84
	$n\text{-}C_4H_9C{\equiv}CH$, $(E)\text{-}CH_3CH{=}CHCOCH_3$	$B\text{-}CH_3O\text{-}9\text{-}BBN$	C_5H_{12}; EA	$n\text{-}C_4H_9C{\equiv}CCH(CH_3)CH_2COCH_3$ (100, —)	87
	, $CH_2{=}CHCOCH_3$	BH_3-THF	H_2O	 (99, 80)	79
	", "		H_2O; [O]	" (65, —)	343
	", "		"	" (81, —)	343
	", "		"	" (61, —)	343
	$(i\text{-}C_3H_7)_3B$, 	—	1. *hν*, −78° 2. $(CH_3)_3NO$	 (23, —)	130
	$CH_3CH{=}CHCH_3$, 	BH_3-THF	H_2O, CH_3I	 (61, 54)	342
	Cyclohexene, $(E)\text{-}CH_3CH{=}CHCOCH_3$	"	Air, H_2O	$C_6H_{11}CH(CH_3)CH_2COCH_3$ (96, —)	84
	", $CH_2{=}C(CH_3)COCH_3$	"	—	$C_6H_{11}CH_2CH(CH_3)COCH_3$ (100, —)	82
	", $(E)\text{-}CH_3CH{=}CHCOCH_3$		H_2O; [O]	$C_6H_{11}CH(CH_3)CH_2COCH_3$ (71, —)	343
	, $CH_2{=}CHCOCH_3$	"	"	 (E)-(70, 64) (Z)-(9, 9)	343
	$t\text{-}C_4H_9C{\equiv}CCH_3$, "	9-BBN	Reflux	$t\text{-}C_4H_9CH{=}C(CH_3)(CH_2)_2COCH_3$ (E)-(69, —)	86
	$(i\text{-}C_3H_7)_3B$, 	—	1. *hν*, −78° 2. $(CH_3)_3NO$	 (83, —)	130
	$(C_6H_{11})_3B$, $(E)\text{-}CH_3CH{=}CHCOCH_3$ (3 eq)	—	DG, $(CH_3CO_2)_2$, H_2O	$C_6H_{11}CH(CH_3)CH_2COCH_3$ (90, —)	83
	", " (2 eq)	—	DG, *hν*, $i\text{-}C_3H_7OH$	" (96, —)	83
	$CH_3CO_2(CH_2)_3CH{=}CH_2$, $CH_2{=}CHCOCH_3$	$(C_6H_5)_2BH\text{-}C_5H_5N$	1. BF_3 etherate, 0° 2. Air, $i\text{-}C_3H_7OH$	$CH_3CO_2(CH_2)_7COCH_3$ (63, —)	287
	$n\text{-}C_4H_9CH{=}CH_2$, $CH_2{=}C(CH_3)COCH_3$	BH_3-THF	—	$n\text{-}C_7H_{15}CH(CH_3)COCH_3$ (65, —)	82
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, $(CH_3)_2CO$	—	—	$n\text{-}C_5H_{11}CH(COCH_3)COH(CH_3)_2$ (—, 15)	135
12	$C_6H_5C{\equiv}CH$, $(E)\text{-}CH_3OCH{=}CHCOCH_3$	9-BBN	C_6H_{14}; [O]	$C_6H_5C{\equiv}CCH{=}CHCOCH_3$ (—, 88)	88
	", $CH_2{=}CHCOCH_3$ (1.2 eq)	$B\text{-}CH_3O\text{-}9\text{-}BBN$	C_5H_{12}; EA	$C_6H_5C{\equiv}C(CH_2)_2COCH_3$ (80, —)	87
	", "	9-BBN	Reflux	$C_6H_5CH{=}CH(CH_2)_2COCH_3$ (E)-(93, —)	86
	$(C_6H_{11})_3B$, 2,5-dihydroxybenzoquinone	—	DMF, 0°	 (—, 172)	141

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

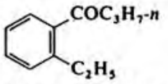
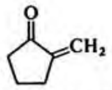
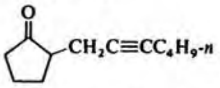
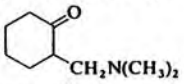
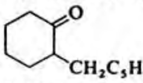
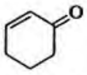
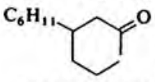
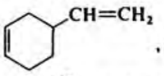
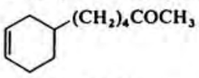
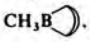
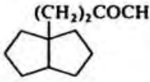
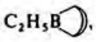
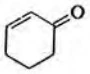
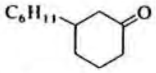
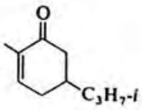
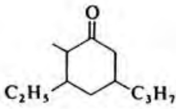
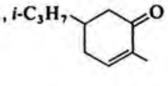
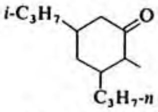
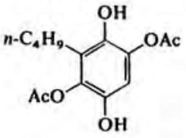
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(C_2H_5)_3B$, C_6H_5MgBr, $n\text{-}C_3H_7COCl$	—	1. Ether, −78° 2. NaOH	 (35, —)	345
	$C_6H_5CH{=}CH_2$, $CH_2{=}CHCOCH_3$	BH_3-THF	40°	$C_6H_5(CH_2)_4COCH_3$ (53, —)	79
	$C_6H_{11}C{\equiv}CH$, (*E*)-$CH_3OCH{=}CHCOCH_3$	9-BBN	C_6H_{14}; [O]	$C_6H_{11}C{\equiv}CCH{=}CHCOCH_3$ (*E*)-(—, 72)	88
	$(n\text{-}C_4H_9)_3B$, C_6H_5MgBr, CH_3COBr	—	1. Ether, −78° 2. NaOH	$o\text{-}CH_3COC_6H_4C_4H_9\text{-}n$ (23, —)	345
	", ", CH_3COCl	—	"	" (19, —)	345
	$n\text{-}C_4H_9C{\equiv}CH$, 	*B*-CH_3O-9-BBN	C_5H_{12}; EA	 (70, —)	87
	$t\text{-}C_4H_9C{\equiv}CH$, (*E*)-$CH_3OCH{=}C(CH_3)COC_2H_5$	9-BBN	C_6H_{14}; [O]	$t\text{-}C_4H_9C{\equiv}CCH{=}C(CH_3)COC_2H_5$ (*E*)-(94, —)	88
	$C_6H_{11}C{\equiv}CH$, $CH_2{=}CHCOCH_3$	*B*-CH_3O-9-BBN	C_5H_{12}; EA	$C_6H_{11}C{\equiv}C(CH_2)_2COCH_3$ (97, —)	87
	Cyclopentene, 	BH_3-THF	H_2O, CH_3I	 (90, 85)	342
	Cyclohexene, 	"	Air, H_2O	 (86, —)	84
	$n\text{-}C_4H_9C{\equiv}CH$, $(CH_3)_2C{=}CHCOCH_3$	*B*-CH_3O-9-BBN	C_5H_{12}; EA	$n\text{-}C_4H_9C{\equiv}CC(CH_3)_2CH_2COCH_3$ (70, —)	87
	, $CH_2{=}CHCOCH_3$	$(C_6H_5)_2BOCH_3$	1. $LiAlH_4$ 2. CH_3SO_3H, 0° 3. Air	 (—, 76)	287
	, ", CH_3Li	—	1. CH_3COCl, 0° 2. Air	 (—, 90)	275
	, ", CH_3Li	—	1. CH_2COCl (2 eq), 0° 2. 40°	" (—, —)	293
	$(C_6H_{11})_3B$,  (3 eq)	—	DG, $(CH_3CO_2)_2$, H_2O	 (62, —)	83
	", " (2 eq)	—	1. DG 2. *hv*, $i\text{-}C_3H_7OH$	" (100, —)	83
	$CH_2{=}CH_2$, 	BH_3-THF	Air, 40°	 (55, —)	346
	$n\text{-}C_6H_{13}CH{=}CH_2$, $CH_2{=}CHCOCH_3$	$(C_6H_5)_2BH\text{-}C_5H_5N$	1. BF_3 etherate, 0° 2. Air, $i\text{-}C_3H_7OH$	$n\text{-}C_{10}H_{21}COCH_3$ (73, —)	287
	", "	BH_3-THF	40°	" (79, 73)	79
	", "	"	H_2O	" (84, 70)	79
	", "	$(C_6H_5)_2BOCH_3$	1. $LiAlH_4$ 2. CH_3SO_3H, 0° 3. Air	" (95, —)	287
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, $n\text{-}C_3H_7CHO$	—	—	$n\text{-}C_5H_{11}CH(COCH_3)CHOHC_3H_7\text{-}n$ (—, 71)	135
13	$C_6H_5C{\equiv}CCH_3$, $CH_2{=}CHCOCH_3$	9-BBN	Reflux	$C_6H_5CH{=}C(CH_3)(CH_2)_2COCH_3$ (*E*)-(62, —)	86
	$(n\text{-}C_3H_7)_3B$, C_6H_5MgBr, $n\text{-}C_3H_7COCl$	—	1. Ether, −78° 2. NaOH	$o\text{-}(n\text{-}C_3H_7)C_6H_4COC_3H_7\text{-}n$ (20, —)	345
	$t\text{-}C_4H_9C{\equiv}CH$, (*E*)-$CH_3OCH{=}CHCOC_4H_9\text{-}t$	9-BBN	C_6H_{14}; [O]	$t\text{-}C_4H_9C{\equiv}CCH{=}CHCOC_4H_9\text{-}t$ (*E*)-(100, —)	88
	$CH_3CH{=}CH_2$, 	BH_3-THF	Air, 40°	 (60, —)	346
	$n\text{-}C_6H_{13}CH{=}CH_2$, $CH_2{=}C(CH_3)COCH_3$	"	—	$n\text{-}C_9H_{19}CH(CH_3)COCH_3$ (68, —)	82
14	$(n\text{-}C_4H_9)_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, 25)	141

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

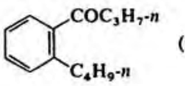
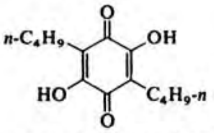
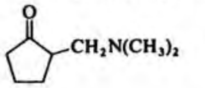
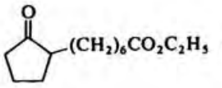
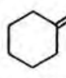
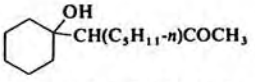
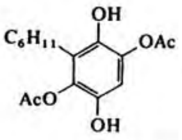
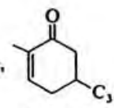
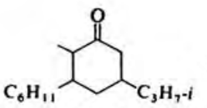
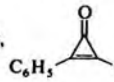
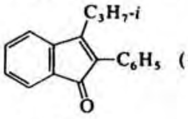
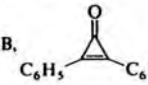
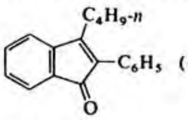
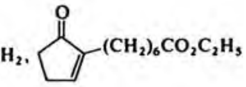
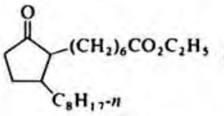
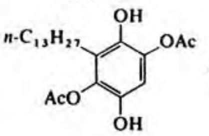
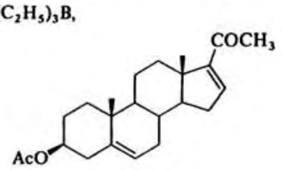
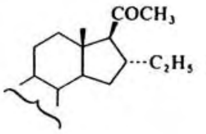
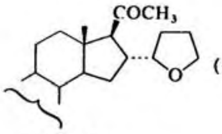
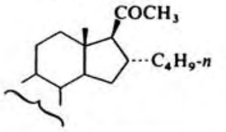
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	", C_6H_5MgBr, n-C_3H_7COCl	—	1. Ether, −78° 2. NaOH	 (22, —)	345
	", 2,5-dihydroxybenzoquinone	—	DMF, air, 0°	 (—, 16)	141
	n-$C_8H_{17}C{\equiv}CH$, (E)-$CH_3OCH{=}CHCOCH_3$	9-BBN	C_6H_{14}; [O]	n-$C_8H_{17}C{\equiv}CCH{=}CHCOCH_3$ (E)-(—, 81)	88
	$CH_2{=}CH(CH_2)_3CO_2C_2H_5$, 	BH_3–THF	CH_3I; [O]	 (—, 65)	347
	$(n$-$C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, 	—	—	 (—, 38)	135
15	t-$C_4H_9C{\equiv}CH$, (E)-$C_6H_5COCH{=}CHOCH_3$	9-BBN	C_6H_{14}; [O]	$C_6H_5COCH{=}CHC{\equiv}CC_4H_9$-$t$ (E)-(65, —)	88
	$(n$-$C_4H_9)_3B$, $CH_2{=}CHCOCH_3$, C_6H_5CHO	—	—	$C_6H_5CHOHCH(C_5H_{11}$-$n)COCH_3$ (—, 91)	135
	$(i$-$C_3H_7)_3B$, $HC{\equiv}CC_5H_{11}$-n, CH_3COCl	—	1. n-C_4H_9Li, reflux 2. Jones reagent[d]	$(i$-$C_3H_7)_2C{=}C(C_5H_{11}$-$n)COCH_3$ (—, 42)	348
16	$(C_6H_{11})_3B$, 2,5-diacetoxybenzoquinone	—	DMF, 0°	 (—, —)	141
	Cyclohexene, 	BH_3–THF	Air, 40°	 (82, —)	346
	$(i$-$C_3H_7)_3B$, $C_6H_5C{\equiv}CH$, CH_3COCl	—	1. n-C_4H_9Li, reflux 2. Jones reagent[d]	$(i$-$C_3H_7)_2C{=}C(C_6H_5)COCH_3$ (—, 36)	141
17	$(n$-$C_4H_9)_3B$, n-$C_5H_{11}C{\equiv}CH$, CH_3COCl	—	"	$(n$-$C_4H_9)_2C{=}C(C_5H_{11}$-$n)COCH_3$ (—, 36)	141
18	$(i$-$C_3H_7)_3B$, 	—	C_6H_6, ether	 (—, 13)	349
	", "	—	C_6H_6, THF, O_2	" (—, 52)	349
	$(n$-$C_4H_9)_3B$, $C_6H_5C{\equiv}CH$, CH_3COCl	—	1. n-C_4H_9Li, reflux 2. Jones reagent[d]	$(n$-$C_4H_9)_2C{=}C(C_6H_5)COCH_3$ (—, 30)	141
	$(s$-$C_4H_9)_3B$, ", "	—	"	$(s$-$C_4H_9)_2C{=}C(C_6H_5)COCH_3$ (—, 28)	58
19	$(n$-$C_4H_9)_3B$, 	—	C_6H_6, ether	 (—, 17)	349
22	n-$C_6H_{13}CH{=}CH_2$, 	BH_3–THF	[O]	 (—, 46)	347
23	$(n$-$C_{13}H_{27})_3B$, 2,5-diacetoxybenzoquinone	—	Reflux	 (—, —)	141

TABLE IV. KETONES. C. THREE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
25	$(C_2H_5)_3B$, 	—	[O]	 (—, 32)	300
27	$(n\text{-}C_4H_9)_3B$, ", THF	—	[O]	 (—, 34)	300
	$(i\text{-}C_4H_9)_3B$, ", "	—	[O]	" (—, 32)	300
	$(n\text{-}C_4H_9)_3B$, "	—	$i\text{-}C_3H_7OH$; [O]	 (—, 40)	300

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[a] Reagents following the semicolon are those used to decompose an intermediate organoborane. Abbreviations are: [O] = oxidation with alkaline hydrogen peroxide, EA = ethanolamine.

[b] The yield was determined by ^1H NMR analysis.

[c] The isomer ratio (Z:E) was 84:16.

[d] Jones reagent is an 8 N solution of chromic acid in sulfuric acid.

TABLE IV. KETONES. D. FOUR-OR-MORE-CARBON HOMOLOGATION

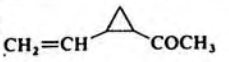
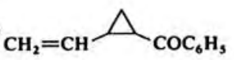
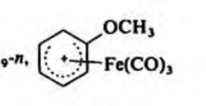
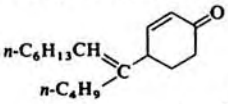
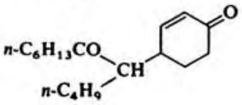
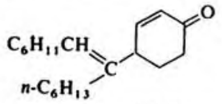
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	$(n\text{-}C_3H_7)_3B$, 	—	Air; [O]	$n\text{-}C_4H_9CH{=}CH(CH_2)_2COCH_3$ (25, —)	181
11	$(s\text{-}C_4H_9)_3B$, "	—	"	$s\text{-}C_4H_9CH_2CH{=}CH(CH_2)_2COCH_3$ (28, —)	181
14	$(C_5H_9)_3B$, $HC{\equiv}CC_4H_9\text{-}n$, $BrCH_2COCH_3$	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7CO_2H$	$C_5H_9CH{=}C(C_4H_9\text{-}n)CH_2COCH_3$ (—, 70)	164
	", ", "	--	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$C_5H_9COCH(C_4H_9\text{-}n)CH_2COCH_3$ (—, 74)	164
15	$(n\text{-}C_3H_7)_3B$, 	—	Air; [O]	$n\text{-}C_4H_9CH{=}CH(CH_2)_2COC_6H_5$ (21, —)	181
	", "	—	CH_3Li, CuBr, 0°; [O]	" (*E*)-(48, —)	63
	", "	—	CH_3Li, CuCl, 0°; [O]	" (*E*)-(38, —)	63
	", "	—	CH_3Li, CuI, 0°; [O]	" (*E*)-(84, —)	63
16	$(n\text{-}C_4H_9)_3B$, "	—	"	$n\text{-}C_5H_{11}CH{=}CH(CH_2)_2COC_6H_5$ (*E*)-(81, —)	63
	$(i\text{-}C_4H_9)_3B$, "	—	"	$i\text{-}C_4H_9CH_2CH{=}CH(CH_2)_2COC_6H_5$ (*E*)-(75,—)	63
17	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}\text{-}n$, $BrCH_2COCH_3$	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7CO_2H$	$n\text{-}C_6H_{13}CH{=}C(C_6H_{13}\text{-}n)CH_2COCH_3$ (—, 75)	164
	", ", "	—	$n\text{-}C_4H_9Li$, DG, 0°;	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2COCH_3$ (—, 75)	164
18	", $HC{\equiv}CC_4H_9\text{-}n$, 	—	1. $n\text{-}C_4H_9Li$ 2. $i\text{-}C_3H_7CO_2H$ 3. Ce^{+4}	 (*Z*)-(—, 47) (*E*)-(—, 25)	166
	", ", ",	—	1. $n\text{-}C_4H_9Li$ 2. $(CH_3)_3NO$ 3. Ce^{+4}	 (—, 46)	166

TABLE IV. KETONES. D. FOUR-OR-MORE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
20	$(C_6H_{11})_3B$, n-$C_6H_{13}C{\equiv}CH$, "	—	1. n-C_4H_9Li 2. i-$C_3H_7CO_2H$ 3. Ce^{+4}	 (*Z*)-(—, 46) (*E*)-(—, 24)	166
22	$(n$-$C_6H_{13})_3B$, ", p-$ClC_6H_4COCH_2Br$	—	1. n-C_4H_9Li, 0° 2. DG, −78 to 40° 3. CH_3CO_2H	n-$C_6H_{13}CH{=}C(C_6H_{13}$-$n)CH_2COC_6H_4Cl$-$p$ (*E*)-(—, 77)	65
	", ", $C_6H_5COCH_2Br$	—	1. n-C_4H_9Li, DG, 0° 2. i-$C_3H_7CO_2H$	n-$C_6H_{13}CH{=}C(C_6H_{13}$-$n)CH_2COC_6H_5$ (—, 74)	164
	", ", "	—	n-C_4H_9Li, DG, 0°; [O]	n-$C_6H_{13}COCH(C_6H_{13}$-$n)CH_2COC_6H_5$ (—, 74)	164

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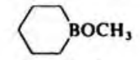
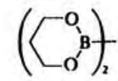
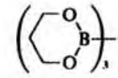
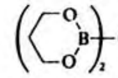
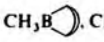
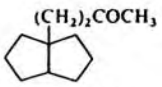
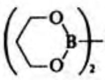
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE IV. KETONES. E. MISCELLANEOUS PREPARATIONS

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5		—	Br_2, CH_2Cl_2, H_2O; [O]	Cyclopentanone (48, −)	27
7	 $-CH_2$, n-$C_5H_{11}Br$, CH_3I	—	1. LTMP, −75° 2. C_6H_{12}, reflux; [O]	n-$C_5H_{11}COCH_3$ (−, 78)	182
	n-$C_6H_{13}B(OC_4H_9$-$n)_2$, CH_3MgBr	—	Br_2, $h\nu$, CCl_4, −78°; [O]	" (−, 70)	350
8	$CH_2{=}CHCH_2C(OC_2H_5){=}CHB(CH_2CH{=}CH_2)_2$	—	1. H_2, Pt; [O] 2. H^+, CrO_3	$CH_3COCH_2CH(C_3H_7$-$n)CO_2H$ (−, −)	351
9	 $-CLi$, C_6H_5CHO, CH_3Li	—	I_2, NaOH; [O]	$C_6H_5CH_2COCH_3$ (−, −)	100
	$C_2H_5C{\equiv}CC_2H_5$, $(CH_3)_3SiCl$	Sia_2BH	LTMP; [O]	$CH_3CH[Si(CH_3)_3]CH_2COC_2H_5$ (90, −)	277
10	 $-CH_2$, n-$C_5H_{11}Br$, n-$C_3H_7CO_2CH_3$	—	1. LTMP, −78° 2. C_6H_{12}, reflux 3. H_2O	n-$C_6H_{13}COC_3H_7$-n (66, −)	182
11	n-$C_4H_9C{\equiv}CCl$, n-$C_3H_7C{\equiv}CH$	$ThexylBH_2$	1. $NaOCH_3$, −25° 2. i-$C_3H_7CO_2H$, reflux	n-$C_3H_7CH{=}CHCOC_5H_{11}$-n (E)-(58, 48)	32
12	, $CH_2{=}CHCOCH_3$	—	1. CH_3Li, C_5H_{12}, −78° 2. CH_3COCl, 0° 3. Air	 (−, 90)	275
13	 $-CH_2$, n-$C_5H_{11}Br$, C_6H_5CHO		1. LTMP, −75° 2. C_6H_{12}, reflux; [O]	n-$C_5H_{11}COCH_2C_6H_5$ (84, −)	182
	", ", $C_6H_5CO_2CH_3$	—	"	n-$C_6H_{13}COC_6H_5$ (99, −)	182
14	n-$C_4H_9C{\equiv}CCl$, $C_6H_{11}C{\equiv}CH$	$ThexylBH_2$	$NaOCH_3$, −25°; [O]	n-$C_5H_{11}COCH{=}CHC_6H_{11}$ (E)-(54, 48)	32

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE V. ALDEHYDES. A. ONE-CARBON HOMOLOGATION

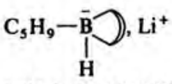
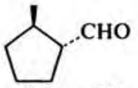
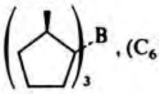
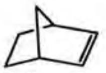
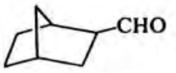
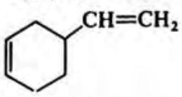
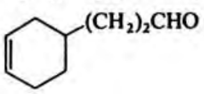
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	$NCCH_2CH{=}CH_2$	9-BBN	1. $LiAlH(OC_4H_9\text{-}t)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$NC(CH_2)_3CHO$ (85, 72)	185
	$CH_3CH{=}CHCH_3$	BH_3–THF	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$s\text{-}C_4H_9CHO$ (94, —)	183
	$(CH_3)_2C{=}CH_2$	"	"	$i\text{-}C_4H_9CHO$ (91, —)	183
	"	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (52, —)	184
6	Cyclopentene	"	"	C_5H_9CHO (79, —)	184
	$(C_5H_9)_3B$, $(C_6H_5S)_2CH_2$	—	1. $n\text{-}C_4H_9Li$, −30° 2. H_2O_2, pH 7 buffer	" (—, 91)	169
		—	CO; [O]	" (85. —)	253
	$(CH_3)_2C{=}CHCH_3$	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$i\text{-}C_3H_7CH(CH_3)CHO$ (60, —)	184
7	Cyclohexene	BH_3–THF	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$C_6H_{11}CHO$ (93, —)	183
	"	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (81, —)	184
		9-BBN	"	 (—, 50)[b]	15
	 , $(C_6H_5S)_2CH_2$		1. $n\text{-}C_4H_9Li$, −30° 2. H_2O_2, pH 7 buffer	" (—, 82)	169
	$(C_6H_{11})_3B$, "	—	"	$C_6H_{11}CHO$ (—, 94)	169
	$AcO(CH_2)_2CH{=}CH_2$	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$AcO(CH_2)_4CHO$ (45, —)	185
	"	"	1. $LiAlH(OC_4H_9\text{-}t)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (92, 84)	185
	$C_2H_5O_2CCH_2CH{=}CH_2$	"	"	$C_2H_5O_2C(CH_2)_3CHO$ (83, 70)	185
	$n\text{-}C_4H_9CH{=}CH_2$	BH_3–THF	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$n\text{-}C_6H_{13}CHO$ (98, —)	183
	"	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (93, —)	184
	$(n\text{-}C_6H_{13})_3B$, $(C_6H_5S)_2CH_2$	—	1. $n\text{-}C_4H_9Li$, −30° 2. H_2O_2, pH 7 buffer	" (—, 79)	169
	$(C_6H_5)_3B$	—	1. $LiAlH(OCH_3)_3$, CO, 0° 2. NaH_2PO_4, K_2HPO_4; H_2O_2	C_6H_5CHO (—, 84)	352
8		BH_3–THF	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	 (87, —)	183
	"	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (59, —)	184
	 , $(C_6H_5S)_2CH_2$	—	1. $n\text{-}C_4H_9Li$, −30° 2. H_2O_2, pH 7 buffer	" (—, 75)	169
	$CH_2{=}CH(CH_2)_2CH{=}CH_2$	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$OHC(CH_2)_6CHO$ (78, —)	184
9	$C_6H_5CH{=}CH_2$	"	"	$C_6H_5(CH_2)_2CHO$ (84, —)	184
		"	"	 (93, —)	184
10	$[C_6H_5CH(CH_3)CH_2]_3B$,	—	1. $n\text{-}C_4H_9Li$, −30° 2. H_2O_2, pH 7 buffer	$C_6H_5CH(CH_3)CH_2CHO$ (—, 95)	169
11	$C_6H_5CO_2CH_2CH{=}CH_2$	9-BBN	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$C_6H_5CO_2(CH_2)_3CHO$ (25, —)	185

TABLE V. ALDEHYDES. A. ONE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$C_6H_5CO_2CH{=}CH_2$	9-BBN	1. $LiAlH(OC_4H_9\text{-}t)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$C_6H_5CO_2(CH_2)_3CHO$ (89, 74)	185
12	$NC(CH_2)_8CH{=}CH_2$	"	"	$NC(CH_2)_{10}CHO$ (99, 83)	185
13	$CH_3O_2C(CH_2)_8CH{=}CH_2$	"	1. $LiAlH(OCH_3)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	$CH_3O_2C(CH_2)_{10}CHO$ (99, –)	185
	"	"	1. $LiAlH(OC_4H_9\text{-}t)_3$, CO 2. NaH_2PO_4, K_2HPO_4; H_2O_2	" (99, 85)	185
	$AcO(CH_2)_8CH{=}CH_2$	"	"	$AcO(CH_2)_{10}CHO$ (99, 87)	185
	"	R_2BH[c]	$KBH(OC_3H_7\text{-}i)_3$, ^{14}CO; [O]	$AcO(CH_2)_{10}{}^{14}CHO$ (–, 59)	291

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The product was isolated as the alcohol.

[c] The structure of the borane reagent is not specified in the original paper. It is presumably 9-BBN, $(C_6H_{11})_2BH$, or Sia_2BH.

TABLE V. ALDEHYDES. B. TWO-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	$(C_2H_5)_3B$, N_2CHCHO	—	—	n-C_3H_7CHO (88, –)	186
6	$(CH_2{=}CHCH_2)_3B$, $CH_3C{\equiv}CH$	—	H^+	$CH_2{=}CHCH_2CH(CH_3)CHO$ (–, –)	321
	$[CH_2{=}C(CH_3)CH_2]_3B$, $HC{\equiv}CH$	—	1. 140–150° 2. H_2O_2, H^+	$CH_2{=}C(CH_3)(CH_2)_2CHO$ (–, 43)[a,b]	307
	$(n$-$C_4H_9)_3B$, N_2CHCHO	—	—	n-$C_5H_{11}CHO$ (77, –)	186
	$(s$-$C_4H_9)_3B$, "	—	—	s-$C_4H_9CH_2CHO$ (33, –)	186
	$(i$-$C_4H_9)_3B$, "	—	—	i-$C_4H_9CH_2CHO$ (67, –)	186
7	$(C_5H_9)_3B$, "	—	—	$C_5H_9CH_2CHO$ (98, –)	186
9	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CC_4H_9$-n	—	H^+	$CH_2{=}CHCH_2CH(C_4H_9$-$n)CHO$ (–, --)	353
	$(n$-$C_4H_9)_3B$, HCO_2CH_3, $N_2CHCO_2C_2H_5$	—	—	n-$C_4H_9CH(CO_2C_2H_5)CHO$ (–, 65)	135
	", $HCO_2C_2H_5$, "	—	—	" (–, 60)	135
	", $HCON(CH_3)_2$, "	—	—	" (–, 40)	135
	", p-$HCO_2C_6H_4NO_2$, "	—	—	" (–, 44)	135
	", $HCON(CH_3)C_6H_5$, "	—	—	" (–, 8)	135

[a] The product was isolated as the 2,4-dinitrophenylhydrazone.

[b] The yield is not given in the original paper. The yield in the table is determined by multiplication of yields in the intermediate steps.

TABLE V. ALDEHYDES. C. THREE-CARBON HOMOLOGATION

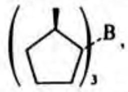
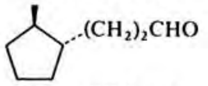
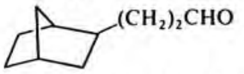
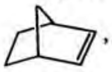
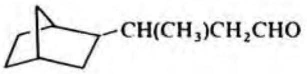
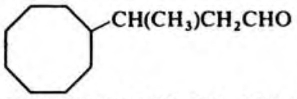
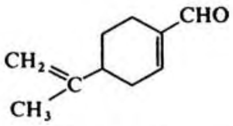
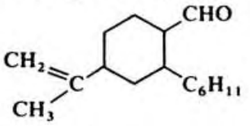
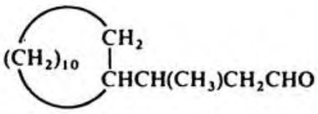
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$(C_2H_5)_3B$, (*E*)-$CH_3CH{=}CHCHO$ (3 eq)	—	DG, $(CH_3CO_2)_2$, H_2O	*s*-$C_4H_9CH_2CHO$ (48, —)	83
	" (1.5 eq), "	—	Air, H_2O	" (50, —)	84
	", " (2 eq)	—	DG, *hν*, *i*-C_3H_7OH	" (60, —)	83
	", $CH_2{=}C(CH_3)CHO$	—	$CH_3COCH_2COCH_3$, 90°	*n*-$C_3H_7CH(CH_3)CHO$ (—, 60)	187
7	$C_2H_5CH{=}CH_2$, $CH_2{=}CBrCHO$	BH_3-THF	H_2O	*n*-$C_5H_{11}CHBrCHO$ (100, 85)[a]	81
	$CH_3CH{=}CHCH_3$, "	"	H_2O	*s*-$C_4H_9CH_2CHBrCHO$ (90, 81)[a]	81
	$(CH_3)_2C{=}CH_2$, "	"	"	*i*-$C_4H_9CH_2CHBrCHO$ (100, 80)[a]	81
	$C_2H_5CH{=}CH_2$, $CH_2{=}CHCHO$	"	"	*n*-$C_6H_{13}CHO$ (47, —)	80
	$CH_3CH{=}CHCH_3$, "	"	"	*s*-$C_4H_9(CH_2)_2CHO$ (96, —)	80
	$(CH_3)_2C{=}CH_2$, "	"	"	*i*-$C_4H_9(CH_2)_2CHO$ (87, —)	80
	(*i*-$C_3H_7)_3B$, $CH_2{=}C(CH_3)CHO$	—	Benzoin, 90°	*i*-$C_4H_9CH(CH_3)CHO$ (—, 98)	187
8	Cyclopentene, $CH_2{=}CHCHO$	BH_3-THF	H_2O	$C_5H_9(CH_2)_2CHO$ (88, —)	80
	$[CH_2{=}CH(CH_2)_2]_3B$, $CH_2{=}C(CH_3)CHO$	—	8-Quinolinol, 90°	$CH_2{=}CH(CH_2)_3CH(CH_3)CHO$ (—, 81)	187
	$[ClCH_2CH(CH_3)CH_2]_3B$, "	—	"	$ClCH_2CH(CH_3)(CH_2)_2CH(CH_3)CHO$ (—, 97)	187
	$CH_3CH{=}CHCH_3$, $CH_2{=}C(CH_3)CHO$	BH_3-THF	H_2O	*s*-$C_4H_9CH_2CH(CH_3)CHO$ (100, 95)	81
	$(CH_3)_2C{=}CH_2$, "	"	"	*i*-$C_4H_9CH_2CH(CH_3)CHO$ (100, 95)	81
	$C_2H_5CH{=}CH_2$ (1.5 eq), (*E*)-$CH_3CH{=}CHCHO$	"	Air, H_2O	*n*-$C_4H_9CH(CH_3)CH_2CHO$ (54, —)	84
	$CH_3CH{=}CHCH_3$, "	"	"	*s*-$C_4H_9CH(CH_3)CH_2CHO$ (90, —)	84
	$(CH_3)_2C{=}CH_2$ (1.5 eq), "	"	"	*i*-$C_4H_9CH(CH_3)CH_2CHO$ (50, —)	84
	(*n*-$C_4H_9)_3B$, "	—	C_5H_5N (3 eq)	*n*-$C_4H_9CH(CH_3)CH_2CHO$ (20, —)	188
	(*i*-$C_4H_9)_3B$, $CH_2{=}C(CH_3)CHO$	—	Benzoin, 90°	*i*-$C_4H_9CH_2CH(CH_3)CHO$ (—, 86)	187
9	Cyclohexene, $CH_2{=}CBrCHO$	BH_3-THF	H_2O	$C_6H_{11}CH_2CHBrCHO$ (90, 65)[a]	81
	Cyclopentene, $CH_3CH{=}CHCHO$	"	C_5H_5N (3 eq)	$C_5H_9CH(CH_3)CH_2CHO$ (99, —)	188
	Cyclohexene, $CH_2{=}CHCHO$	"	H_2O	$C_6H_{11}(CH_2)_2CHO$ (77, —)	80
	 "	—	—	 (—, 91)	15
	n-$C_4H_9CH{=}CH_2$, "	BH_3-THF	H_2O	*n*-$C_8H_{17}CHO$ (65, —)	80
10	 "	"	"	 (80, —)	80
	Cyclohexene, $CH_3CH{=}CHCHO$	"	α,α-Dipyridyl (3 eq)	$C_6H_{11}CH(CH_3)CH_2CHO$ (16, —)	188
	", "	"	2-Picoline (3 eq)	" (47, —)	188
	", "	"	$(C_2H_5)_3N$ (3 eq)	" (48, —)	188
	", "	"	3-Picoline (3 eq)	" (48, —)	188
	", "	"	2,6-Lutidine	" (83, —)	188
	", "	"	4-Picoline	" (96, —)	188
	", "	"	Pyridine (3 eq)	" (97, —)	188
	", "	"	Air, H_2O	" (96, —)	84
	", $CH_2{=}C(CH_3)CHO$	"	H_2O	$C_6H_{11}CH_2CH(CH_3)CHO$ (100, 92)	81
	$(C_6H_{11})_3B$, (*E*)-$CH_3CH{=}CHCHO$ (3 eq)	—	DG, $(CH_3CO_2)_2$, H_2O	$C_6H_{11}CH(CH_3)CH_2CHO$ (86, —)	83
	", " (2 eq)	—	*hν*, DG, *i*-C_3H_7OH	" (100, —)	83
	", $CH_2{=}C(CH_3)CHO$	—	CH_3OH	$C_6H_{11}CH_2CH(CH_3)CHO$ (—, 93)	187
	(*n*-$C_3H_7)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7$-*i* (3 eq)	—	Air, CH_3OH	*n*-$C_3H_7CH(CH_3)CH_2CH{=}NC_3H_7$-*i* (69, —)	215
11	(*n*-$C_4H_9)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7$-*i* (3 eq)	—	"	*n*-$C_4H_9CH(CH_3)CH_2CH{=}NC_3H_7$-*i* (76, —)	215
	$(C_6H_5CH_2)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7$-*i* (3 eq)	—	1. CH_3OH 2. $(CH_3)_3NO$	$C_6H_5CH_2CH(CH_3)CH_2CHO$ (—, 75)	187
	 , $CH_3CH{=}CHCH{=}NC_3H_7$-*i* (3 eq)	BH_3-THF	H_2O	 (100, 97)	81

TABLE V. ALDEHYDES. C. THREE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
12	Cyclooctene, $CH_3CH{=}CHCHO$	"	C_5H_5N, (3 eq)	 (23, –)	188
	$(C_5H_9)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7$-*i* (3 eq)	–	Air, CH_3OH	$C_5H_9CH(CH_3)CH_2CH{=}NC_3H_7$-*i* (53, –)	215
	$(n\text{-}C_5H_{11})_3B$, "	–	"	$n\text{-}C_5H_{11}CH(CH_3)CH_2CH{=}NC_3H_7$-*i* (83, –)	215
16	Cyclohexene, 	–	Air, 40°	 (70, –)	346
	Cyclododecene, $CH_3CH{=}CHCHO$	–	C_5H_5N, (3 eq)	 (81, –)	188

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[a] The yield is based on ^1H NMR analysis.

TABLE V. ALDEHYDES. D. MISCELLANEOUS PREPARATIONS

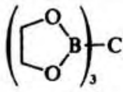
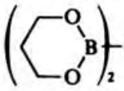
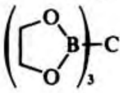
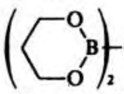
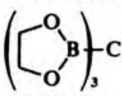
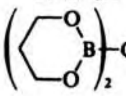
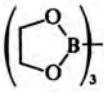
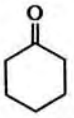
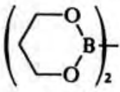
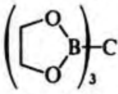
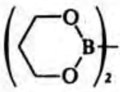
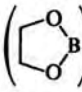
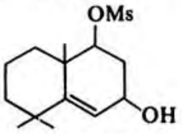
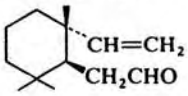
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	 —CH, $(CH_3)_2CO$	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	i-C_3H_7CHO (63, —)	99
5	 —CH_2, $Cl(CH_2)_4I$	—	LTMP, −75°; [O]	$Cl(CH_2)_4CHO$ (83, —)	182
	 —CH, n-C_3H_7CHO	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	n-C_4H_9CHO (85, —)	99
	 —CH_2, n-C_4H_9Br	—	LTMP, −75°; [O]	" (79, —)	182
	", n-C_4H_9I	—	"	" (86, —)	182
	$Cl_2CHB(OC_3H_7$-$i)_2$, n-C_4H_9Li	—	1. −78° 2. H_2O_2, pH 7	" (85, —)	189
	", t-C_4H_9Li	—	"	t-C_4H_9CHO (35, —)	189
6	 —CH, $CH_2{=}CH(CH_2)_2CHO$	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	$CH_2{=}CH(CH_2)_3CHO$ (79, —)	99
	", $(C_2H_5)_2CO$	—	"	$(C_2H_5)_2CHCHO$ (—, 74)	99
	 —CH_2, n-$C_5H_{11}Br$	—	LTMP, −75°; [O]	n-$C_5H_{11}CHO$ (80, 62)	182

TABLE V. ALDEHYDES. D. MISCELLANEOUS PREPARATIONS (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	$Cl_2CHB(OC_3H_7\text{-}i)_2$, C_6H_5MgBr	—	1. −78° 2. H_2O_2, pH 8.8	C_6H_5CHO (70, —)	189
	 —CH, 	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	$C_6H_{11}CHO$ (97, —)	99
	", $CH_3COCH{=}C(CH_3)_2$	—		$(CH_3)_2C{=}CHCH(CH_3)CHO$ (—, 81)	99
8	", C_6H_5CHO	—	"	$C_6H_5CH_2CHO$ (97, 77)	99
	 —CH_2, $C_6H_5CH_2Br$	—	LTMP, −75°; [O]	" (71, —)	182
	 —CH, $CH_3CO(CH_2)_2CO_2C_2H_5$	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	$OHCCH(CH_3)(CH_2)_2CO_2C_2H_5$ (—, 65)	99
	", $n\text{-}C_6H_{13}CHO$	—	"	$n\text{-}C_7H_{15}CHO$ (87, 83)	99
	 —CH_2, $n\text{-}C_7H_{15}I$	—	LTMP, −75°; [O]	" (82, —)	182
	", $n\text{-}C_7H_{15}OTs$	—	"	" (76, —)	182
	$n\text{-}C_3H_7C{\equiv}CH$, $(CH_3)_3SiCl$	Sia_2BH	LTMP; [O]	$C_2H_5CH[Si(CH_3)_3]CH_2CHO$ (72, —)	277
9	 —CH, $C_6H_5COCH_3$	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	$C_6H_5CH(CH_3)CHO$ (—, 80)	99
	", $n\text{-}C_7H_{15}CHO$	—	"	$n\text{-}C_8H_{17}CHO$ (94, —)	99
	$n\text{-}C_4H_9C{\equiv}CH$, $(CH_3)_3SiCl$	Sia_2BH	LTMP; [O]	$n\text{-}C_3H_7CH[Si(CH_3)_3]CH_2CHO$ (77, —)	277
11	$n\text{-}C_6H_{13}C{\equiv}CH$, "	"	"	$n\text{-}C_5H_{11}CH[Si(CH_3)_3]CH_2CHO$ (75, —)	277
13		BH_3–THF	NaOH	 (—, 40)	354

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. A. ONE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	n-$C_4H_9C{\equiv}CH$	DCHB (2 eq)	1. n-C_4H_9Li (2 eq) 2. CO_2	n-$C_5H_{11}CH(CO_2H)_2$ (—, 65–70)	98
10	$C_6H_5C{\equiv}CH$	"	"	$C_6H_5CH_2CH(CO_2H)_2$ (—, 65–70)	98
12	n-$C_8H_{17}C{\equiv}CH$	"	"	n-$C_9H_{19}CH(CO_2H)_2$ (—, 65–70)	98

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. B. TWO-CARBON HOMOLOGATION

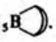
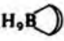
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	$CH_3Li, Br_2CHCO_2C_2H_5$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 0°	$CH_3CHBrCO_2C_2H_5$ (40, –)	173
	$(n\text{-}C_3H_7)_3B, C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$n\text{-}C_4H_9CO_2H$ (81, –)	191
6	$CH_2{=}CH_2, Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 0°	$C_2H_5CHBrCO_2C_2H_5$ (97, –)	16
	$(C_2H_5)_3B, N_2CHCO_2C_2H_5$	–	Br_2, CCl_4, 0°, dark	" (83, –)[b]	179
	", $Br_2CHCO_2C_2H_5$	–	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (96, –)	196
	C_2H_5B, "	–	"	" (83, –)	196
	$CH_2{=}CH_2, Cl_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 0°	$C_2H_5CHClCO_2C_2H_5$ (98, –)	16
	", $Br_2CHCO_2C_2H_5$	"	"	$n\text{-}C_3H_7CO_2C_2H_5$ (98, –)	190
	" "	9-BBN	"	" (51, –)	192
	$(C_2H_5)_3B$, "	–	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (95, –)	196
	C_2H_5B, "	–	"	" (70, –)	196
	$s\text{-}C_4H_9B$, $C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$s\text{-}C_4H_9CH_2CO_2H$ (39, –)	191
	$(n\text{-}C_4H_9)_3B$, "	–	"	$n\text{-}C_5H_{11}CO_2H$ (100, –)	191
	$(s\text{-}C_4H_9)_3B$, "	–	"	$s\text{-}C_4H_9CH_2CO_2H$ (17, –)	191
	$(i\text{-}C_4H_9)_3B$, "	–	"	$i\text{-}C_4H_9CH_2CO_2H$ (67, –)	191
7	$(C_2H_5)_3B, NCCHBrCO_2C_2H_5$	–	0°[c]	$C_2H_5CH(CN)CO_2C_2H_5$ (91, –)	202
	C_2H_5B, "	–	"	" (94, –)	202
	$(CH_2{=}CHCH_2)_3B, N_2CHCO_2C_2H_5$ (2 eq)	–	Low temp	$CH_2{=}CH(CH_2)_2CO_2C_2H_5$ (–, 75)	355
	$(C_5H_9)_3B, C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$C_5H_9CH_2CO_2H$ (97, –)	191
8	$(CH_3CH{=}CHCH_2)_3B, N_2CHCO_2C_2H_5$ (2 eq)	–	Low temp	$CH_3CH{=}CH(CH_2)_2CO_2C_2H_5$ (–, 67)	355
	$[CH_2{=}C(CH_3)CH_2]_3B$, " (2 eq)	–	"	$CH_2{=}C(CH_3)(CH_2)_2CO_2C_2H_5$ (–, 86)	355
	$C_6H_{11}B$, $C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$C_6H_{11}CH_2CO_2H$ (36, –)	191
	$CH_3CH{=}CH(CH_2)_3B$, "	"	"	$CH_3CH{=}CH(CH_2)_4CO_2H$ (93, –)	191
	$CH_3CH{=}CHCH_3, Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 0°	$s\text{-}C_4H_9CHBrCO_2C_2H_5$ (80, –)	16
	$(CH_3)_2C{=}CH_2$, "	"	"	$i\text{-}C_4H_9CHBrCO_2C_2H_5$ (85, –)	16
	$i\text{-}C_4H_9B$, "	–	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (81, –)	196
	$(n\text{-}C_4H_9)_3B, N_2CHCO_2C_2H_5$	–	Br_2, CCl_4, 0°, dark	$n\text{-}C_4H_9CHBrCO_2C_2H_5$ (76, –)[b]	179
	$CH_2 = CH_2$ (2 eq), $Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 50°	$(C_2H_5)_2CHCO_2C_2H_5$ (69, –)	16
	", $C_2H_5CHBrCO_2C_2H_5$	"	"	" (87, –)	16
	$C_2H_5CH{=}CH_2, BrCH_2CO_2C_2H_5$	"	$t\text{-}C_4H_9OK, t\text{-}C_4H_9OH$, 0°	$n\text{-}C_5H_{11}CO_2C_2H_5$ (93, –)	190
	$CH_3CH{=}CHCH_3$, "	"	"	$s\text{-}C_4H_9CH_2CO_2C_2H_5$ (80, –)	190
	$(CH_3)_2C{=}CH_2$, "	"	"	$i\text{-}C_4H_9CH_2CO_2C_2H_5$ (98, –)	190
	$C_2H_5CH{=}CH_2$, "	9-BBN	"	$n\text{-}C_5H_{11}CO_2C_2H_5$ (59, –)	192
	$CH_3CH{=}CHCH_3$, "	"	"	$s\text{-}C_4H_9CH_2CO_2C_2H_5$ (68, –)	192
	$(CH_3)_2C{=}CH_2$, "	"	"	$i\text{-}C_4H_9CH_2CO_2C_2H_5$ (53, –)	192
	$n\text{-}C_4H_9BCl_2, N_2CHCO_2C_2H_5$	–	Ether, –62°	$n\text{-}C_5H_{11}CO_2C_2H_5$ (57, –)	194
	$(C_2H_5)_3B$ (2 eq), $Br_2CHCO_2C_2H_5$	–	(2 eq), THF, $t\text{-}C_4H_9OH$, 0°[c]	$(C_2H_5)_2CHCO_2C_2H_5$ (66, –)	196

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. B. TWO-CARBON HOMOLOGATION (*Continued*)

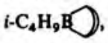
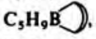
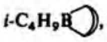
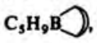
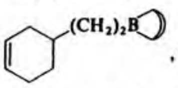
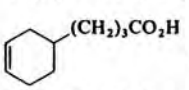
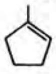
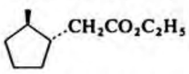
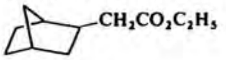
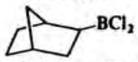
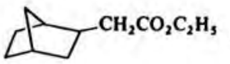
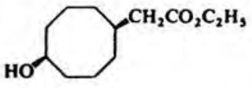
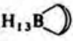
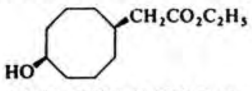
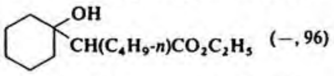
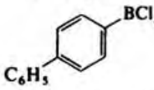
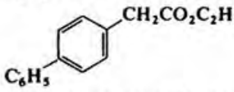
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_4H_9)_2BCl$, $N_2CHCO_2C_2H_5$	—	−78°	$n\text{-}C_5H_{11}CO_2C_2H_5$ (89, —)	193
	$(s\text{-}C_4H_9)_2BCl$, "	—	−78°	$s\text{-}C_4H_9CH_2CO_2C_2H_5$ (89, —)	193
	$(i\text{-}C_4H_9)_2BCl$, "	—	−78°	$i\text{-}C_4H_9CH_2CO_2C_2H_5$ (88, —)	193
	, $BrCH_2CO_2C_2H_5$	—	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (56, —)	196
	$(n\text{-}C_6H_{13})_3B$, $C_6H_5OCH_2CO_2H$	—	1. LDA, 0° 2. Reflux; [O]	$n\text{-}C_7H_{15}CO_2H$ (77, —)	191
9	Cyclopentene, $Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_5H_9CHBrCO_2C_2H_5$ (93, —)	16
	, "	—	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (78, —)	196
	$(C_5H_9)_3B$, "	—	"	" (76, —)	196
	Cyclopentene, $Cl_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_5H_9CHClCO_2C_2H_5$ (54, —)	16
	", "	9-BBN	"	" (90, —)	192
	", $N_2CHCO_2C_2H_5$	BH_3-THF	THF, D_2O	$C_5H_9CHDCO_2C_2H_5$ (97, —)	18
	, $NCCHBrCO_2C_2H_5$	—	0°[c]	$i\text{-}C_4H_9CHCNCO_2C_2H_5$ (48, —)	202
	Cyclopentene, $N_2CHCO_2C_2H_5$	BH_3-THF	H_2O, 0°	$C_5H_9CH_2CO_2C_2H_5$ (58, —)	203
	", $BrCH_2CO_2C_2H_5$	"	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	" (95, 75)	190
	", "	9-BBN	"	" (63, —)	192
	", $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	BH_3-THF	Reflux	" (35, —)	19
	$C_5H_9BCl_2$, $N_2CHCO_2C_2H_5$	—	Ether, −62°	" (71, —)	194
	$(C_5H_9)_2BCl$, "	—	−78°	" (94, 78)	193
	, $BrCH_2CO_2C_2H_5$	—	THF, $t\text{-}C_4H_9OH$, 0°[c]	" (57, —)	196
	$(C_5H_9)_3B$, "	—	"	" (75, —)	196
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, HCO_2CH_3	—	—	$n\text{-}C_4H_9CH(CHO)CO_2C_2H_5$ (—, 65)	135
	", ", $HCO_2C_2H_5$	—	—	" (—, 60)	135
	", ", $HCON(CH_3)_2$	—	—	" (—, 40)	135
	", ", $p\text{-}HCO_2C_6H_4NO_2$	—	—	" (—, 44)	135
	", ", $HCON(CH_3)C_6H_5$	—	—	" (—, 8)	135
10	C_6H_5Li, $Br_2CHCO_2C_2H_5$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_6H_5CHBrCO_2C_2H_5$ (65, —)	173
	$p\text{-}ClC_6H_4BCl_2$, $N_2CHCO_2C_2H_5$ (1.1 eq)	—	−25°	$p\text{-}ClC_6H_4CH_2CO_2C_2H_5$ (100, 91)	194
	C_6H_5Li, $BrCH_2CO_2C_2H_5$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_6H_5CH_2CO_2C_2H_5$ (50, —)	173
	$C_6H_5BCl_2$, $N_2CHCO_2C_2H_5$	—	Ether, −62°	" (87, —)	194
	", " (1.1 eq)	—	−25°	" (100, 98)	194
	$(C_6H_5)_3B$, $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	—	Reflux	" (45, —)	19
	$n\text{-}C_4H_9C\equiv CH$, $N_2CHCO_2C_2H_5$	BF_3-ether	1. $n\text{-}C_4H_9Li$, −20° 2. H_2O	$n\text{-}C_4H_9C\equiv CCH_2CO_2C_2H_5$ (100, 88)	195
	$t\text{-}C_4H_9C\equiv CH$, "	"	"	$t\text{-}C_4H_9C\equiv CCH_2CO_2C_2H_5$ (83, 63)	195
	, $C_6H_5OCH_2CO_2H$	—	1. LDA, 0° 2. Reflux; [O]	 (60, —)	191
	Cyclohexene, $Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_6H_{11}CHBrCO_2C_2H_5$ (47, —)	16
	", "	9-BBN	"	" (68, —)	192
	", $Cl_2CHCO_2C_2H_5$	"	"	$C_6H_{11}CHClCO_2C_2H_5$ (88, 67)	192
	", $BrCH_2CO_2C_2H_5$	BH_3-THF	"	$C_6H_{11}CH_2CO_2C_2H_5$ (80, —)	190
	, "	9-BBN	$t\text{-}C_4H_9OK$	 (60, 54)	15,192
	Cyclohexene, "	9-BBN	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$C_6H_{11}CH_2CO_2C_2H_5$ (62, —)	192
	$C_6H_{11}BCl_2$, $N_2CHCO_2C_2H_5$	—	Ether, −62°	" (57, —)	194
	$(C_6H_{11})_2BCl$, "	—	−78°	" (93, —)	193
	$(n\text{-}C_4H_9)_3B$, ", CH_3CN	—	—	$n\text{-}C_4H_9CH(COCH_3)CO_2C_2H_5$ (—, 57)	135
	$n\text{-}C_4H_9CH{=}CH_2$, $N_2CDCO_2C_2H_5$	BH_3-THF	THF, D_2O	$n\text{-}C_6H_{13}CD_2CO_2C_2H_5$ (98, —)	18
	", $Br_2CHCO_2C_2H_5$	"	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$n\text{-}C_6H_{13}CHBrCO_2C_2H_5$ (98, —)	16
	", $Cl_2CHCO_2C_2H_5$	"	"	$n\text{-}C_6H_{13}CHClCO_2C_2H_5$ (98, —)	16
	", $N_2CHCO_2C_2H_5$	"	THF, D_2O	$n\text{-}C_6H_{13}CHDCO_2C_2H_5$ (98, —)	18
	", "	"	H_2O, 0°	$n\text{-}C_7H_{15}CO_2C_2H_5$ (83, —)	203
	$n\text{-}C_3H_7C(CH_3){=}CH_2$, "	"	"	$n\text{-}C_3H_7CH(CH_3)(CH_2)_2CO_2C_2H_5$ (40, —)	203
	$n\text{-}C_4H_9CH{=}CH_2$, $BrCH_2CO_2C_2H_5$	"	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$n\text{-}C_7H_{15}CO_2C_2H_5$ (93, —)	190
	", "	9-BBN	"	" (74, —)	192
	", $ClCH_2CO_2C_2H_5$	"	"	" (74, —)	192
	", $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	BH_3-THF	Reflux	" (49, —)	19

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. B. TWO-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$n\text{-}C_3H_7C(CH_3)=CH_2$, "	"	"	$n\text{-}C_3H_7CH(CH_3)(CH_2)_2CO_2C_2H_5$ (40, –)	19
	$n\text{-}C_3H_7CH(CH_3)CH_2BCl_2$, $N_2CHCO_2C_2H_5$	–	Ether, –62°	$n\text{-}C_3H_7CH(CH_3)(CH_2)_2CO_2C_2H_5$ (61, –)	194
	$n\text{-}C_3H_7CH(C_2H_5)BCl_2$, "	–	"	$n\text{-}C_3H_7CH(C_2H_5)CH_2CO_2C_2H_5$ (60, –)	194
	$(n\text{-}C_8H_{17})_3B$, $C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$n\text{-}C_9H_{19}CO_2H$ (90, –)	191
11	$p\text{-}CH_3C_6H_4Li$, $BrCH_2CO_2C_2H_5$	9-BBN	1. CH_3SO_3H, 0° 2. $t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$p\text{-}CH_3C_6H_4CH_2CO_2C_2H_5$ (73, –)	173
	$p\text{-}CH_3C_6H_4BCl_2$, $N_2CHCO_2C_2H_5$ (1.1 eq)	–	–25°	" (100, 95)	194
	$[C_6H_5CH(CH_3)CH_2]_3B$, $C_6H_5OCH_2CO_2H$	–	1. LDA, 0° 2. Reflux; [O]	$C_6H_5CH(CH_3)(CH_2)_2CO_2H$ (65, –)	191
	$C_6H_{11}B$, $NCCHBrCO_2C_2H_5$	–	0°[c]	$C_6H_{11}CH(CN)CO_2C_2H_5$ (22, –)	202
	, $BrCH_2CO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°[c]	 (85, –)	190
	", $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	"	Reflux	" (31, –)	19
	, $N_2CHCO_2C_2H_5$	–	Ether, –62°	" (60, –)	194
	$n\text{-}C_5H_{11}C\equiv CH$, "	BF_3-ether	1. $n\text{-}C_4H_9Li$, –20° 2. H_2O	$n\text{-}C_5H_{11}C\equiv CCH_2CO_2C_2H_5$ (97, 87)	195
	, "	–	–78°	 (92, –)	193
	$n\text{-}C_5H_{11}CH=CH_2$, $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	BH_3-THF	Reflux	$n\text{-}C_8H_{17}CO_2C_2H_5$ (52, 45)	19
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, $(CH_3)_2CO$	–	–	$(CH_3)_2COHCH(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 73)	73
12	$C_6H_5C\equiv CH$, $N_2CHCO_2C_2H_5$	BF_3-ether	1. $n\text{-}C_4H_9Li$, –20° 2. H_2O	$C_6H_5C\equiv CCH_2CO_2C_2H_5$ (100, 92)	195
	HB, $C_6H_5C\equiv CH$, $N_2CHCO_2C_2H_5$	–	[O]	 (40, –)	175
	", $n\text{-}C_4H_9C\equiv CH$, "	–	[O]	" (54, –)	175
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, $n\text{-}C_3H_7CN$	–	–	$n\text{-}C_4H_9CH(COC_3H_7\text{-}n)CO_2C_2H_5$ (–, 54)	135
	$n\text{-}C_6H_{13}B$, $N_2CHCO_2C_2H_5$	–	[O]	 (77, –)	175
	$CH_2=CH_2$, $n\text{-}C_6H_{13}CHBrCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 50°	$n\text{-}C_6H_{13}CH(C_2H_5)CO_2C_2H_5$ (72, –)	16
	$n\text{-}C_4H_9CH=CH_2$, $C_2H_5CHBrCO_2C_2H_5$	"	"	" (63, –)	16
	$n\text{-}C_6H_{13}CH=CH_2$, $N_2CHCO_2C_2H_5$	"	H_2O, 0°	$n\text{-}C_9H_{19}CO_2C_2H_5$ (78, –)	203
	", $(CH_3)_2\overset{+}{S}\overset{-}{C}HCO_2C_2H_5$	"	Reflux	" (48, –)	19
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, $n\text{-}C_3H_7CHO$	–	–	$n\text{-}C_4H_9CH(CO_2C_2H_5)CHOHC_3H_7\text{-}n$ (–, 87)	73
14	", ", cyclohexanone	–	–	 (–, 96)	73
	$n\text{-}C_8H_{17}CH=CH_2$, $Br_2CHCO_2C_2H_5$	BH_3-THF	$t\text{-}C_4H_9OK$, $t\text{-}C_4H_9OH$, 0°	$n\text{-}C_{10}H_{21}CHBrCO_2C_2H_5$ (92, –)	16
15	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, C_6H_5CN	–	–	$C_6H_5COCH(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 71)	135
	", ", C_6H_5CHO	–	–	$C_6H_5CHOHCH(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 81)	73,72
16	, $N_2CHCO_2C_2H_5$ (1.1 eq)	–	–25°	 (100, 91)	194
	$(n\text{-}C_4H_9)_3B$, $N_2CHCO_2C_2H_5$, $C_6H_5CH_2CN$	–	–	$C_6H_5CH_2COCH(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 61)	135
17	$(C_6H_{11})_3B$, ", C_6H_5CHO	–	–	$C_6H_5CHOHCH(C_6H_{11})CO_2C_2H_5$ (–, 87)	73
	$(n\text{-}C_4H_9)_3B$, ", $C_6H_5COC_2H_5$	–	–	$C_6H_5COH(C_2H_5)CH(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 68)	73
20	", $N_2CHCOSCH_2C_6H_5$, C_6H_5CHO	–	–	$C_6H_5CHOHCH(C_4H_9\text{-}n)COSCH_2C_6H_5$ (–, 51)	135
22	", $N_2C(CH_2C_6H_5)CO_2C_2H_5$, C_6H_5CHO	–	–	$C_6H_5CHOHC(CH_2C_6H_5)(C_4H_9\text{-}n)CO_2C_2H_5$ (–, 70)	73

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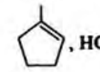
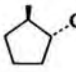
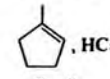
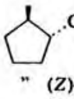
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The yield is based on ^1H NMR analysis.

[c] Potassium 2,6-di-*tert*-butylphenoxide was used as the base.

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. C. THREE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	$(n\text{-}C_3H_7)_3B$, $HC{\equiv}CCO_2C_2H_5$	—	CH_3Li, CuI, DME, 0°; [O]	$n\text{-}C_3H_7CH{=}CHCO_2C_2H_5$ *(E)*-(63, —)	198
	$(n\text{-}C_3H_7)_3\bar{B}CH_3Li^+$, *(E)*-$BrCH{=}CHCO_2C_2H_5$	—	CuBr, 0°; [O]	" *(E)*-(60, —)	61
	", "	—	CuCl, 0°; [O]	" *(E)*-(42, —)	61
	", "	—	CuI, 0°; [O]	" *(E)*-(80, —)	61
	$(n\text{-}C_3H_7)_3B$, $CH_2{=}CHCO_2C_2H_5$	—	CH_3Li, CuBr, 0°; [O]	$n\text{-}C_5H_{11}CO_2C_2H_5$ (44, —)	63
	", "	—	e^-, $(n\text{-}C_4H_9)_4NI$, CH_3CN	" (77, —)	197
	$(CH_3)_2C{=}CHCH_3$, $HC{\equiv}CCO_2C_2H_5$	$ThexylBH_2$	$NaOCH_3$; [O]	$i\text{-}C_3H_7CH(CH_3)CHOHCH_2CO_2H$ (72, 68)	89
9	$(n\text{-}C_4H_9)_3B$, "	—	CH_3Li, CuI, DME, 0°; [O]	$n\text{-}C_4H_9CH{=}CHCO_2C_2H_5$ *(E)*-(61, —)	198
	$(i\text{-}C_4H_9)_3B$, "	—	"	$i\text{-}C_4H_9CH{=}CHCO_2C_2H_5$ *(E)*-(53, —)	198
	$(n\text{-}C_4H_9)_3\bar{B}CH_3Li^+$, *(E)*-$BrCH{=}CHCO_2C_2H_5$	—	CuI, 0°; [O]	$n\text{-}C_4H_9CH{=}CHCO_2C_2H_5$ *(E)*-(98, —)	61
	$(i\text{-}C_4H_9)_3\bar{B}CH_3Li^+$, *(E)*-$BrCH{=}CHCO_2C_2H_5$	—	"	$i\text{-}C_4H_9CH{=}CHCO_2C_2H_5$ *(E)*-(65, —)	61
	, $HC{\equiv}CCO_2C_2H_5$	$ThexylBH_2$	$NaOCH_3$; [O]	$CHOHCH_2CO_2H$ (81, 69)	89
	Cyclohexene, "	"	"	$C_6H_{11}CHOHCH_2CO_2H$ (74, 60)	89
	$(n\text{-}C_3H_7)_3B$, $CH_2{=}C(CH_3)CO_2C_2H_5$	—	e^-, $(n\text{-}C_4H_9)_4NI$, CH_3CN	$n\text{-}C_4H_9CH(CH_3)CO_2C_2H_5$ (85, 73)	197
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}CHCO_2C_2H_5$	—	"	$n\text{-}C_6H_{13}CO_2C_2H_5$ (57, —)	197
	$(s\text{-}C_4H_9)_3B$, "	—	"	$s\text{-}C_4H_9(CH_2)_2CO_2C_2H_5$ (65, 59)	197
	$n\text{-}C_3H_7C(CH_3){=}CH_2$, $HC{\equiv}CCO_2C_2H_5$	$ThexylBH_2$	$NaOCH_3$; [O]	$n\text{-}C_3H_7CH(CH_3)CH_2CHOHCH_2CO_2H$ (46, —)	89
10	, "	"	"	$CHOHCH_2CO_2H$ (57, 51)	89
	$(CH_3)_2C{=}CHCH_3$, "	"	Br_2, heat	$i\text{-}C_3H_7CH(CH_3)CH{=}CHCO_2C_2H_5$ *(E)*-(55, 46)	48
	", "	"	1. Br_2 2. $NaOC_2H_5$	" *(Z)*-(65, —)	48
	$(C_5H_9)_3B$, $CH_2{=}CHCO_2C_2H_5$	—	e^-, $(n\text{-}C_4H_9)_4NI$, CH_3CN	$C_5H_9(CH_2)_2CO_2C_2H_5$ (51, —)	197
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}C(CH_3)CO_2C_2H_5$	—	"	$n\text{-}C_5H_{11}CH(CH_3)CO_2C_2H_5$ (64, 60)	197
	$(n\text{-}C_5H_{11})_3B$, $CH_2{=}CHCO_2C_2H_5$	—	"	$n\text{-}C_7H_{15}CO_2C_2H_5$ (86, —)	197
	$(n\text{-}C_4H_9)_3B$, $CH_3COCH_2CO_2C_2H_5$ (3 eq)	—	$h\nu$, C_6H_6; [O]	$n\text{-}C_4H_9COH(CH_3)CH_2CO_2C_2H_5$ (—, 60)	265
11	, $HC{\equiv}CCO_2C_2H_5$	$ThexylBH_2$	Br_2, heat	$CH{=}CHCO_2C_2H_5$ *(E)*-(49, 42) *(Z)*-(3, 3)	48
	", "	"	Br_2, $NaOC_2H_5$	" *(Z)*-(49, 48) *(E)*-(8, 5)	48
	Cyclohexene, "	"	Br_2, heat	$C_6H_{11}CH{=}CHCO_2C_2H_5$ *(E)*-(65, —)	48
	", "	"	Br_2, $NaOC_2H_5$	" *(Z)*-(69, —), *(E)*-(4, —)	48
	$(C_5H_9)_3B$, $CH_2{=}C(CH_3)CO_2C_2H_5$	—	e^-, $(n\text{-}C_9H_9)_4NI$, CH_3CN	$C_5H_9CH_2CH(CH_3)CO_2C_2H_5$ (51, —)	197
	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CCO_2C_2H_5$	—	CH_3Li, CuI, DME, 0°; [O]	$n\text{-}C_6H_{13}CH{=}CHCO_2C_2H_5$ *(E)*-(42, —)	198
	$(n\text{-}C_4H_9)_3B$, $CH_2{=}C(CH_3)CO_2C_2H_5$	—	e^-, $(n\text{-}C_4H_9)_4NI$, CH_3CN	$n\text{-}C_6H_{13}CH(CH_3)CO_2C_2H_5$ (94, —)	197
12	, $HC{\equiv}CCO_2C_2H_5$	$ThexylBH_2$	Br_2, heat	$CH{=}CHCO_2C_2H_5$ *(E)*-(68, 58)	48
	", "	"	Br_2, $NaOC_2H_5$	" *(Z)*-(68, 54), *(E)*-(8, 6)	48
	$(C_6H_{11})_3B$, $CH_3COCH_2CO_2C_2H_5$	—	$h\nu$, C_6H_6; [O]	$C_6H_{11}COH(CH_3)CH_2CO_2C_2H_5$ (—, 33)	265
13	$(n\text{-}C_8H_{17})_3\bar{B}CH_3Li^+$, *(E)*-$BrCH{=}CHCO_2C_2H_5$	—	CuI, 0°; [O]	$n\text{-}C_8H_{17}CH{=}CHCO_2C_2H_5$ *(E)*-(81, —)	61
17	$[CH_3O_2C(CH_2)_{10}]_3\bar{B}CH_3Li^+$, *(E)*-$BrCH{=}CHCO_2C_2H_5$	—	"	$CH_3O_2C(CH_2)_{10}CH{=}CHCO_2C_2H_5$ *(E)*-(55, —)	61

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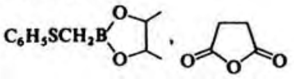
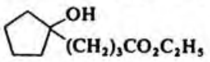
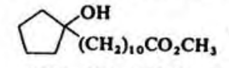
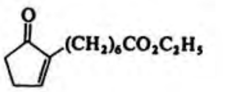
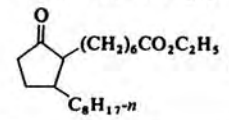
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. D. FOUR-OR-MORE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	$CH_3SOCH_2\bar{B}(C_4H_9\text{-}n)_3Li^+$, $ClCO(CH_2)_2CO_2CH_3$	—	THF, C_6H_{14}	$CH_3SOCH_2CO(CH_2)_2CO_2CH_3$ (—, 61)	56
8	$(C_2H_5)_3B$, $BrCH_2CH{=}CHCO_2C_2H_5$	—	0°[b]	$C_2H_5CH{=}CHCH_2CO_2C_2H_5$ (78, —)	199
9	$n\text{-}C_4H_9\bar{B}(C_5H_9)_3Li^+$, $ClCO(CH_2)_2CO_2CH_3$	—	THF, C_6H_{14}	$n\text{-}C_4H_9CO(CH_2)_2CO_2CH_3$ (76, —)	56
10	$(n\text{-}C_4H_9)_3B$, $BrCH_2CH{=}CHCO_2C_2H_5$	—	0°[b]	$n\text{-}C_4H_9CH{=}CHCH_2CO_2C_2H_5$ (72, 60)	199
	$(s\text{-}C_4H_9)_3B$, "	—	"	$s\text{-}C_4H_9CH{=}CHCH_2CO_2C_2H_5$ (89, —)	199
	$(i\text{-}C_4H_9)_3B$, "	—	"	$i\text{-}C_4H_9CH{=}CHCH_2CO_2C_2H_5$ (82, —)	199
11		—	1. LDA 2. H^+	$C_6H_5SCH_2CO(CH_2)_2CO_2H$ (74, —)	298
	$(C_5H_9)_3B$, $BrCH_2CH{=}CHCO_2C_2H_5$	—	0°[b]	$C_5H_9CH{=}CHCH_2CO_2C_2H_5$ (81, —)	199
	$(CH_3)_2C{=}CH_2$, $CH_2{=}CHCH_2CO_2C_2H_5$	ThexylBH_2	CO, H_2O, 70 atm, 50°; [O]	$i\text{-}C_4H_9CO(CH_2)_3CO_2C_2H_5$ (98, 84)	154
	Cyclopentene, $CH_2{=}CHCH_2CO_2C_2H_5$	"	Br_2, CH_2Cl_2, H_2O; [O]	 (90, 72)	26
12	$(C_6H_{11})_3B$, $BrCH_2CH{=}CHCO_2C_2H_5$	—	0°[b]	$C_6H_{11}CH{=}CHCH_2CO_2C_2H_5$ (73, —)	199
13	$(n\text{-}C_4H_9)_3B$, $p\text{-}BrCH_2C_6H_4CO_2CH_3$	—	CH_3Li, CuCN; [O]	$p\text{-}(n\text{-}C_5H_{11})C_6H_4CO_2CH_3$ (52, —)	60
	$(C_6H_{11})_2BH$, $CH_2{=}CHCH_2CO_2C_2H_5$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_3CO_2C_2H_5$ (—, 54)	153
15	$(C_5H_9)_3B$, $HC{\equiv}CC_4H_9\text{-}n$, $BrCH_2CO_2C_2H_5$	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7OH$	$C_5H_9CH{=}C(C_4H_9\text{-}n)CH_2CO_2C_2H_5$ (—, 67)	164
	", ", "	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$C_5H_9COCH(C_4H_9\text{-}n)CH_2CO_2C_2H_5$ (—, 74)	164
17	", $CH_2{=}CH(CH_2)_8CO_2CH_3$	ThexylBH_2	Br_2, CH_2Cl_2, H_2O; [O]	 (—, 75)	26
18	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}\text{-}n$, $BrCH_2CO_2C_2H_5$	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7OH$	$n\text{-}C_6H_{13}CH{=}C(C_6H_{13}\text{-}n)CH_2CO_2C_2H_5$ (—, 69)	164
	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}\text{-}n$, $BrCH_2CO_2C_2H_5$	—	$n\text{-}C_4H_9Li$, DG, 0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CO_2C_2H_5$ (—, 78)	164
19	$(C_6H_{11})_2BH$, $CH_2{=}CH(CH_2)_8CO_2CH_3$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_{10}CO_2CH_3$ (—, 53)	153
21	$C_6H_5CH{=}CH_2$, "	ThexylBH_2	CO, H_2O, 70 atm, 50°; [O]	$C_6H_5(CH_2)_2CO(CH_2)_{10}CO_2CH_3$ (—, 73)	154
22	$n\text{-}C_6H_{13}CH{=}CH_2$, 	BH_3-THF	[O]	 (—, 46)	347

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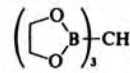
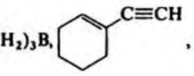
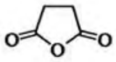
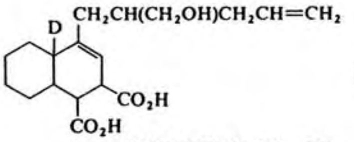
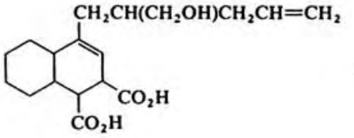
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] Potassium 2,6-di-*tert*-butylphenoxide was used as a base.

TABLE VI. CARBOXYLIC ACIDS AND DERIVATIVES. E. MISCELLANEOUS PREPARATIONS

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	 CH, $CH_3CO(CH_2)_2CO_2C_2H_5$	—	CH_3Li, CH_2Cl_2, THF, −78° to room temp; [O]	$OHCCH(CH_3)(CH_2)_2CO_2C_2H_5$ (—, 65)	99
	$CH_2{=}CHCH_2C(OC_2H_5){=}CHB(CH_2CH{=}CH_2)_2$	—	1. H_2, Pt; [O] 2. H^+, CrO_3	$CH_3COCH_2CH(C_3H_7\text{-}n)CO_2H$ (—, —)	351
18	$(CH_2{=}CHCH_2)_3B$, , 	—	1. H_2, Pt black, CH_3OH, 0° 2. CH_3OD, CD_3CO_2D; [O]	 (—, —)	319
	", ", "	—	CH_3CO_2H, CH_3OH, 0°; [O]	 (—, 8)	319

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE VII. NITRILES. A. TWO-CARBON HOMOLOGATION

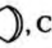
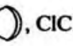
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	$(C_2H_5)_3B$, Cl_2CHCN	—	[b], 0°	$C_2H_5CHClCN$ (89, —)	201
	C_2H_5B, "	—	[b], 0°	" (87, —)	201
	$(C_2H_5)_3B$, $ClCH_2CN$	—	[b], 0	n-C_3H_7CN (95, —)	200
5	", $BrCH(CN)_2$	—	[b], 0°	$C_2H_5CH(CN)_2$ (96, —)	202
	C_2H_5B, "	—	[b], 0°	" (79, —)	202
6	n-C_4H_9B, Cl_2CHCN	—	[b], 0°	n-$C_4H_9CHClCN$ (75, —)	201
	s-C_4H_9B, "	—	[b], 0°	s-$C_4H_9CHClCN$ (69, —)	201
	i-C_4H_9B, "	—	[b], 0°	i-$C_4H_9CHClCN$ (73, —)	201
	$(C_2H_5)_3B$ (2 eq), "	—	[b], 0°	$(C_2H_5)_2CHCN$ (96, —)	201
	C_2H_5B (2 eq), "	—	[b],	" (97, —)	201
	n-C_4H_9B, $ClCH_2CN$	—	[b], 0°	n-$C_5H_{11}CN$ (76, —)	200
	s-C_4H_9B, "	—	[b], 0°	s-$C_4H_9CH_2CN$ (65, —)	200
	i-C_4H_9B, "	—	[b], 0°	i-$C_4H_9CH_2CN$ (57, —)	200
	$(n\text{-}C_4H_9)_3B$, "	—	[b], 0°	n-$C_5H_{11}CN$ (89, —)	200
	", CH_3CN	—	e^-, $(C_2H_5)_4NI$; [O]	" (44, —)	103
	$(s\text{-}C_4H_9)_3B$, "	—	"	s-$C_4H_9CH_2CN$ (47, —)	103

TABLE VII. NITRILES. A. TWO-CARBON HOMOLOGATION (*Continued*)

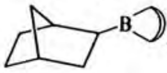
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	*n*-C_4H_9B, $BrCH(CN)_2$	—	^{b}, 0°	*n*-$C_4H_9CH(CN)_2$ (75, —)	202
	s-C_4H_9B, "	—	^{b}, 0°	*s*-$C_4H_9CH(CN)_2$ (87, —)	202
	i-C_4H_9B, "	—	^{b}, 0°	*i*-$C_4H_9CH(CN)_2$ (91, —)	202
	(*n*-$C_4H_9)_3B$, "	—	^{b}, 0°	*n*-$C_4H_9CH(CN)_2$ (92, 73)	202
	C_5H_9B, Cl_2CHCN	—	^{b}, 0°	$C_5H_9CHClCN$ (76, —)	201
	Cyclopentene, N_2CHCN (1.5 eq)	BH_3-THF	KOH, 0°	$C_5H_9CH_2CN$ (99, 81)	203
	C_5H_9B, $ClCH_2CN$	—	^{b}, 0°	", (72, —)	200
	$(C_5H_9)_3B$, "	—	^{b}, 0°	" (67, 50)	200
	$(C_2H_5)_3B$, $BrCH(CN)CO_2C_2H_5$	—	^{b}, 0°	$C_2H_5CH(CN)CO_2C_2H_5$ (91, —)	202
	C_2H_5B, "	—	^{b}, 0°	" (94, —)	202
8	C_6H_5B, $ClCH_2CN$	—	^{b}, 0°	$C_6H_5CH_2CN$ (75, —)	200
	C_5H_9B, $BrCH(CN)_2$	—	^{b}, 0°	$C_5H_9CH(CN)_2$ (87, —)	202
	$C_6H_{11}B$, Cl_2CHCN	—	^{b}, 0°	$C_6H_{11}CHClCN$ (78, —)	201
	", $ClCH_2CN$	—	^{b}, 0°	$C_6H_{11}CH_2CN$ (77, —)	200
	n-$C_4H_9CH{=}CH_2$, N_2CHCN (1.5 eq)	BH_3-THF	KOH, 0°	*n*-$C_7H_{15}CN$ (95, —)	203
	(*E*)-$C_2H_5CH{=}CHC_2H_5$, " (1.5 eq)	"	"	*n*-$C_3H_7CH(C_2H_5)CH_2CN$ (54, —)	203
	n-$C_3H_7C(CH_3){=}CH_2$, " (1.5 eq)	"	"	*n*-$C_3H_7CH(CH_3)(CH_2)_2CN$ (97, —)	203
	$(C_2H_5)_3B$, *s*-$C_4H_9CHClCN$	—	^{b}	*s*-$C_4H_9CH(C_2H_5)CN$ (91, —)	201
	", *i*-$C_4H_9CHClCN$	—	^{b}	*i*-$C_4H_9CH(C_2H_5)CN$ (88, —)	201
	s-C_4H_9B, $(C_2H_5)_3B$, Cl_2CHCN	—	^{b}	*s*-$C_4H_9CH(C_2H_5)CN$ (69, —)	201
	i-C_4H_9B, ", "	—	^{b}	*i*-$C_4H_9CH(C_2H_5)CN$ (52,)	201
	(*n*-$C_6H_{13})_3B$, CH_3CN	—	e^-, $(C_2H_5)_4NI$; [O]	*n*-$C_7H_{15}CN$ (52,)	103
	", "	—	e^-, KBr; [O]	" (trace, —)	103
	", "	—	e^-, KI; [O]	" (19, —)	103
9	$C_6H_{11}B$, $BrCH(CN)_2$	—	^{b}, 0°	$C_6H_{11}CH(CN)_2$ (85, —)	202
	, $ClCH_2CN$	—	^{b}, 0°	 (65, —)	200
	$(C_2H_5)_3B$, $C_5H_9CHClCN$	—	^{b}	$C_5H_9CH(C_2H_5)CN$ (83, —)	201
	", C_5H_9B, Cl_2CHCN	—	^{b}	" (52, —)	201
	i-C_4H_9B, $BrCH(CN)CO_2C_2H_5$	—	^{b}, 0°	*i*-$C_4H_9CH(CN)CO_2C_2H_5$ (48, —)	202
	n-$C_5H_{11}CH{=}CH_2$, N_2CHCN (1.5 eq)	BH_3-THF	KOH, 0°	*n*-$C_8H_{17}CN$ (93, —)	203
	(*n*-$C_6H_{13})_3B$, C_2H_5CN	—	e^-, $(C_2H_5)_4NI$; [O]	*n*-$C_6H_{13}CH(CH_3)CN$ (27, —)	103
10	$(C_2H_5)_3B$, $C_6H_{11}CHClCN$	—	^{b}	$C_6H_{11}CH(C_2H_5)CN$ (85, —)	201
	n-C_4H_9B (2 eq), Cl_2CHCN	—	^{b}	(*n*-$C_4H_9)_2CHCN$ (85, —)	201
	s-C_4H_9B (2 eq), "	—	^{b}, reflux	(*s*-$C_4H_9)_2CHCN$ (46, —)	201
	i-C_4H_9B (2 eq), "	—	^{b}, reflux	(*i*-$C_4H_9)_2CHCN$ (66, —)	201

TABLE VII. NITRILES. A. TWO-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_8H_{17})_3B$, CH_3CN	—	e^-, $(C_2H_5)_4NBr$; [O]	$n\text{-}C_9H_{19}CN$ (48, —)	103
	", "	—	e^-, $(C_2H_5)_4NI$; [O]	" (51, —)	103
	", "	—	e^-, $(n\text{-}C_4H_9)_4NBr$; [O]	" (42, —)	103
	", "	—	e^-, $(n\text{-}C_4H_9)_4NI$; [O]	" (56, —)	103
11	$C_6H_{11}B$, $BrCH(CN)CO_2C_2H_5$	—	[b], 0°	$C_6H_{11}CH(CN)CO_2C_2H_5$ (22, —)	202
12	C_5H_9B, $C_5H_9CHClCN$	—	[b], reflux	$(C_5H_9)_2CHCN$ (56, —)	201
	$C_6H_{11}B$, $ClCH(CN)CH(CH_3)C_2H_5$	—	[b], reflux	$C_6H_{11}CH(CN)CH(CH_3)C_2H_5$ (61, —)	201

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] Potassium 2,6-di-*tert*-butylphenoxide is used as a base.

TABLE VII. NITRILES. B. THREE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$(n\text{-}C_3H_7)_3B$, $CH_2{=}CHCN$	—	CH_3Li, CuBr, 0°; [O]	$n\text{-}C_5H_{11}CN$ (84, —)	63
	", "	—	CH_3Li, CuCl, 0°; [O]	" (65, —)	63
	", "	—	CH_3Li, CuI, 0°; [O]	" (19, —)	63
7	$(n\text{-}C_4H_9)_3B$, "	—	CH_3Li, CuBr, 0°; [O]	$n\text{-}C_6H_{13}CN$ (88, —)	63
	$(i\text{-}C_4H_9)_3B$, "	—	"	$i\text{-}C_4H_9(CH_2)_2CN$ (88, —)	63
8	$(n\text{-}C_5H_{11})_3B$, "	—	"	$n\text{-}C_7H_{15}CN$ (89, —)	63
9	$(n\text{-}C_6H_{13})_3B$, "	—	"	$n\text{-}C_8H_{17}CN$ (93, —)	63

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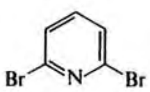
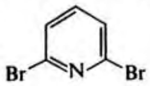
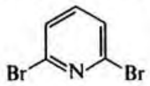
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE VII. NITRILES. C. FOUR-OR-MORE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	$(n\text{-}C_3H_7)_3B$, 		1. $n\text{-}C_4H_9Li$, −60° 2. CH_3CO_2H, reflux	$n\text{-}C_3H_7CH{=}CHCH{=}CHCN$ (Z), (E)-(—, 80)	204
	$(i\text{-}C_3H_7)_3B$, "	—	"	$i\text{-}C_3H_7CH{=}CHCH{=}CHCN$ (Z), (E)-(60, —)	204
9	$(n\text{-}C_4H_9)_3B$, "	—	"	$n\text{-}C_4H_9CH{=}CHCH{=}CHCN$ (Z), (E)-(93, —)	204
10	Cyclopentene, $CH_2{=}CHCH_2CN$	ThexylBH_2	CO, H_2O, 70 atm, 50°; [O]	$C_5H_9CO(CH_2)_3CN$ (50, 45)	154
11	$(n\text{-}C_3H_7)_3B$, 	—	1. $n\text{-}C_4H_9Li$, −60° 2. NaOH, I_2	$(n\text{-}C_3H_7)_2C{=}CHCH{=}CHCN$ (Z)-(58, —), (E)-(9, —)	356
	$(i\text{-}C_3H_7)_3B$, "	—	"	$(i\text{-}C_3H_7)_2C{=}CHCH{=}CHCN$ (Z)-(38, —), (E)-(19, —)	356
	$(C_6H_{11})_2BH$, $CH_2{=}CHCH_2CN$	—	CO, H_2O, 45°; [O]	$C_6H_{11}CO(CH_2)_3CN$ (—, 45)	153
	$(n\text{-}C_3H_7)_3B$, 		1. $n\text{-}C_4H_9Li$, −60° 2. NaOH	$(n\text{-}C_3H_7)_2C{=}CH(CH_2)_2CN$ (—, 94)	356
	$(i\text{-}C_3H_7)_3B$, "	"	"	$(i\text{-}C_3H_7)_2C{=}CH(CH_2)_2CN$ (75, —)	356
13	$(n\text{-}C_4H_9)_3B$, "	—	$n\text{-}C_4H_9Li$, −60°; [O]	$(n\text{-}C_4H_9)_2C{=}CHCH{=}CHCN$ (Z)-(44, —), (E)-(6, —)	356
	", "	—	1. $n\text{-}C_4H_9Li$, −60° 2. NaOH	$(n\text{-}C_4H_9)_2C{=}CH(CH_2)_2CN$ (—, 69)	356
14	C_6H_5Br, $p\text{-}ClCOC_6H_4CN$	R_3B[b]	Li, C_6H_6; [O]	$C_6H_5COC_6H_4CN\text{-}p$ (—, 70)	57
15	$m\text{-}CH_3C_6H_4Br$, "	"[b]	"	$m\text{-}CH_3C_6H_4COC_6H_4CN\text{-}p$ (78, 68)	57
	$(C_5H_9)_3B$, $HC{\equiv}CC_6H_{13}\text{-}n$, ICH_2CN	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7OH$	$C_5H_9CH{=}C(C_6H_{13}\text{-}n)CH_2CN$ (Z)-(—, 64)	67
	", ", "	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $(CH_3)_3NO$, 50°	$C_5H_9COCH(C_6H_{13}\text{-}n)CH_2CN$ (—, 62)	67
16	$(n\text{-}C_6H_{13})_3B$, ", "	—	1. CH_3Li, DG, 0° 2. $i\text{-}C_3H_7OH$	$n\text{-}C_6H_{13}CH{=}C(C_6H_{13}\text{-}n)CH_2CN$ (Z)-(—, 72)	67
	", ", "	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $(CH_3)_3NO$, 50°	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH_2CN$ (—, 71)	67
	$(n\text{-}C_8H_{17})_3B$, $HC{\equiv}CC_4H_9\text{-}n$, "	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $i\text{-}C_3H_7OH$	$n\text{-}C_8H_{17}CH{=}C(C_4H_9\text{-}n)CH_2CN$ (Z)-(—, 68)	67
	", ", "	—	1. $n\text{-}C_4H_9Li$, DG, 0° 2. $(CH_3)_3NO$, 50°	$n\text{-}C_8H_{17}COCH(C_4H_9\text{-}n)CH_2CN$ (—, 70)	67

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] R_3B = Trinorbornylborane.

TABLE VIII. AMINES. A. DIRECT FUNCTIONALIZATION

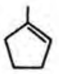
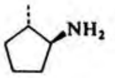
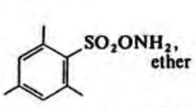
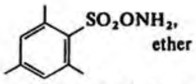
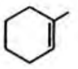
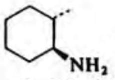
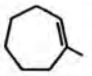
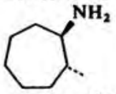
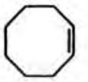
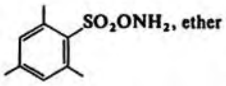
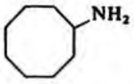
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	(*Z*)-$CH_3CH{=}CHCH_3$	DIPCB	DG, H_2NOSO_3H, 90°	$C_2H_5CH(CH_3)NH_2$ (*R*)-(−)-(−, 13)[a]	357
5	Cyclopentene	BH_3–THF	1. NaOH, H_2O, chloramine 2. HCl	$C_5H_9NH_2$ (−, 50)	205
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (−, 59)	205
6		BH_3–DG	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	 (56, 45)	206
	Cyclohexene (2 eq)	BH_3–THF	 SO_2ONH_2, ether	$C_6H_{11}NH_2$ (−, 31)	207
	", "	"	1. NaOH, H_2O, chloramine 2. HCl	" (−, 49)	205
	", "	"	1. H_2NOSO_3H, reflux 2. HCl	" (−, 55)	205
	n-$C_3H_7C(CH_3){=}CH_2$	"	1. NaOH, H_2O, chloramine 2. HCl	*n*-$C_3H_7CH(CH_3)CH_2NH_2$ (−, 28)	205
	", "	"	1. H_2NOSO_3H, reflux 2. HCl	" (−, 59)	205
	$(C_2H_5)_3B$, *n*-$C_4H_9N_3$	—	1. Xylene, reflux 2. HCl, ether 3. NaOH	$C_2H_5NHC_4H_9$-*n* (72, —)	209
	", *s*-$C_4H_9N_3$	—	"	$C_2H_5NHC_4H_9$-*s* (80, —)	209
	", *i*-$C_4H_9N_3$	—	"	$C_2H_5NHC_4H_9$-*i* (78, —)	209
	$(C_6H_5)_3B$	—	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	$C_6H_5NH_2$ (−, 105)	352
7		BH_3–DG	"	 (57, 48)	206
	" (3 eq)	BH_3–THF	 SO_2ONH_2, ether	" (−, 49)	207
	"	"	1. NaOH, H_2O, chloramine 2. HCl	" (−, 51)	205
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (−, 52)	205
	$(C_2H_5)_3B$, $C_5H_9N_3$	—	1. Xylene, reflux 2. HCl, ether 3. NaOH	$C_5H_9NHC_2H_5$ (77, —)	209
		BH_3–THF	1. NaOH, H_2O, chloramine 2. HCl	 (−, 8)	205
	"	BH_3–DG	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	" (58, 45)	206
8	$C_6H_5BCl_2$, $I(CH_2)_2N_3$	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	C_6H_5N (73, —)[b]	113
	$(C_2H_5)_3B$, $C_6H_5N_3$	—	1. Xylene, reflux 2. HCl, ether 3. NaOH	$C_6H_5NHC_2H_5$ (78, —)	209
	", $C_6H_{11}N_3$	—	"	$C_6H_{11}NHC_2H_5$ (73, —)	209
		BH_3–DG	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	 (45, 40)	206
	, (2 eq)	BH_3–THF	 SO_2ONH_2, ether	 (−, 40)	207

TABLE VIII. AMINES. A. DIRECT FUNCTIONALIZATION (*Continued*)

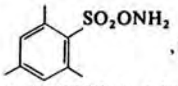
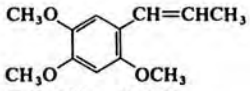
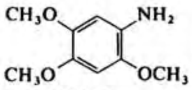
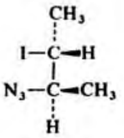
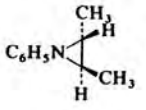
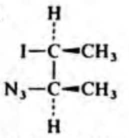
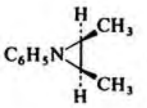
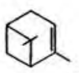
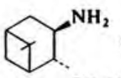
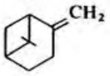
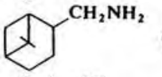
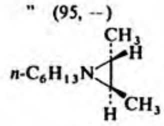
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$t\text{-}C_4H_9CH_2C(CH_3){=}CH_2$	"	1. NaOH, H_2O, chloramine 2. HCl	$t\text{-}C_4H_9CH_2CH(CH_3)CH_2NH_2$ (—, 28)	205
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (—, 58)	205
	$n\text{-}C_6H_{13}CH{=}CH_2$	"	"	$n\text{-}C_8H_{17}NH_2$ (—, 64)	205
	$n\text{-}C_4H_9BCl_2$, $n\text{-}C_4H_9N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$(n\text{-}C_4H_9)_2NH$ (84, —)	210
	$(n\text{-}C_4H_9)_2BCl$, "	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	" (71, —)	358
	$(n\text{-}C_4H_9)_3B$	—	NO, heptane, 60–70°	" (—, 35)	211
9	$C_6H_5C(CH_3){=}CH_2$ (3 eq)	BH_3-THF	 , ether	$C_6H_5CH(CH_3)CH_2NH_2$ (—, 43)	207
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (—, 58)	205
	"	"	1. NaOH, H_2O, chloramine 2. HCl	" (—, 58)	205
		"	H_2NOSO_3H	 (—, 20)	359
	$C_5H_9BCl_2$, $n\text{-}C_4H_9N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_5H_9NHC_4H_9\text{-}n$ (96, —)	210
	$(C_5H_9)_2BCl$, "	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	" (80, —)	358
10	$C_6H_5BCl_2$, 	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	 (76, 72)	113
	", 	—	"	 (83, —)	113
	$n\text{-}C_4H_9BCl_2$, $C_6H_5N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_5NHC_4H_9\text{-}n$ (89, —)	210
	$C_6H_5BCl_2$, $n\text{-}C_4H_9N_3$	—	"	" (100, —)	210
	$(n\text{-}C_4H_9)_2BCl$, $C_6H_5N_3$	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	" (72, —)	358
		BH_3-DG	1. H_2NOSO_3H, 100° 2. HCl 3. NaOH	 (58, 45)	358
		BH_3-THF	1. NaOH, H_2O, chloramine 2. HCl	 (—, 48)	205
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (—, 55)	205
	$n\text{-}C_4H_9BCl_2$, $C_6H_{11}N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_{11}NHC_4H_9\text{-}n$ (92, —)	210
	$C_6H_{11}BCl_2$, $n\text{-}C_4H_9N_3$	—	"	" (95, —)	210
	$n\text{-}C_6H_{13}BCl_2$, $CH_3CH(N_3)CHICH_3$	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	 (92, —)	113

TABLE VIII. AMINES. A. DIRECT FUNCTIONALIZATION (*Continued*)

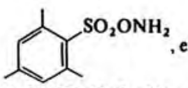
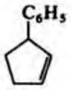
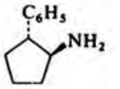
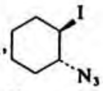
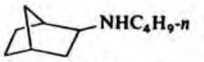
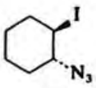
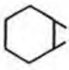
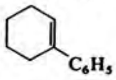
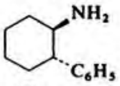
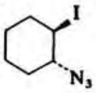
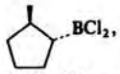
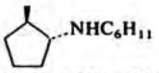
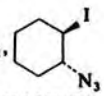
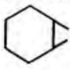
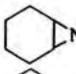
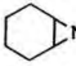
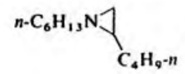
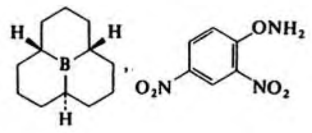
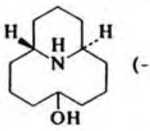
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(n\text{-}C_4H_9)_2BCl$, $C_6H_{11}N_3$	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	$C_6H_{11}NHC_4H_9\text{-}n$ (72, —)	358
	$(s\text{-}C_4H_9)_2BCl$, "	—	"	$C_6H_{11}NHC_4H_9\text{-}s$ (51, —)	358
	$(i\text{-}C_4H_9)_2BCl$, "	—	"	$C_6H_{11}NHC_4H_9\text{-}i$ (73, —)	358
	$n\text{-}C_8H_{17}CH{=}CH_2$ (3 eq)	BH_3-THF	, ether	$n\text{-}C_{10}H_{21}NH_2$ (—, 24)	207
	"	"	1. NaOH, H_2O, chloramine 2. HCl	" (—, 51)	205
11	$C_5H_9BCl_2$, $C_6H_5N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_5NHC_5H_9$ (84, —)	210
	$(C_5H_9)_2BCl$, "	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	" (74, —)	358
		BH_3-DG	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	 (47, 43)	206
	$C_5H_9BCl_2$, 	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	NC_5H_9 (94, —)	113
	", $C_6H_{11}N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_{11}NHC_5H_9$ (88, —)	210
	, $n\text{-}C_4H_9N_3$	—	"	 (86, —)	210
	$(C_5H_9)_2BCl$, $C_6H_{11}N_3$	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	$C_6H_{11}NHC_5H_9$ (80, —)	358
12	$C_6H_5BCl_2$, 		1. C_6H_6, 80° 2. HCl 3. KOH, reflux	NC_6H_5 (73, —)	113
	Cyclopentene, $p\text{-}CH_3C_6H_4SO_2NHCl$	BH_3-THF	NaOH, H_2O, 60°	$p\text{-}CH_3C_6H_4SO_2NHC_5H_9$ (—, 74)	208
	$C_6H_5BCl_2$, $C_6H_{11}N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_5NHC_6H_{11}$ (96, —)	210
	$C_6H_{11}BCl_2$, $C_6H_5N_3$	—	"	" (94, 91)	210
		BH_3-DG	1. H_2NOSO_3H, DG, 100° 2. HCl 3. NaOH	 (42, 38)	206
	$C_6H_{11}BCl_2$, 	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	NC_6H_{11} (86, 81)	113
	, $C_6H_{11}N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	 (90, —)	210
	$C_6H_{11}BCl_2$, "	—	"	$(C_6H_{11})_2NH$ (92, —)	210
	$n\text{-}C_6H_{13}BCl_2$, 	—	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	$NC_6H_{13}\text{-}n$ (92, —)	113
	$n\text{-}C_3H_7CH(CH_3)CH_2BCl_2$, "	—	"	$NCH_2CH(CH_3)C_3H_7\text{-}n$ (87, —)	113
	$n\text{-}C_3H_7CH(C_2H_5)BCl_2$, "	—	"	$NCH(C_2H_5)C_3H_7\text{-}n$ (86, —)	113
	$(C_6H_{11})_2BCl$, $C_6H_{11}N_3$	—	1. $C_6H_5CH_3$, ether, reflux 2. H_2O, HCl 3. NaOH	$(C_6H_{11})_2NH$ (76, —)	358
	$(C_6H_{11})_3B$, $C_6H_{11}NO$	—	60°	" (—, 26)	360
	$n\text{-}C_3H_7CH(CH_3)CH_2BCl_2$, $C_6H_{11}N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	$C_6H_{11}NHCH_2CH(CH_3)C_3H_7\text{-}n$ (92, —)	210
	$n\text{-}C_3H_7CH(C_2H_5)BCl_2$, "	—	"	$C_6H_{11}NHCH(C_2H_5)C_3H_7\text{-}n$ (85, —)	210

TABLE VIII. AMINES. A. DIRECT FUNCTIONALIZATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	n-$C_6H_{13}BCl_2$, n-$C_4H_9CHICH_2N_3$	–	1. C_6H_6, 80° 2. HCl 3. KOH, reflux	 (91, 83)	113
		—	t-C_4H_9OCl, CH_2Cl_2, −78 to 25°; [O][c]	 (--, 50)	212
13	, $C_6H_5N_3$	—	1. C_6H_6 2. H_2O, HCl 3. NaOH	 (92, —)	210
	Cyclohexene, p-$CH_3C_6H_4SO_2NClNa$	BH_3-THF	60°; [O][c]	p-$CH_3C_6H_4SO_2NHC_6H_{11}$ (, 72)	208
	n-$C_4H_9CH{=}CH_2$, "	"	"	p-$CH_3C_6H_4SO_2NHC_6H_{13}$-$n$ (, 84)	208
	$C_2H_5O_2C(CH_2)_8CH{=}CH_2$	"	1. Chloramine, NaOH, H_2O 2. HCl	$C_2H_5O_2C(CH_2)_{10}NH_2$ (-, 30)	205
	"	"	1. H_2NOSO_3H, reflux 2. HCl	" (-, 30)	205
14	$(C_6H_5)_2C{=}CH_2$	"	"	$(C_6H_5)_2CHCH_2NH_2$ (, 27)	205
	$(C_6H_5CH_2)_3B$, p-$CH_3C_6H_4SO_2NClNa$	—	60°, NaOH	p-$CH_3C_6H_4SO_2NHCH_2C_6H_5$ (-, 69)	208
15	n-$C_6H_{13}CH{=}CH_2$, "	BH_3-THF	"	p-$CH_3C_6H_4SO_2NHC_8H_{17}$-$n$ (, 80)	208

[a] The optical purity is 76%

[b] The yield is based on ^1H NMR analysis.

[c] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE VIII. AMINES. B. ONE-CARBON HOMOLOGATION

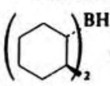
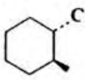
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
13	$(CH_3)_2C{=}CH_2$, $HC{\equiv}CC_4H_9$-*n*, KCN	ThexylBH_2	1. TFAA, −78° 2. NaOH	*i*-$C_4H_9CH(NHCOCF_3)CH{=}CHC_4H_9$-*n* (*E*)-(–, 67)	214
	", $C_2H_5C{\equiv}CC_2H_5$, KCN	"	"	*i*-$C_4H_9CH(NHCOCF_3)C(C_2H_5){=}CHC_2H_5$ (*E*)-(–, 74)	214
14	Cyclopentene, $HC{\equiv}CC_4H_9$-*n*, KCN	"	"	$C_5H_9CH(NHCOCF_3)CH{=}CHC_4H_9$-*n* (*E*)-(–, 83)	214
15	Cyclohexene, ", KCN	"	"	$C_6H_{11}CH(NHCOCF_3)CH{=}CHC_4H_9$-*n* (*E*)-(–, 82)	214
	", $C_2H_5C{\equiv}CC_2H_5$, KCN	"	"	$C_6H_{11}CH(NHCOCF_3)C(C_2H_5){=}CHC_2H_5$ (*E*)-(–, 77)	214
	$(C_6H_{11})_2BH$, $HC{\equiv}CC_4H_9$-*n*, KCN	—	"	$C_6H_{11}CH(NHCOCF_3)CH{=}CHC_4H_9$-*n* (*E*)-(–, 90)	214
	", $C_2H_5C{\equiv}CC_2H_5$, KCN	—	"	$C_6H_{11}CH(NHCOCF_3)C(C_2H_5){=}CHC_2H_5$ (*E*)-(–, 76)	214
16	 , $HC{\equiv}CC_4H_9$-*n*, KCN	—	"	 $CH(NHCOCF_3)CH{=}CHC_4H_9$-*n* (*E*)-(–, 63)	214

TABLE VIII. AMINES. C. TWO-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	$(C_2H_5)_3B$, i-$C_3H_7COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	—	DMSO, NaOH	$C_2H_5CH(COC_3H_7$-$i)CH_2N(CH_3)_2$ (94, —)	180
13	$(C_2H_5)_3B$, $C_6H_5COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	—	"	$C_2H_5CH(COC_6H_5)CH_2N(CH_3)_2$ (92, 70)	180
14	n-$C_4H_9CH{=}CH_2$, i-$C_3H_7COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	BH_3-THF	"	n-$C_6H_{13}CH(COC_3H_7$-$i)CH_2N(CH_3)_2$ (84, —)	180
15	n-$C_5H_{11}CH{=}CH_2$, i-$C_3H_7COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	"	"	n-$C_7H_{15}CH(COC_3H_7$-$i)CH_2N(CH_3)_2$ (100, —)	180
17	n-$C_4H_9CH{=}CH_2$, $C_6H_5COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	"	"	n-$C_6H_{13}CH(COC_6H_5)CH_2N(CH_3)_2$ (86, —)	180
18	n-$C_5H_{11}CH{=}CH_2$, $C_6H_5COCHN_2$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	"	"	n-$C_7H_{15}CH(COC_6H_5)CH_2N(CH_3)_2$ (80, —)	180

TABLE VIII. AMINES. D. THREE-OR-MORE-CARBON HOMOLOGATION

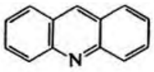
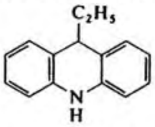
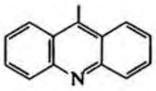
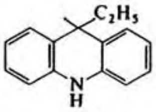
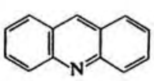
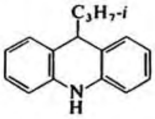
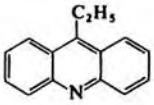
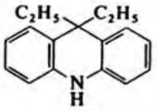
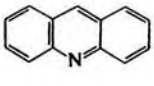
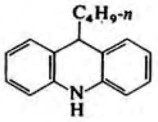
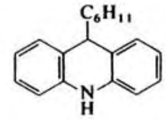
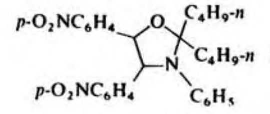
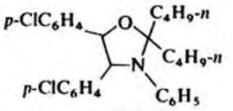
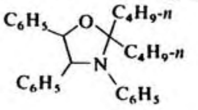
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	$(n\text{-}C_3H_7)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7\text{-}i$ (3 eq)	—	Air, CH_3OH	$n\text{-}C_3H_7CH(CH_3)CH_2CH{=}NC_3H_7\text{-}i$ (69, —)	215
	$(C_2H_5)_3B$, $CH_2{=}C(CH_3)COCH_3$, $CH_2{=}\overset{+}{N}(CH_3)_2I^-$	—	DMSO, NaOH	$n\text{-}C_3H_7C(CH_3)(COCH_3)CH_2N(CH_3)_2$ (87, —)	180
11	$(n\text{-}C_4H_9)_3B$, $CH_3CH{=}CHCH{=}NC_3H_7\text{-}i$ (3 eq)	—	Air, CH_3OH	$n\text{-}C_4H_9CH(CH_3)CH_2CH{=}NC_3H_7\text{-}i$ (76, —)	215
12	$(C_5H_9)_3B$, "	—	"	$C_5H_9CH(CH_3)CH_2CH{=}NC_3H_7\text{-}i$ (53, —)	215
	$(n\text{-}C_5H_{11})_3B$, "	--	"	$n\text{-}C_5H_{11}CH(CH_3)CH_2CH{=}NC_3H_7\text{-}i$ (83, —)	215
15	$(C_2H_5)_3B$, 	—	$h\nu$, C_6H_6; [O]	 (72, —)	130
16	$p\text{-}BrC_6H_4N(CH_3)_2$	$BH_3 \cdot THF$	1. KOH, CH_3OH, reflux 2. $AgNO_3$	$p\text{-}(CH_3)_2NC_6H_4C_6H_4N(CH_3)_2\text{-}p$ (—, 71)	255
	$(C_2H_5)_3B$, 	—	$h\nu$, C_6H_6; [O]	 (75, —)	130
	$(i\text{-}C_3H_7)_3B$, 	—	"	 (86, —)	130
17	$(C_2H_5)_3B$, 	—	"	 (72, —)	130
	$(n\text{-}C_4H_9)_3B$, 	—	"	 (65, —)	129

TABLE VIII. AMINES. D. THREE-OR-MORE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
19	$(C_6H_{11})_3B$, "	—	"	 (90, —)	129
29	$(n\text{-}C_4H_9)_3B$, $p\text{-}O_2NC_6H_4CHO$ (2 eq), C_6H_5NC	—	Ether	 (—, 66)	326
	", $p\text{-}ClC_6H_4CHO$ (2 eq), "	—	"	 (—, 72)	326
	", C_6H_5CHO (2 eq), "	—	"	 (—, 72)	326

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE IX. MISCELLANEOUS NITROGEN COMPOUNDS

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
3	$CH_3CH{=}CH_2$	$BH_3 \cdot THF$	1. NaN_3 (3 eq), $Fe(SO_4)_3$ (1.5 eq) 2. H_2O_2, 0°; [O]	$n\text{-}C_3H_7N_3$ (57, –)	216
4	$(n\text{-}C_3H_7)_3B$, CH_3NO_2	—	e^-, $(C_2H_5)_4NI$	$n\text{-}C_4H_9NO_2$ (28, –)	104
	$(s\text{-}C_4H_9)_3B$, "	—		$s\text{-}C_4H_9NO_2$ (25, –)	104
	$C_2H_5CH{=}CH_2$	$BH_3 \cdot THF$	1. NaN_3 (3 eq), $Fe(SO_4)_3$ (1.5 eq) 2. H_2O_2, 0°; [O]	$n\text{-}C_4H_9N_3$ (56, –)	216
	$CH_3CH{=}CHCH_3$	"	"	$s\text{-}C_4H_9N_3$ (100, –)	216
5	$(C_5H_9)_3B$, CH_3NO_2	—	e^-, $(C_2H_5)_4NI$	$C_5H_9NO_2$ (50, –)	104
	Cyclopentene	$BH_3\text{-}THF$	1. NaN_3 (3 eq), $Fe(SO_4)_3$ (1.5 eq) 2. H_2O_2, 0°; [O]	$C_5H_9N_3$ (100, –)	216
6	$n\text{-}C_4H_9CH{=}CH_2$	"	"	$n\text{-}C_6H_{13}N_3$ (85, –)	216
7	$(n\text{-}C_6H_{13})_3B$, CH_3NO_2	—	e^-, $(C_2H_5)_4NI$	$n\text{-}C_7H_{15}NO_2$ (39, –)	104
8	$n\text{-}C_6H_{13}CH{=}CH_2$	$BH_3\text{-}THF$	1. NaN_3 (3 eq), $Fe(SO_4)_3$ (1.5 eq) 2. H_2O_2, 0°; [O]	$n\text{-}C_8H_{17}N_3$ (75, –)	216
	$(n\text{-}C_3H_7)_3B$, *N*-methylpyrrole	—	1. $n\text{-}C_4H_9Li$, TMEDA, ether 2. I_2, –78°; [O]	2-*n*-Propyl-*N*-methylpyrrole (92, –)	361
9	$(n\text{-}C_8H_{17})_3B$, CH_3NO_2	—	e^-, $(C_2H_5)_4NI$	$n\text{-}C_9H_{19}NO_2$ (31, –)	104,361
	$(s\text{-}C_4H_9)_3B$, *N*-methylpyrrole	—	1. $n\text{-}C_4H_9Li$, –25° 2. I_2; EA	2-*s*-Butyl-*N*-methylpyrrole (95, –)	325
	$s\text{-}C_4H_9B$, *N*-methylpyrrole	—	"	" (53, –)	325
	$(n\text{-}C_4H_9)_3B$, "	—	1. $n\text{-}C_4H_9Li$, TMEDA, ether 2. I_2, –78°; [O]	2-*n*-Butyl-*N*-methylpyrrole (98, –)	361
	$(i\text{-}C_4H_9)_3B$, "	—	"	2-Isobutyl-*N*-methylpyrrole (80, –)	361
10	$t\text{-}C_4H_9C{\equiv}CB$, CH_3NCO (2 eq)	—	Ether, 0° to room temp;	$CH_3NHCON(CH_3)COC{\equiv}CC_4H_9\text{-}t$ (–, 49)	362
	$(C_5H_9)_3B$, *N*-methylpyrrole	—	1. $n\text{-}C_4H_9Li$, –25° 2. I_2; EA	2-Cyclopentyl-*N*-methylpyrrole (73, –)	361,325
	C_5H_9B, "	—	"	" (45, –)	325

TABLE IX. MISCELLANEOUS NITROGEN COMPOUNDS (*Continued*)

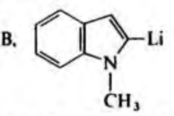
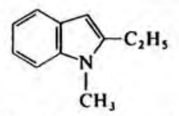
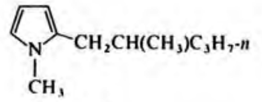
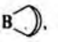
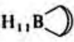
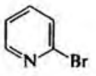
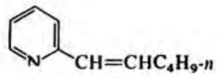
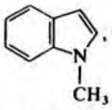
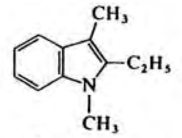
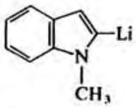
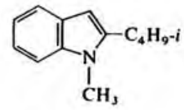
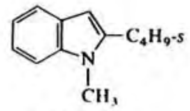
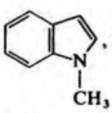
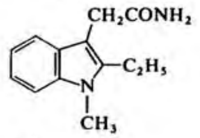
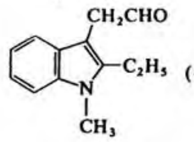
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
11	$(C_2H_5)_3B$, 	—	I_2, −80° to room temp; [O]	 (79, –)	363
	$(n\text{-}C_6H_{13})_3B$, *N*-methylpyrrole	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	2-*n*-Hexyl-*N*-methylpyrrole (59, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. I_2; EA	" (70, –)	325,361
	$n\text{-}C_6H_{13}B$, "	—	"	" (39, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	" (44, –)	325
	$[n\text{-}C_3H_7CH(CH_3)CH_2]_3B$, "		"	 (66, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. I_2; EA	" (72, –)	325
	$n\text{-}C_3H_7CH(CH_3)CH_2B$, "	—	"	" (41, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	" (39, –)	325
	$(C_6H_{11})_3B$, *N*-methylpyrrole	—	"	2-Cyclohexyl-*N*-methylpyrrole (63, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. I_2; EA	" (86, –)	325
	$C_6H_{11}B$, "	—	"	" (52, –)	325
	", "	—	1. $n\text{-}C_4H_9Li$, −25° 2. NCS; EA	" (42, –)	325
	$n\text{-}C_4H_9C{\equiv}CH$, 	CATBH	1. $Pd[P(C_6H_5)_3]_4$, C_6H_6 2. $NaOC_2H_5$, C_2H_5OH, reflux; [O]	 (*E*)-(83, –)	364
12	$(C_2H_5)_3B$, , CH_3I	—	1. $n\text{-}C_4H_9Li$, reflux 2. −80° to room temp; [O]	 (80, –)	365
13	$(i\text{-}C_4H_9)_3B$, 		I_2, −80° to room temp; [O]	 (71, –)	363
	$i\text{-}C_4H_9B$ "	—	"	" (85, –)	363
	$(s\text{-}C_4H_9)_3B$, "	—	"	 (71, –)	363
	$s\text{-}C_4H_9B$, "	—	"	" (78, –)	363
	$(C_2H_5)_3B$, , ICH_2CONH_2	—	1. $n\text{-}C_4H_9Li$, reflux 2. −80° to room temp; [O]	 (–, 53)	365
	", ", ICH_2CN	—	"	" (–, 61)	365
	", ", $BrCH_2CH(OC_2H_5)_2$	—	", then HCl	 (–, 54)	365

TABLE IX. MISCELLANEOUS NITROGEN COMPOUNDS (*Continued*)

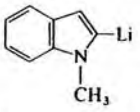
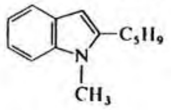
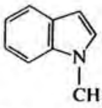
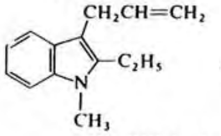
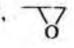
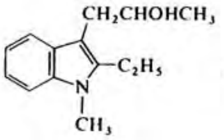
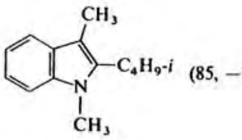
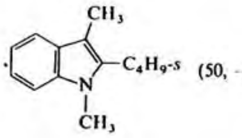
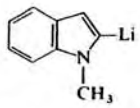
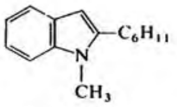
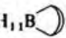
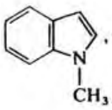
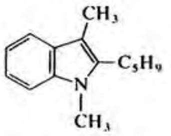
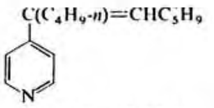
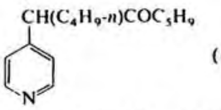
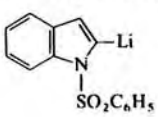
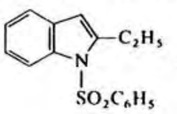
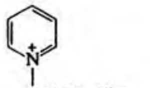
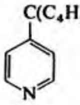
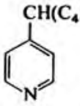
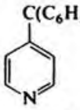
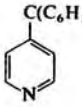
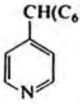
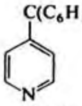
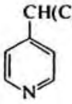
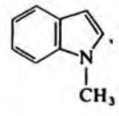
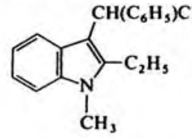
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions^a	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
14	p-$O_2NC_6H_4CH_2I$	$(C_2H_5)_3B$	Air	p-$O_2NC_6H_4(CH_2)_2C_6H_4NO_2$-$p$ (–, 43)	366
	$(C_5H_9)_3B$, 	...	I_2, –80° to room temp; [O]	 (79, –)	363
	C_5H_9B "	—	"	" (60, –)	363
	$(C_2H_5)_3B$, , $CH_2{=}CHCH_2Br$	—	1. n-C_4H_9Li, reflux 2. –80° to room temp; [O]	 (94, –)	365
	", ", 	—	"	 (–, 66)	365
	$(i$-$C_4H_9)_3B$, ", CH_3I	—	"	 (85, –)	365
	i-C_4H_9B, ", "	—	"	" (64, –)	365
	$(s$-$C_4H_9)_3B$, ", "	—	"	 (50, –)	365
15	$(C_6H_{11})_3B$, 	—	I_2, –80° to room temp; [O]	 (96, –)	363
	$C_6H_{11}B$, "	—	"	" (78, –)	363
	$(C_5H_9)_3B$, , CH_3I		1. n-C_4H_9Li, reflux 2. –80° to room temp; [O]	 (84, –)	365
	C_5H_9B, ", "	—	"	" (26, –)	364
16	$(C_5H_9)_3B$, $LiC{\equiv}CC_4H_9$-n, pyridine	—	1. CH_3COCl, –78° to room temp 2. AcOH; [O]	 (–, 78)	165
	", ", "		CH_3COCl, –78° to room temp; [O]	 (–, 74)	165
	", $LiC{\equiv}CC_6H_{13}$-n, $CH_3CH{=}CHNO_2$	—	0°; [O]	$C_5H_9COCH(C_6H_{13}$-$n)CH(CH_3)CH_2NO_2$ (–, 75)	90
	$(n$-$C_5H_{11})_3B$, ", "	—	0°; [O]	n-$C_5H_{11}COCH(C_6H_{13}$-$n)CH(CH_3)CH_2NO_2$ (–, 75)	90
	$(n$-$C_6H_{13})_3B$, ", $CH_2{=}CHNO_2$	—	0°; [O]	n-$C_6H_{13}COCH(C_6H_{13}$-$n)(CH_2)_2NO_2$ (–, 80)	90
	$(C_2H_5)_3B$, 	—	I_2, –80° to room temp; [O]	 (–, 57)	363

TABLE IX. MISCELLANEOUS NITROGEN COMPOUNDS (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
17	$(n\text{-}C_6H_{13})_2BC(CH_3)_2C_3H_7\text{-}i$, $LiC\equiv CC_4H_9\text{-}n$, 	—	1. −78° to room temp 2. H^+	$C(C_4H_9\text{-}n)=CHC_6H_{13}\text{-}n$  (*Z*)-(—, 63) (*E*)-(—, 9)	367
	$(n\text{-}C_6H_{13})_3B$, $LiC\equiv CC_4H_9\text{-}n$, pyridine	—	1. CH_3COCl, −78° to room temp 2. CH_3CO_2H; [O]	" (—, 72)	165
	", ", "	—	CH_3COCl, −78° to room temp; [O]	$CH(C_4H_9\text{-}n)COC_6H_{13}\text{-}n$  (—, 76)	165
	", $LiC\equiv CC_6H_{13}\text{-}n$, $CH_2=C(CH_3)NO_2$	—	0°, $i\text{-}C_3H_7CO_2H$	$n\text{-}C_6H_{13}CH=C(C_6H_{13}\text{-}n)CH_2CH(CH_3)NO_2$ (—, 5)	90
	", ", $CH_3CH=CHNO_2$	—	"	$n\text{-}C_6H_{13}CH=C(C_6H_{13}\text{-}n)CH(CH_3)CH_2NO_2$ (—, 82)	90
	", ", "	—	0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)CH(CH_3)CH_2NO_2$ (—, 93)	90
19	", $LiC\equiv CC_6H_5$, pyridine		1. CH_3COCl, −78° to room temp 2. CH_3CO_2H; [O]	$C(C_6H_5)=CHC_6H_{13}\text{-}n$  (—, 66)	165
	$(C_6H_{11})_3B$, $LiC\equiv CC_6H_{13}\text{-}n$, "	—	"	$C(C_6H_{13}\text{-}n)=CHC_6H_{11}$  (—, 71)	165
	", ", "	—	CH_3COCl, −78° to room temp; [O]	$CH(C_6H_{13}\text{-}n)COC_6H_{11}$  (—, 68)	165
	$(n\text{-}C_6H_{13})_3B$, ", "	—	1. CH_3COCl, −78° to room temp 2. CH_3CO_2H: [O]	$C(C_6H_{13}\text{-}n)=CHC_6H_{13}\text{-}n$  (—, 68)	165
	", ", "	—	CH_3COCl, −78° to room temp; [O]	$CH(C_6H_{13}\text{-}n)COC_6H_{13}\text{-}n$  (—, 72)	165
26	$(C_2H_5)_3B$,  $C_6H_5CH=CHCOC_6H_5$		1. $n\text{-}C_4H_9Li$, reflux 2. $TiCl_4$, −80° to room temp; [O]	$CH(C_6H_5)CH_2COC_6H_5$  (—, 50)	365

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[a] Reagents after the semicolon are those used to decompose an intermediate organoborane; abbreviations are: [O] oxidation with alkaline hydrogen peroxide. EA = ethanolamine.

TABLE X. HALIDES. A. DIRECT FUNCTIONALIZATION

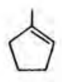
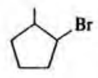
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
2	$(C_2H_5)_3B$, $CH_2{=}CHCH_2I$	—	Air	C_2H_5I (100, -)	366
4	$C_2H_5CH{=}CH_2$	BH_3-THF	Br_2 (1.1 eq), dark	n-C_4H_9Br (80, —), s-C_4H_9Br (11, —)	222
	"	"	$CuBr_2$, H_2O	n-C_4H_9Br (90, -)	225
	"	"	1. Br_2 (4 eq), 0° 2. $NaOCH_3$, CH_3OH, 0°	" (91, —)	219
	$CH_3CH{=}CHCH_3$	"	1. $NaOCH_3$, CH_3OH 2. Br_2 (3 eq)	s-C_4H_9Br (74, —)	219
	"	"	$CuBr_2$, H_2O	" (83, —)	225
	"	"	Br_2 (1.1 eq), dark	" (88, —)	222
	$(CH_3)_2C{=}CH_2$	"	"	i-C_4H_9Br (85, —)	222
	"	"	$CuBr_2$, H_2O, 65°	" (90, —)	225
	$CH_3CH{=}CHCH_3$	9-BBN	1. Br_2, CH_2Cl_2, dark 2. NaOH	s-C_4H_9Br (85, —)	223
	(s-$C_4H_9)_3B$	—	$CuBr_2$ (6 eq), 55°	" (55, —)	224
	"	—	NCl_3, CCl_4, 0°	s-C_4H_9Cl (94, —)	202
	$C_2H_5CH{=}CH_2$	BH_3-THF	1. I_2 (3 eq) 2. CH_3OH, NaOH (3 eq)	n-C_4H_9I (65, —)	217
	"	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	" (79, —)	218
	$CH_3CH{=}CHCH_3$	BH_3-THF	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	s-C_4H_9I (30, —)	217
	"	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	" (66, —)	218
	$(CH_3)_2C{=}CH_2$	BH_3-THF	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	i-C_4H_9I (63, —)	217
	"	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	" (80, —)	218
	(Z)-$CH_3CH{=}CHCH_3$	DIPCB	"	s-C_4H_9I (49, —)[b]	220
	(n-$C_4H_9)_3B$, $CH_2{=}CHCH_2I$	—	Air	n-C_4H_9I (97, —)	366
	", n-C_4H_9Li	—	I_2, −78°; [O]	" (100, —)	368
	(n-$C_4H_9)_2BC_6H_5$, "	—	"	" (98, —)	368
5	Cyclopentene	BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (4 eq), CH_3OH, 0°	C_5H_9Br (31, —)	219
	"	"	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	" (69, —)	219
	"	"	$CuBr_2$, H_2O	" (75, —)	225
	"	"	Br_2 (3 eq), dark	" (84, —)	222
	n-$C_3H_7C{\equiv}CH$	Sia_2BH	Br_2, CCl_4, reflux	n-$C_3H_7CH{=}CHBr$ (E)-(40, —)	369
	"	"	1. Br_2, CCl_4, 0° 2. NaOH	" (Z)-(63, —), (E)-(2, —)	369
	Cyclopentene	BH_3-THF	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	C_5H_9I (33, —)	217
	"	BH_3-DMS	1. I_2 (3 eq) 2. NaOH (3 eq), CH_3OH	" (64, —)	218
	$(CH_3)_2C{=}CHCH_3$	9-BBN	1. Br_2, CH_2Cl_2, dark 2. NaOH	i-$C_3H_7CHBrCH_3$ (88, —)	223
	(n-$C_5H_{11})_3B$	—	$CuBr_2$ (6 eq), 55°	n-$C_5H_{11}Br$ (72, 63), n-$C_3H_7CHBrCH_3$ (5, 4)	224
	[i-$C_3H_7CH(CH_3)]_2BC_6H_{13}$-n	—	$CuBr_2$, H_2O	i-$C_3H_7CHBrCH_3$ (35, —)	225
	(n-$C_5H_{11})_3B$	—	$FeCl_2$ (6 eq), 55°	n-$C_5H_{11}Cl$ (59, 48), n-$C_3H_7CHClCH_3$ (4, 2)	224
	", $CH_2{=}CHCH_2I$	—	Air	n-$C_5H_{11}I$ (98, —)	336
6	Cyclohexene	BH_3-THF	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	$C_6H_{11}Br$ (64, —)	219
	"	"	$CuBr_2$, H_2O	" (92, —)	225
	"	"	Br_2 (1.1 eq), dark	" (99, —)	222
	$C_2H_5C{\equiv}CC_2H_5$	CATBH	1. Br_2, CH_2Cl_2, −20° 2. NaOH, CH_3OH	$C_2H_5CH{=}CBrC_2H_5$ (Z)-(85, —)	228
	n-$C_4H_9C{\equiv}CH$	Sia_2BH	Br_2, CCl_4, reflux	n-$C_4H_9CH{=}CHBr$ (E)-(66, —), (Z)-(9, —)	369
	"	"	1. Br_2, CCl_4, 0° 2. NaOH	" (Z)-(64, —), (E)-(3, —)	369
		9-BBN	1. Br_2, CH_2Cl_2, dark 2. NaOH	 (80, —)	223
	Cyclohexene	"	"	$C_6H_{11}Br$ (84, —)	223
	$(C_6H_{11})_3B$	—	$CuBr_2$ (6 eq), 55°	" (83, —)	224
	$(C_6H_{11})_2BC_6H_{13}$-n	—	$CuBr_2$, H_2O	" (87, —)	225
	Cyclohexene	BH_3-THF	$CuCl_2$, 65°	$C_6H_{11}Cl$ (63, —)	225
	"	"	1. NaOH, H_2O 2. N-Chloropiperidine	" (—, 53)	370

TABLE X. HALIDES. A. DIRECT FUNCTIONALIZATION (*Continued*)

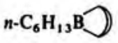
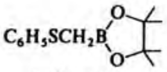
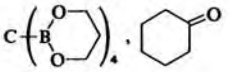
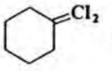
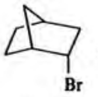
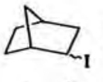
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
	$(C_6H_{11})_3B$	—	$FeCl_2$ (6 eq), H_2O_2 (6 eq), 55°	" (61, 52)	224
	"	—	$CuCl_2$ (6 eq), 55°	" (62, —)	224
	"	—	$FeCl_2$ (6 eq), 55°	" (73, 65)	224
	$(C_6H_{11})_2BC_6H_{13}$-*n*	—	$CuCl_2$, H_2O	" (56, —)	225
	Cyclohexene	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	$C_6H_{11}I$ (72, —)	218
	n-$C_4H_9C{\equiv}CH$	CATBH	1. NaOH, H_2O 2. I_2, ether, 0°	*n*-$C_4H_9CH{=}CHI$ (*E*)-(89, —)	227
	$(C_6H_{11})_3B$, $CH_2{=}CHCH_2I$	—	Air	$C_6H_{11}I$ (75, —)	366
	n-$C_4H_9CH{=}CH_2$	BH_3-THF	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	*n*-$C_6H_{13}Br$ (85, —)	219
	"	"	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), 0°	" (93, —)	219
	n-$C_3H_7C(CH_3){=}CH_2$	"	"	*n*-$C_3H_7CH(CH_3)CH_2Br$ (99, —)	219
	i-$C_3H_7CH{=}CHCH_3$	9-BBN	1. Br_2, CH_2Cl_2, dark 2. NaOH	*i*-$C_3H_7CH_2CHBrCH_3$ (88, —)	223
		—	$CuBr_2$, H_2O	*n*-$C_6H_{13}Br$ (7, —)	225
	(*n*-$C_6H_{13})_3B$	—	$CuBr_2$ (6 eq), 55°	*n*-$C_6H_{13}Br$ (86, 78), *n*-$C_4H_9CHBrCH_3$ (4, 3)	224
	", $CH_2{=}CHCH_2Br$	—	Air	*n*-$C_6H_{13}Br$ (12, —)	366
	", $C_6H_5CH_2Br$	—	Air	" (24, —)	366
	n-$C_4H_9CH{=}CH_2$	BH_3-THF	$CuCl_2$, 65°	*n*-$C_6H_{13}Cl$ (77, —)	225
	t-$C_4H_9CH{=}CH_2$	"	$CuCl_2$, H_2O	*t*-$C_4H_9(CH_2)_2Cl$ (71, —)	225
	i-$C_3H_7C(CH_3)_2B(C_4H_9$-*n*$)_2$	—	NCl_3, CCl_4, 0°	*i*-$C_3H_7C(CH_3)_2Cl$ (44, —)	226
	(*n*-$C_6H_{13})_3B$	—	$FeCl_2$ (6 eq), H_2O_2 (6 eq), 55°	*n*-$C_6H_{13}Cl$ (56, 51), *n*-$C_4H_9CHClCH_3$ (5, 3)	224
	"	—	$FeCl_2$ (6 eq), 55°	*n*-$C_6H_{13}Cl$ (60, 54), *n*-$C_4H_9CHClCH_3$ (5, 4)	224
	"	—	$CuCl_2$ (6 eq), 55°	*n*-$C_6H_{13}Cl$ (63, —), *n*-$C_4H_9CHClCH_3$ (4, —)	224
	", $CH_2{=}CHCH_2Cl$	—	Air	*n*-$C_6H_{13}Cl$ (trace, —)	366
	n-$C_4H_9CH{=}CH_2$	Sia_2BH	1. I_2 2. NaOH, CH_3OH	*n*-$C_6H_{13}I$ (95, —)	217
	(*n*-$C_6H_{13})_3B$, CH_3I	—	Air	" (40, —)	366
	", C_2H_5I	—	"	" (54, —)	366
	", $CH_2{=}CHCH_2I$	—	"	" (100, —)	366
	", *i*-C_3H_7I	—	"	" (64, —)	366
	", *t*-C_4H_9I	—	"	" (85, —)	366
	$(C_6H_5)_3B$	—	1. I_2 (5.5 eq), NaOH, CH_3OH 2. $Na_2S_2O_3$	C_6H_5I (—, 40)	352
	"	—	1. Br_2, $NaOCH_3$, CH_3OH 2. $Na_2S_2O_3$	C_6H_5Br (—, 84)	352
7		—	SO_2Cl_2, CH_2Cl_2	$C_6H_5SCH_2Cl$ (—, 94)	320
		—	1. CH_3Li, −70° 2. I_2, NaOH, 0°	 (—, 71)	371
		BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	 *endo*-(—, —)	221
	"	"	$CuBr_2$, H_2O	" (77, —)	225
	"	"	Br_2 (1.1 eq), dark	" (88, —)	222
	"	9-BBN	1. Br_2, CH_2Cl_2, dark 2. NaOH	" (90, —)	223
	"	BH_3-THF	$CuCl_2$, H_2O	 (43, —)	225
		—	NCl_3, CCl_4, 0°	" (—, —)	226
		BH_3-THF	1. I_2 2. $NaOCH_3$, CH_3OH	 *endo*-(—, 62) *exo*-(—, 16)	220
	t-$C_4H_9C{\equiv}CH$	CATBH	1. Br_2, CH_2Cl_2, −20° 2. $NaOCH_3$, CH_3OH	*t*-$C_4H_9CH{=}CBrCH_3$ (*Z*)-(96, —)	228
	n-$C_5H_{11}C{\equiv}CH$	Sia_2BH	Br_2, CCl_4, reflux	*n*-$C_5H_{11}CH{=}CHBr$ (*E*)-(53, —), (*Z*)-(7, —)	369
	"	"	1. Br_2, CCl_4, 0° 2. NaOH	" (*Z*)-(74, —), (*E*)-(2, —)	369
	$C_2H_5CHClC{\equiv}CH$	CATBH	Br_2 (2 eq), $NaOCH_3$ (2 eq), CH_3OH, −78°	$C_2H_5CHClCHBrCH(OCH_3)_2$ (82, —)	148

TABLE X. HALIDES. A. DIRECT FUNCTIONALIZATION (*Continued*)

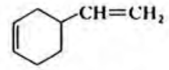
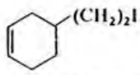
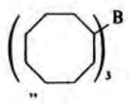
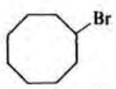
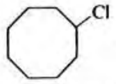
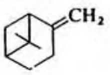
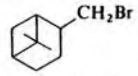
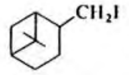
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	t-$C_4H_9CH_2C(CH_3)=CH_2$	BH_3-THF	Br_2 (1.1 eq), dark	t-$C_4H_9CH_2CH(CH_3)CH_2Br$ (82, —)	222
	$C_6H_5C\equiv CH$	CATBH	1. Br_2, CH_2Cl_2, −40° 2. $NaOCH_3$, CH_3OH	$C_6H_5CH=CHBr$ (90, —)	228
	"	Sia_2BH	1. Br_2, CCl_4, 0° 2. NaOH	" (E)-(84, —), (Z)-(4, —)	369
	"	"	Br_2, CCl_4, reflux	" (Z)-(63, —), (E)-(15, —)	369
	"	CATBH	1. NaOH, H_2O 2. I_2, ether, 0°	$C_6H_5CH=CHI$ (E)-(79, —)	227
	$C_6H_{11}C\equiv CH$	"	1. Br_2, CH_2Cl_2, −40° 2. $NaOCH_3$, CH_3OH	$C_6H_{11}CH=CHBr$ (Z)-(85, —)	228
	"	"	1. H_2O 2. Br_2, CH_2Cl_2, −40° 3. $NaOCH_3$, CH_3OH	" (Z)-(88, —)	228
	"	"	1. NaOH, H_2O 2. I_2, ether, 0°	$C_6H_{11}CH=CHI$ (E)-(93,)	227
		Sia_2BH	I_2 (2 eq), NaOH (2 eq), CH_3OH	 (66, 60)	217
	n-$C_6H_{13}C\equiv CH$	CATBH	1. H_2O 2. Br_2, CH_2Cl_2, −20° 3. $NaOCH_3$, CH_3OH	n-$C_6H_{13}CH=CHBr$ (Z)-(85,)	228
	"	"	1. Br_2, CH_2Cl_2, 0° 2. NaOH, CH_3OH	" (Z)-(90, 82)	228
	"	Sia_2BH	Br_2, CCl_4, reflux	" (E)-(47,), (Z)-(3, —)	369
	"	"	1. Br_2, CCl_4, 0° 2. NaOH	" (Z)-(67, —), (E)-(1, —)	369
		—	$CuBr_2$ (6 eq), 55°	 (24, —)	224
	"	—	$FeCl_2$ (6 eq), 55°	 (81, —)	224
	"	—	$FeCl_2$ (6 eq), H_2O_2 (6 eq), 55°	" (60, —)	224
	n-$C_6H_{13}C\equiv CH$	CATBH	1. NaOH, H_2O 2. I_2, ether, 0°	n-$C_6H_{13}CH=CHI$ (E)-(90, 71)	227
	n-$C_6H_{13}CH=CH_2$	BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	n-$C_8H_{17}Br$ (94,)	219
	t-$C_4H_9CH_2C(CH_3)=CH_2$	"	"	t-$C_4H_9CH_2CH(CH_3)CH_2Br$ (80, —)	219
	"	"	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	" (80, 70)	219
	$(n$-$C_8H_{17})_3B$	—	$CuBr_2$ (6 eq), 55°	n-$C_8H_{17}Br$ (51, —), n-$C_6H_{13}CHBrCH_3$ (3, —)	224
	n-$C_4H_9C\equiv CH$	CATBH	Br_2 (2 eq), $NaOCH_3$ (2 eq), CH_3OH, −78°	n-$C_4H_9CHBrCH(OCH_3)_2$ (82,)	148
	t-$C_4H_9C\equiv CH$	"	"	t-$C_4H_9CHBrCH(OCH_3)_2$ (49,)	148
	n-$C_6H_{13}CH=CH_2$	BH_3-THF	$CuCl_2$, H_2O	n-$C_8H_{17}Cl$ (68, —)	225
	"	"	NaOH, H_2O, $(C_2H_5)_2NCl$	" (—, 40)	370
	$(n$-$C_8H_{17})_3B$	—	$FeCl_2$ (6 eq), 55°	" (55, —), n-$C_6H_{13}CHClCH_3$ (4, —)	224
	t-$C_4H_9CH_2C(CH_3)=CH_2$	BH_3-THF	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	t-$C_4H_9CH_2CH(CH_3)CH_2I$ (63, 54)	217
	"	Sia_2BH	1. I_2 (1.1 eq) 2. NaOH (1.1 eq), CH_3OH	" (92,)	217
9	$C_6H_5C(CH_3)=CH_2$	BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	$C_6H_5CH(CH_3)CH_2Br$ (68, —)	219
	"	"	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	" (74, 63)	219
	"	"	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	$C_6H_5CH(CH_3)CH_2I$ (63, 50)	217

TABLE X. HALIDES. A. DIRECT FUNCTIONALIZATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10		"	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	 (55, –)	219
	"	"	1. $NaOCH_3$ (3.3 eq), CH_3OH 2. Br_2 (3 eq)	" (65, 59)	219
	"	"	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	 (60, 40)	217
	"	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	" (72,)	218
	$C_6H_{11}C{\equiv}CH$	CATBH	Br_2 (2 eq), $NaOCH_3$ (2 eq), CH_3OH, −78°	$C_6H_{11}CHBrCH(OCH_3)_2$ (81, –)	148
	n-$C_8H_{17}CH{=}CH_2$	BH_3-THF	1. I_2 (2 eq) 2. NaOH (2 eq), CH_3OH	n-$C_{10}H_{21}I$ (65, –)	217
	"	Sia_2BH	I_2, NaOH, CH_3OH	" (95, –)	217
	n-$C_6H_{13}C{\equiv}CH$	CATBH	Br_2 (2 eq), $NaOCH_3$ (2 eq), CH_3OH, −78°	n-$C_6H_{13}CHBrCH(OCH_3)_2$ (82, 55)	148
11	$Cl(CH_2)_9CH{=}CH_2$	BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	$Cl(CH_2)_{11}Br$ (–, 75)	219
12	$CH_3O_2C(CH_2)_8CH{=}CH_2$	"	"	$CH_3O_2C(CH_2)_{10}Br$ (92, 85)	219
	"	BH_3-DMS	1. I_2 (3 eq) 2. $NaOCH_3$ (3 eq), CH_3OH	$CH_3O_2C(CH_2)_{10}I$ (80, 68)	218
13	$CH_3O_2C(CH_2)_9CH{=}CH_2$	BH_3-THF	1. Br_2 (4 eq), 0° 2. $NaOCH_3$ (5 eq), CH_3OH, 0°	$CH_3O_2C(CH_2)_{11}Br$ (–, 77)	219

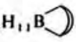
[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The optical purity is 84%.

TABLE X. HALIDES. B. ONE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
4	$(C_2H_5)_3B$, Cl_2CHCN	—	[b], 0°	$C_2H_5CHClCN$ (89, —)	201
	C_2H_5B, "	—	"	" (87, —)	201
5	$(C_2H_5)_3B$, $N_2CHCOCH_3$	—	1. NBS, 0° 2. NaOH	$C_2H_5CHBrCOCH_3$ (83, —)	176
	", "	—	1. NCS, 0° 2. NaOH	$C_2H_5CHClCOCH_3$ (86, —)	176
	CH_3Li, $Br_2CHCO_2C_2H_5$	9-BBN	1. CH_3SO_3H, 0° 2. t-C_4H_9OK, t-C_4H_9OH, 0°	$CH_3CHBrCO_2C_2H_5$ (40, —)	173
6	n-C_4H_9B, Cl_2CHCN	—	[b], 0°	n-$C_4H_9CHClCN$ (75, —)	201
	s-C_4H_9B, "	—	"	s-$C_4H_9CHClCN$ (69, —)	201
	i-C_4H_9B, "	—	"	i-$C_4H_9CHClCN$ (73, —)	201
	$CH_2{=}CH_2$, $Br_2CHCO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	$C_2H_5CHBrCO_2C_2H_5$ (97, —)	16
	$(C_2H_5)_3B$, $N_2CHCO_2C_2H_5$	—	Br_2, CCl_4, 0°, dark	" (83, —)[c]	179
	", $Br_2CHCO_2C_2H_5$	—	[b], THF, t-C_4H_9OH, 0°	" (96, —)	196
	C_2H_5B, "	—	"	" (83, —)	196
	$CH_2{=}CH_2$, $Cl_2CHCO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	$C_2H_5CHClCO_2C_2H_5$ (98, —)	16
7	C_5H_9B, Cl_2CHCN	—	[b], 0°	$C_5H_9CHClCN$ (76, —)	201
	$(C_2H_5)_3B$, $N_2CHCOC_3H_7$-i	—	1. NCS, 0° 2. NaOH	$C_2H_5CHClCOC_3H_7$-i (93, —)	176

TABLE X. HALIDES. B. ONE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
8	$C_6H_{11}B$, Cl_2CHCN	–	[b], 0°	$C_6H_{11}CHClCN$ (78, –)	201
	$CH_3CH{=}CHCH_3$, $Br_2CHCO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	s-$C_4H_9CHBrCO_2C_2H_5$ (80, –)	16
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CHBrCO_2C_2H_5$ (85, –)	16
	i-C_4H_9B, "	--	[b], THF, t-C_4H_9OH, 0°	" (81, –)	196
	$(n$-$C_4H_9)_3B$, $N_2CHCO_2C_2H_5$	–	Br_2, CCl_4, 0°, dark	n-$C_4H_9CHBrCO_2C_2H_5$ (76, –)[c]	179
9	Cyclopentene, $Br_2CHCO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	$C_5H_9CHBrCO_2C_2H_5$ (93, –)	16
	C_5H_9B, "	--	[b], THF, t-C_4H_9OH, 0°	" (78, –)	196
	$(C_5H_9)_3B$, "	–	"	" (76, –)	196
	Cyclopentene, $Cl_2CHCO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	$C_5H_9CHClCO_2C_2H_5$ (54, –)	16
	", "	9-BBN	"	" (90, –)	192
10	$(C_2H_5)_3B$, $N_2CHCOC_6H_5$	--	1. NBS, 0° 2. NaOH	$C_2H_5CHBrCOC_6H_5$ (76, –)	176
	C_6H_5Li, $Br_2CHCO_2C_2H_5$	9-BBN	Pentane; EA	$C_6H_5CHBrCO_2C_2H_5$ (65, –)	173
	Cyclohexene, "	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH, 0°	$C_6H_{11}CHBrCO_2C_2H_5$ (47, –)	16
	", "	9-BBN	"	" (68, –)	192
	", $Cl_2CHCO_2C_2H_5$	"	"	$C_6H_{11}CHClCO_2C_2H_5$ (88, 67)	192
	n-$C_4H_9CH{=}CH_2$, $Br_2CHCO_2C_2H_5$	BH_3-THF	"	n-$C_6H_{13}CHBrCO_2C_2H_5$ (98, –)	16
	n-$C_4H_9CH{=}CH_2$, $Cl_2CHCO_2C_2H_5$	"	"	n-$C_6H_{13}CHClCO_2C_2H_5$ (98, –)	16
11	", $N_2CHCOC_3H_7$-i	"	1. NBS, 0° 2. NaOH	n-$C_6H_{13}CHBrCOC_3H_7$-i (80, 63)	176
12	n-$C_5H_{11}CH{=}CH_2$, "	"	"	n-$C_7H_{15}CHBrCOC_3H_7$-i (84, –)	176
	", "	"	1. NCS, 0° 2. NaOH	n-$C_7H_{15}CHClCOC_3H_7$-i (88, –)	176
14	n-$C_4H_9CH{=}CH_2$, $N_2CHCOC_6H_5$	"	1. NBS, 0° 2. NaOH	n-$C_6H_{13}CHBrCOC_6H_5$ (79, –)	176
	n-$C_8H_{17}CH{=}CH_2$, $Br_2CHCO_2C_2H_5$	"	t-C_4H_9OK, t-C_4H_9OH, 0°	n-$C_{10}H_{21}CHBrCO_2C_2H_5$ (92, –)	16
15	n-$C_5H_{11}CH{=}CH_2$, $N_2CHCOC_6H_5$	"	1. NBS, 0° 2. NaOH	n-$C_7H_{15}CHBrCOC_6H_5$ (83, –)	176

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[a] The abbreviation EA signifies decomposition of an intermediate organoborane with ethanolamine.

[b] Potassium 2,6-di-*tert*-butylphenoxide is used as a base.

[c] The yield is based on ^1H NMR analysis.

TABLE X. HALIDES. C. TWO-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
6	$CH_2=CHCH_2B(C_2H_5)_2, (CF_3)_2CO$	—	0°; TEA	$CH_2=CHCH_2COH(CF_3)_2$ (—, 78)	254
	$(CH_2=CHCH_2)_3B$, "	—	$HC\equiv CC_3H_7\text{-}n$; TEA	" (—, 83)	254
7	$CH_2=C(CH_3)CH_2B(C_3H_7\text{-}n)_2$, "	—	0°; TEA	$CH_2=C(CH_3)CH_2COH(CF_3)_2$ (—, 89)	254
	$[CH_2=C(CH_3)CH_2]_3B$, "	—	$HC\equiv CH$, 140°; TEA	" (—, 69)	254
	$(CH_3CH=CHCH_2)_3B$, "	—	1. 0° 2. $n\text{-}C_9H_{19}OH$	$CH_2=CHCH(CH_3)COH(CF_3)_2$ (—, 87)	254
	$CH_3CH=CHCH_2B(C_4H_9\text{-}n)_2$, "	—	"	" (—, 88)	254
	$C_2H_5CH=CH_2, CH_2=CBrCHO$	$BH_3\text{-}THF$	H_2O	$n\text{-}C_5H_{11}CHBrCHO$ (100, 85)[b]	81
	$CH_3CH=CHCH_3$, "	"	"	$s\text{-}C_4H_9CH_2CHBrCHO$ (90, 81)[b]	81
	$(CH_3)_2C=CH_2$, "	"	"	$i\text{-}C_4H_9CH_2CHBrCHO$ (100, 80)[b]	81
	$(n\text{-}C_3H_7)_3B, CH_2=CHCOCH_3$	—	1. Air 2. Br_2, CCl_4, 0°, dark 3. CH_3OH	$n\text{-}C_4H_9CHBrCOCH_3$ (78, —)[b]	179
8	$n\text{-}C_3H_7CH=C=CHB(OC_4H_9\text{-}n)_2, CCl_3CHO$	—	Ether, HCl	$HC\equiv CCH(C_3H_7\text{-}n)CHOHCCl_3$ (—, 72)	261
	$(n\text{-}C_4H_9)_3B, CH_2=CHCOCH_3$	—	1. Air 2. Br_2, CCl_4, 0°, dark 3. CH_3OH	$n\text{-}C_5H_{11}CHBrCOCH_3$ (74, —)[b]	179
	$(s\text{-}C_4H_9)_3B$, "	—	"	$s\text{-}C_4H_9CH_2CHBrCOCH_3$ (85, —)[b]	179
	$(i\text{-}C_4H_9)_3B$, "	—	"	$i\text{-}C_4H_9CH_2CHBrCOCH_3$ (56, —)[b]	179
9	Cyclohexene, $CH_2=CBrCHO$	$BH_3\text{-}THF$	H_2O	$C_6H_{11}CH_2CHBrCHO$ (90, 65)[b]	81
	$(n\text{-}C_4H_9)_3B, CH_2=C(CH_3)COCH_3$	—	1. Air 2. Br_2, CCl_4, 0°, dark 3. CH_3OH	$n\text{-}C_5H_{11}C(CH_3)BrCOCH_3$ (98, —)[b]	179
	$(s\text{-}C_4H_9)_3B$, "	—	"	$s\text{-}C_4H_9CH_2C(CH_3)BrCOCH_3$ (94, —)[b]	179

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[a] The abbreviation TEA signifies decomposition of an intermediate organoborane with triethanolamine.

[b] The yield is based on ^1H NMR analysis.

TABLE X. HALIDES. D. THREE-OR-MORE-CARBON HOMOLOGATION

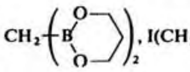
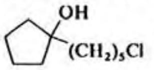
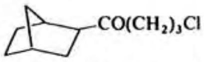
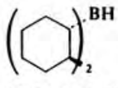
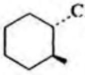
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	, I(CH$_2$)$_4$Cl	—	1. LTMP, −75° 2. NaBO$_3$, H$_2$O	OHC(CH$_2$)$_4$Cl (83, —)	182
7	CH$_2$=CHCH$_2$B(C$_2$H$_5$)$_2$, CH$_3$COCH=CHCl	—	0°; [O]	CH$_2$=CHCH$_2$C(CH$_3$)OHCH=CHCl (—, 73)	254
	(n-C$_4$H$_9$)$_3$B, LiCH=CH$_2$, CH$_2$O	—	1. 45° 2. PCl$_5$, −15°; [O]	n-C$_4$H$_9$CHOH(CH$_2$)$_2$Cl (—, 53)	68
10	(n-C$_3$H$_7$)$_3$B, o-ClC$_6$H$_4$COCl	—	1. CH$_3$Li 2. CuCl, COD; [O]	o-ClC$_6$H$_4$COC$_3$H$_7$-n (80, —)	151
	", p-ClC$_6$H$_4$COCl	—	"	p-ClC$_6$H$_4$COC$_3$H$_7$-n (90, —)	151
	[i-C$_3$H$_7$CH(CH$_3$)]$_2$BH, HC≡C(CH$_2$)$_3$Cl	—	Pd(OAc)$_2$, (C$_2$H$_5$)$_3$N	i-C$_3$H$_7$CH(CH$_3$)CH=CH(CH$_2$)$_3$Cl (E)-(—, 61)	372
	Cyclopentene, CH$_2$=CH(CH$_2$)$_3$Cl	ThexylBH$_2$	1. Br$_2$, CH$_2$Cl$_2$, H$_2$O 2. NaOH, C$_2$H$_5$OH; [O]	OH (CH$_2$)$_5$Cl (89, —)	26
11	(n-C$_4$H$_9$)$_3$B, p-BrC$_6$H$_4$CH$_2$Br	—	1. CH$_3$Li 2. CuCN; [O]	p-BrC$_6$H$_4$C$_5$H$_{11}$-n (59, —)	60
	, CH$_2$=CHCH$_2$Cl	Thexyl BH$_2$	CO, H$_2$O, 70 atm, 50°; [O]	CO(CH$_2$)$_3$Cl (75, 63)	154
12	m-ClC$_6$H$_4$I	BH$_3$-THF	1. Mg, reflux 2. KOH, CH$_3$OH 3. AgNO$_3$	m-ClC$_6$H$_4$C$_6$H$_4$Cl-m (—, 60)	235
13	m-ClC$_6$H$_4$Br, m-FC$_6$H$_4$COCl	BH$_3$-THF	Li, C$_6$H$_6$; [O]	m-ClC$_6$H$_4$COC$_6$H$_4$F-m (—, 68)	57
	(CH$_3$)$_2$C=CH$_2$, HC≡CC$_4$H$_9$-n, KCN	ThexylBH$_2$	1. TFAA, −78° 2. NaOH	i-C$_4$H$_9$CH(NHCOCF$_3$)CH=CHC$_4$H$_9$-n (E)-(—, 67)	214
	", C$_2$H$_5$C≡CC$_2$H$_5$, KCN	"	"	i-C$_4$H$_9$CH(NHCOCF$_3$)C(C$_2$H$_5$)=CHC$_2$H$_5$ (E)-(—, 74)	214

TABLE X. HALIDES. D. THREE-OR-MORE-CARBON HOMOLOGATION (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
14	$C_6H_5CH_2\bar{B}(C_4H_9\text{-}n)_3Li^+$, $p\text{-}IC_6H_4COCl$	—	THF, hexane	$C_6H_5CH_2COC_6H_4I\text{-}p$ (—, 72)	56
	Cyclopentene, $HC{\equiv}CC_4H_9\text{-}n$, KCN	ThexylBH$_2$	1. TFAA, −78° 2. NaOH	$C_5H_9CH(NHCOCF_3)CH{=}CHC_4H_9\text{-}n$ (*E*)-(—, 83)	214
	", $CH_2{=}CH(CH_2)_6Cl$, NaCN	"	TFAA, −78° to room temp; [O]	$C_5H_9CO(CH_2)_8Cl$ (—, 76)	297
	", $CH_2{=}CH(CH_2)_6I$, NaCN	"	"	$C_5H_9CO(CH_2)_8I$ (—, 76)	297
15	Cyclohexene, $HC{\equiv}CC_4H_9\text{-}n$, KCN	ThexylBH$_2$	1. TFAA, 2. NaOH	$C_6H_{11}CH(NHCOCF_3)CH{=}CHC_4H_9\text{-}n$ (*E*)-(—, 82)	214
	", $C_2H_5C{\equiv}CC_2H_5$, KCN	"	"	$C_6H_{11}CH(NHCOCF_3)C(C_2H_5){=}CHC_2H_5$ (*E*)-(—, 77)	214
	$(C_6H_{11})_2BH$, $HC{\equiv}CC_4H_9\text{-}n$, KCN	"	"	$C_6H_{11}CH(NHCOCF_3)CH{=}CHC_4H_9\text{-}n$ (*E*)-(—, 90)	214
	", $C_2H_5C{\equiv}CC_2H_5$, KCN	"	"	$C_6H_{11}CH(NHCOCF_3)C(C_2H_5){=}CHC_2H_5$ (*E*)-(—, 76)	214
16	 , $HC{\equiv}CC_4H_9\text{-}n$, KCN	—	"	 $CH(NHCOCF_3)CH{=}CHC_4H_9\text{-}n$ (*E*)-(—, 63)	214
20	$(C_6H_{11})_3B$, $ClCH{=}C(C_6H_4Cl\text{-}p)_2$	—	$n\text{-}C_4H_9Li$; [O]	$C_6H_{11}COCH(C_6H_4Cl\text{-}p)_2$ (—, 22)	336
22	$(n\text{-}C_6H_{13})_3B$, $HC{\equiv}CC_6H_{13}\text{-}n$, $p\text{-}ClC_6H_4COCH_2Br$	—	1. $n\text{-}C_4H_9Li$, 0° 2. DG, −78 to 40° 3. AcOH	$n\text{-}C_6H_{13}CH{=}C(C_6H_{13}\text{-}n)CH_2COC_6H_4Cl\text{-}p$ (—, 77)	65

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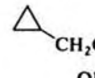
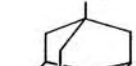
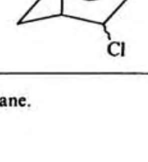
[a] The abbreviation [O] signifies oxidation with alkaline peroxide to decompose an intermediate organoborane.

TABLE X. HALIDES. E. MISCELLANEOUS PREPARATIONS

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
3	$CH_2{=}CHCHCl_2$	9-BBN	NaOH, H_2O	 (90, –)	93
4	$CH_2{=}CHCHClCH_2Cl$	"	"	 (81, –)	93
10	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CCH_2Cl$	—	1. 130° 2. CH_3OH, B_2H_6 3. CO, EG, 70 atm, 150°; [O]	 (–, –)	305

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE XI. SULFUR DERIVATIVES. A. DIRECT FUNCTIONALIZATION

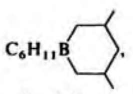
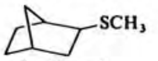
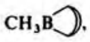
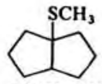
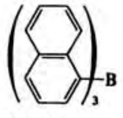
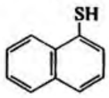
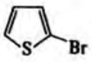
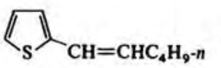
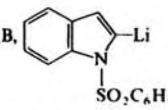
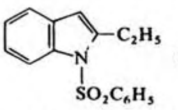
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
5	$C_2H_5CH{=}CH_2$	BH_3-THF	KSCN (6 eq), $Fe(NH_4)(SO_4)_2$ (18 eq), H_2O, reflux	n-C_4H_9SCN (75, –)	224
	$CH_3CH{=}CHCH_3$	"	"	s-C_4H_9SCN (72, 67)	224
	$C_2H_5CH{=}CH_2$, $(CH_3S)_2$ (2 eq)	"	Air	n-$C_4H_9SCH_3$ (71, –)	229
	", " (2 eq)	"	Hexane, *hv*	" (91, –)	229
	$CH_3CH{=}CHCH_3$, " (2 eq)	"	Air	s-$C_4H_9SCH_3$ (83, –)	229
	", " (2 eq)	"	Hexane, *hv*	" (95, –)	229
	$(CH_3)_2C{=}CH_2$, " (2 eq)	"	Air	i-$C_4H_9SCH_3$ (68, –)	229
	", " (2 eq)	"	Hexane, *hv*	" (91, –)	229
6	$(CH_2{=}CHCH_2)_3B$, "	–	Sulfur, 130°	$(CH_2{=}CHCH_2S)_2$ (–, 2)	373
	$(CH_3)_2C{=}CHCH_3$	BH_3-THF	KSCN (6 eq), $Fe(NH_4)(SO_4)_2$ (18 eq), H_2O, reflux	i-$C_3H_7CH(CH_3)SCN$ (98, –)	224
	Cyclopentene, $(CH_3S)_2$ (2 eq)	"	Air	$C_5H_9SCH_3$ (81, 74)	229
	", " (2 eq)	"	Hexane, *hv*	" (93, –)	229
7	Cyclohexene	"	KSCN (6 eq), $Fe(NH_4)(SO_4)_2$ (18 eq), H_2O, reflux	$C_6H_{11}SCN$ (200, 191)	224
	n-$C_4H_9CH{=}CH_2$	"	"	n-$C_6H_{13}SCN$ (77, 80)	224
	Cyclohexene, $(CH_3S)_2$ (2 eq)	"	Air	$C_6H_{11}SCH_3$ (88, 77)	229
	, " (2 eq)	–	*hv*	" (94, –)	229
	", " (2 eq)	BH_3-THF	Hexane, *hv*	" (93, –)	229
8	, " (2 eq)	"	Air	 (78, 75)	229
	", " (2 eq)	"	Hexane, *hv*	" (95, –)	229
9	, ", $LiCH_3$	–	1. Pentane, −78° 2. CH_3COCl, 0° 3. *hv*	 (–, 91)	275
	n-$C_6H_{13}CH{=}CH_2$, " (2 eq)	BH_3-THF	Air	n-$C_8H_{17}SCH_3$ (84, 75)	229
	", " (2 eq)	"	Hexane, *hv*	" (95, –)	229
	$(n$-$C_8H_{17})_3B$, " (2 eq)	–	*hv*	" (82, –)	229
10	$(n$-$C_4H_9)_3B$, $(C_6H_5S)_2$ (2 eq)	–	Air	n-$C_4H_9SC_6H_5$ (95, –)	229
	$(s$-$C_4H_9)_3B$, " (2 eq)	–	"	s-$C_4H_9SC_6H_5$ (98, –)	229
		–	Sulfur, 130°	 (–, 34)	
12	$(C_6H_5)_3B$	–	"	$(C_6H_5S)_2$ (–, 64)	373
	$(C_6H_{11})_3B$	–	"	$(C_6H_{11}S)_2$ (–, 33)	373
14	$(n$-$C_8H_{17})_3B$, C_6H_5SCl	–	$(n$-$C_4H_9)_2O$, heat	n-$C_8H_{17}SC_6H_5$ (20, –)	374
15	", p-$CH_3C_6H_4SCl$	–	"	n-$C_8H_{17}SC_6H_4CH_3$-p (37, –)	374
16	$[C_6H_5(CH_2)_2]_3B$	–	Sulfur, 130°	$[C_6H_5(CH_2)_2S]_2$ (–, 31)	373
	$(n$-$C_8H_{17})_3B$	–	"	$(n$-$C_8H_{17}S)_2$ (–, 47)	373

TABLE XI. SULFUR DERIVATIVES. B. ONE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
7	$C_2H_5CH{=}CH_2$, $BrCH_2SO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	n-$C_5H_{11}SO_2C_2H_5$ (—, 78)	230
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH_2SO_2C_2H_5$ (—, 81)	230
	$(n$-$C_3H_7)_3B$, thiophene (1.2 eq)	—	1. n-C_4H_9Li, TMEDA, ether 2. I_2, −78°; [O]	2-n-Propylthiophene (62, —)	361
8	Cyclopentene, $BrCH_2SO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	$C_5H_9CH_2SO_2C_2H_5$ (—, 78)	230
	$(n$-$C_4H_9)_3B$, thiophene (1.2 eq)	—	1. n-C_4H_9Li, TMEDA, ether 2. I_2, −78°; [O]	2-n-Butylthiophene (91, —)	361
	$(i$-$C_4H_9)_3B$, " (1.2 eq)	—	"	2-Isobutylthiophene (95, —)	361
	$(s$-$C_4H_9)_3B$, " (1.2 eq)	—	"	2-*sec*-Butylthiophene (100, —)	361
9	Cyclohexene, $BrCH_2SO_2C_2H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	$C_6H_{11}CH_2SO_2C_2H_5$ (—, 65)	230
	n-$C_4H_9CH{=}CH_2$, "	"	"	n-$C_7H_{15}SO_2C_2H_5$ (—, 91)	230
	$C_2H_5CH{=}CH_2$, $BrCH_2SO_2N(C_2H_5)_2$	"	"	n-$C_5H_{11}SO_2N(C_2H_5)_2$ (—, 84)	230
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH_2SO_2N(C_2H_5)_2$ (—, 82)	230
	$(C_5H_9)_3B$, thiophene (1.2 eq)	—	1. n-C_4H_9Li, TMEDA, ether 2. I_2, −78°; [O]	2-Cyclopentylthiophene (100, —)	361
10	Cyclopentene, $BrCH_2SO_2N(C_2H_5)_2$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	$C_5H_9CH_2SO_2N(C_2H_5)_2$ (—, 68)	230
	$C_2H_5CH{=}CH_2$, $BrCH_2SO_3CH_2C_4H_9$-t	"	"	n-$C_5H_{11}SO_3CH_2C_4H_9$-t (—, 76)	230
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH_2SO_3CH_2C_4H_9$-t (—, 59)	230
	$(C_6H_5)_3B$, thiophene	—	1. n-C_4H_9Li, TMEDA, ether 2. I_2, −78°; [O]	2-Phenylthiophene (42, —)	361
	n-$C_4H_9C{\equiv}CH$, 	CATBH	1. $Pd[P(C_6H_5)_3]_4$, C_6H_6 2. $NaOCH_3$, C_2H_5OH, reflux; [O]	 (*E*)-(86, —)	364
11	$C_2H_5CH{=}CH_2$, $BrCH_2SO_2C_6H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	n-$C_5H_{11}SO_2C_6H_5$ (—, 99)	230
	$(CH_3)_2C{=}CH_2$, "	"	"	i-$C_4H_9CH_2SO_2C_6H_5$ (—, 92)	230
	Cyclopentene, $BrCH_2SO_3CH_2C_4H_9$-t	"	"	$C_5H_9CH_2SO_3CH_2C_4H_9$-t (—, 73)	230
	Cyclohexene, $BrCH_2SO_2N(C_2H_5)_2$	"	"	$C_6H_{11}CH_2SO_2N(C_2H_5)_2$ (—, 72)	230
	n-$C_6H_{13}CH{=}CH_2$, $BrCH_2SO_2C_2H_5$	"	"	n-$C_9H_{19}SO_2C_2H_5$ (—, 81)	230
	n-$C_4H_9CH{=}CH_2$, $BrCH_2SO_2N(C_2H_5)_2$	"	"	n-$C_7H_{15}SO_2N(C_2H_5)_2$ (—, 85)	230
12	Cyclopentene, $BrCH_2SO_2C_6H_5$	"	"	$C_5H_9CH_2SO_2C_6H_5$ (—, 82)	230
	Cyclohexene, $BrCH_2SO_3CH_2C_4H_9$-t	"	"	$C_6H_{11}CH_2SO_3CH_2C_4H_9$-$t$ (—, 60)	230
	n-$C_4H_9CH{=}CH_2$, "	"	"	n-$C_7H_{15}SO_3CH_2C_4H_9$-t (—, 76)	230
	$(n$-$C_8H_{17})_3B$, thiophene, (1.2 eq)	—	1. n-C_4H_9Li, TMEDA, ether 2. I_2, −78°; [O]	2-n-Octylthiophene (66, —)	361
13	Cyclohexene, $BrCH_2SO_2C_6H_5$	BH_3-THF	t-C_4H_9OK, t-C_4H_9OH; [O]	$C_6H_{11}CH_2SO_2C_6H_5$ (—, 37)	230
	n-$C_4H_9CH{=}CH_2$, "	"	"	n-$C_7H_{15}SO_2C_6H_5$ (—, 96)	230
	n-$C_6H_{13}CH{=}CH_2$, $BrCH_2SO_2N(C_2H_5)_2$	"	"	n-$C_9H_{19}SO_2N(C_2H_5)_2$ (—, 77)	230
14	", $BrCH_2SO_3CH_2C_4H_9$-t	"	"	n-$C_9H_{19}SO_3CH_2C_4H_9$-t (—, 75)	230
15	", $BrCH_2SO_2C_6H_5$	"	"	n-$C_9H_{19}SO_2C_6H_5$ (—, 79)	230

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE XI. SULFUR DERIVATIVES. C. TWO-OR-MORE-CARBON HOMOLOGATION

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
16	$(C_2H_5)_3B$, 	—	I_2, −80° to room temp; [O]	 (—, 57)	363
22	$(n\text{-}C_6H_{13})_3B$, $LiC{\equiv}CC_6H_{13}\text{-}n$, $CH_2{=}CHSOC_6H_5$	--	0°; [O]	$n\text{-}C_6H_{13}COCH(C_6H_{13}\text{-}n)(CH_2)_2SOC_6H_5$ (—, 10)	90

[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

TABLE XII. ALKANES, CYCLOALKANES, AND ARENES

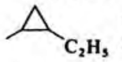
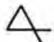
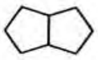
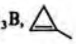
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
3	$CH_2{=}CHCH_2Br$	$(n\text{-}C_3H_7)_2BH$	$NaB(C_2H_5)_4$	Cyclopropane (—, 69)	92
	$CH_2{=}CHCH_2Cl$	"	"	" (—, 66)	92
	"	$NaBH_4$, BF_3-ether	0°, DG; [O]	" (—, 43)	91
4	$CH_2{=}C(CH_3)CH_2Cl$	"	"	Methylcyclopropane (—, 71)	91
	"	$(n\text{-}C_3H_7)_2BH$	$NaB(C_2H_5)_4$	" (—, 96)	92
	$CH_2{=}CHCHClCH_3$	9-BBN	NaOH, H_2O	" (85, —)	93
	$(C_2H_5)_3B$	—	Ag_2O, NaOH, H_2O	$n\text{-}C_4H_{10}$ (74, —)	231
5	$CH_2{=}CHC(CH_3)_2Cl$	9-BBN	NaOH, H_2O	1,1-Dimethylcyclopropane (75, —)	93
6	$CH_2{=}CH(CH_2)_2CH{=}CH_2$	BH_3-THF	1. KOH, CH_3OH 2. $AgNO_3$	Cyclohexane (66, —)	234
	$CH_2{=}C(CH_3)CH_2CH{=}CH_2$	"	"	Methylcyclopentane (85, —)	234
	$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	"	"	1,2-Dimethylcyclobutane (79, —)	234
	$n\text{-}C_3H_7C(CH_2Cl){=}CH_2$	$NaBH_4$, BF_3-ether	0°, DG; [O]	n-Propylcyclopropane (—, 61)	91
	"	$(n\text{-}C_3H_7)_2BH$	$NaB(C_2H_5)_4$	" (—, 88)	92
	$C_2H_5CHClC(CH_3){=}CH_2$	"	"	 (E)-(—, 43) (Z)-(—, 43)	92
7	$CH_2{=}CH(CH_2)_3CH{=}CH_2$	BH_3-THF	1. KOH, CH_3OH 2. $AgNO_3$	Cycloheptane (67, —)	234
	$(CH_2{=}CHCH_2)_3B$, 	—	1. CH_3OH, −60° 2. $(CH_3O)_3B$, 100–200° 3. $C_9H_{19}CO_2H$	 $-C_3H_7$-n (—, 34)[b]	375
8	CH_3B, $LiCH_3$	—	1. Pentane, −78° 2. CH_3COCl, 0° 3. hν, $n\text{-}C_3H_7SH$, CH_3OH	 (—, 75)	275
	$(CH_3CH{=}CHCH_2)_3B$, 	—	1. −50° 2. CH_3OH, reflux 3. $C_9H_{19}CO_2H$, 160–170°	 $CH(CH_3)CH{=}CH_2$ (—, 79)[b]	132
	$CH_2{=}C(CH_3)(CH_2)_2C(CH_3){=}CH_2$	BH_3-THF	1. KOH, CH_3OH 2. $AgNO_3$	1,4-Dimethylcyclohexane (49, —)	234
	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	"	"	Cyclooctane (42, —)	234
	$(CH_2{=}CHCH_2)_3B$, HC≡CH	—	1. H_2, Pt, 130° 2. $C_6H_5CO_2H$	1,3-Dimethylcyclohexane (—, 50)[b]	303
	$C_2H_5CH{=}CH_2$	BH_3-DG	1. KOH, CH_3OH 2. $AgNO_3$	$n\text{-}C_8H_{18}$ (68–80, —)	232
	$CH_3CH{=}CHCH_3$	"	"	$C_2H_5CH(CH_3)CH(CH_3)C_2H_5$ (35–50, —)	232
	$(CH_3)_2C{=}CH_2$	"	"	$i\text{-}C_3H_7(CH_2)_2C_3H_7\text{-}i$ (60–80, —)	232
9	$C_6H_5C(CH_2Cl){=}CH_2$	$NaBH_4$, BF_3-ether	DG, 0°; [O]	Phenylcyclopropane (—, 55)	91
	"	9-BBN	NaOH, H_2O	" (92, —)	93
	$C_6H_5CHClCH{=}CH_2$	"	"	" (91, —)	93
	$(CH_2{=}CHCH_2)_3B$, $HC{\equiv}CCH_2Cl$	—	1. 130° 2. CH_3OH 3. $n\text{-}C_{17}H_{35}CO_2H$, 230°	1,3,5-Trimethylbenzene (—, 53)[b]	376
	", "	—	1. 130° 2. $n\text{-}C_4H_9OH$ 3. H_2, PtO_2 4. $n\text{-}C_{17}H_{35}CO_2H$	1,3,5-Trimethylcyclohexane (—, —)	377
	", "	—	1. 130° 2. CH_3OH, H_2, Pd-$SrCO_3$ 3. $n\text{-}C_{17}H_{35}CO_2H$, 200°	" (—, 39)[b]	376
	", $CH_2{=}C{=}CH_2$	—	1. Heat 2. CH_3OH, H_2, Pt 3. $n\text{-}C_{17}H_{35}CO_2H$	" (—, 34)[b]	312
	", $HC{\equiv}CCH_3$	—	1. 130° 2. CH_3OH, H_2, Ni, 90° 3. $C_6H_5CO_2H$	" (—, 54)[b]	303
	", $HC{\equiv}CCH_2Cl$	—	1. H_2, Pt 2. H_2, Pd-$SrCO_3$ 3. $n\text{-}C_{17}H_{35}CO_2H$, 200°	$i\text{-}C_4H_9CH(CH_3)C_3H_7\text{-}n$ (—, 41)[b]	378 377
	$CH_3CH{=}CHCH_2Li$, $BrCH_2CH{=}C(CH_3)_2$	B-$n\text{-}C_4H_9$-9-BBN	Ether, −78° to room temp	$CH_3CH(CH{=}CH_2)CH_2CH{=}C(CH_3)_2$ (—, 53)	379

TABLE XII. ALKANES, CYCLOALKANES, AND ARENES (*Continued*)

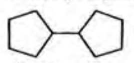
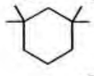
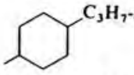
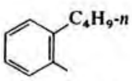
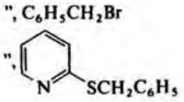
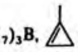
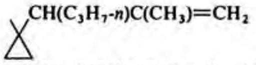
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
10	$C_6H_5CH_2C(CH_2Cl)=CH_2$	$NaBH_4$, BF_3-ether	DG, 0°; [O]	Benzylcyclopropane (—, 45)	91
	$C_6H_5CHClC(CH_3)=CH_2$	9-BBN	NaOH, H_2O	1-Methyl-2-phenylcyclopropane (92, —)	93
	Cyclopentene	BH_3-DG	1. KOH, CH_3OH 2. $AgNO_3$	 (—, 35-50)	232
	$[CH_2=C(CH_3)CH_2]_3B$, $HC\equiv CH$	—	1. 140-150° 2. CH_3OH, H_2, Ni, 100° 3. n-$C_{17}H_{35}CO_2H$, 180-260°	 (—, 29)[b]	307
	$(CH_3)_2C=CH(CH_2)_2C(CH_3)=CHCH_2OAc$	BH_3-THF	1. KOH, CH_3OH 2. $AgNO_3$	 (83, —)	234 309
	n-$C_3H_7CH=CH_2$	"	KOH, CH_3OH, e^-; [O]	n-$C_{10}H_{22}$ (46, —)	233
	$C_2H_5C(CH_3)=CH_2$	BH_3-DG	1. KOH, CH_3OH 2. $AgNO_3$	i-$C_3H_7CH(CH_3)CH(CH_3)C_3H_7$-$i$ (—, 35-50)	232
11	$(C_2H_5)_3B$, $LiCH=CH_2$, C_6H_5CHO	—	1. 45° 2. PCl_5, −15° 3. NaOH	1-Ethyl-2-phenylcyclopropane (—, 35)	68
	$(n$-$C_4H_9)_3B$, C_6H_5Li, CH_3OSO_2F	—	NaOH, H_2O_2, reflux	 (38, —)	70
	", ", "	—	$(CH_3)_3NO$ (3 eq), H_3PO_4, H_2O, reflux	" (52, —)	70
	", $C_6H_5CH_2Br$	—	CH_3Li, CuCN; [O]	$C_6H_5C_5H_{11}$-n (68, —)	60
	", 		1. n-C_4H_9Li, −75° 2. Reflux; [O]	" (—, 63)	236
	", $C_6H_5SCH_2C_6H_5$	—	"	" (—, 71)	236
	", "	—	1. n-C_4H_9Li, −75° 2. CuI, reflux; [O]	" (—, 92)	236
	", "	—	1. n-C_4H_9Li, −75° 2. $(CH_3)_2SO_4$, reflux; [O]	" (—, 78)	236
	$(n$-$C_3H_7)_3B$,  (2 eq)	—	1. Neat 2. n-$C_{17}H_{35}CO_2H$	 (—, 50)	380
	$(CH_2=CHCH_2)_3B$, $(CH_3)_2C=C=CHCl$	—	1. CH_3OH, H_2, Pt 2. n-$C_{17}H_{35}CO_2H$	n-$C_6H_{13}C(CH_3)_2C_2H_5$ (—, 32)[b]	310
	$(n$-$C_6H_{13})_3B$, $(n$-$C_5H_{11})_3B$	—	KOH, CH_3OH, e^-; [O]	n-$C_{11}H_{24}$ (19, —)	233
12	C_6H_5Br	BH_3-THF	1. Reflux 2. KOH, CH_3OH 3. $AgNO_3$	$C_6H_5C_6H_5$ (—, 59)	235
	$(n$-$C_4H_9)_3B$, m-$CH_3C_6H_4CH_2Br$	—	CH_3Li, CuCN; [O]	m-$CH_3C_6H_4C_5H_{11}$-n (61, —)	60
	$[Cl(CH_2)_5]_3B$, $C_6H_5CH_2Br$	—	"	$C_6H_5(CH_2)_6Cl$ (65, —)	60
	Cyclohexene	BH_3-DG	1. KOH, CH_3OH 2. $AgNO_3$	$C_6H_{11}C_6H_{11}$ (—, 30-50)	232
	"	BH_3-THF	KOH, CH_3OH, e^-; [O]	" (23, —)	233
	$C_6H_{11}Br$	"	1. Reflux 2. KOH, CH_3OH 3. $AgNO_3$	" (71, —)	235
	n-$C_4H_9CH=CH_2$	"	KOH, CH_3OH, e^-; [O]	n-$C_{12}H_{26}$ (56, —)	233
	"	BH_3-DG	1. KOH, H_2O 2. $AgNO_3$	" (66, —)	232
	n-$C_3H_7C(CH_3)=CH_2$	"	"	n-$C_3H_7CH(CH_3)(CH_2)_2CH(CH_3)C_3H_7$-$n$ (71, 61)	232
	n-$C_6H_{13}Br$	BH_3-THF	1. Reflux 2. KOH, CH_3OH 3. $AgNO_3$	" (94, —)	235
	$CH_2=CHCH_2Li$, $C_6H_5CH=CHCH_2Cl$	B-n-C_4H_9-9-BBN	Ether, −78° to room temp	$C_6H_5CH=CH(CH_2)_2CH=CH_2$ (—, 60)	379
	n-$C_4H_9C\equiv CH$, C_6H_5I	CATBH	1. $Pd[P(C_6H_5)_3]_4$, C_6H_6 2. $NaOC_2H_5$, C_2H_5OH, reflux; [O]	$C_6H_5CH=CHC_4H_9$-n (*E*)-(100, —)	364
	", C_6H_5Br	"	"	" (*E*)-(98, —)	364
	", C_6H_5Cl	"	"	" (*E*)-(3, —)	364
	$C_2H_5C\equiv CC_2H_5$, C_6H_5Br	"	"	$C_6H_5C(C_2H_5)=CHC_2H_5$ (*E*)-(87, —)	364
	n-$C_4H_9C\equiv CH$, p-ClC_6H_4Br	"	"	p-$ClC_6H_4CH=CHC_4H_9$-n (*E*)-(100, —)	364

TABLE XII. ALKANES, CYCLOALKANES, AND ARENES (*Continued*)

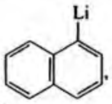
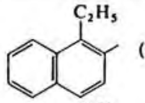
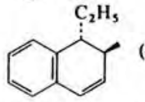
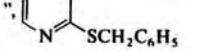
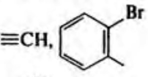
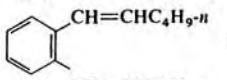
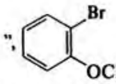
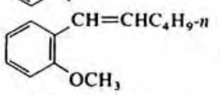
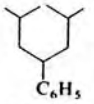
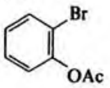
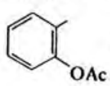
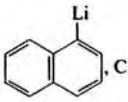
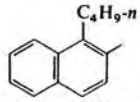
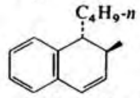
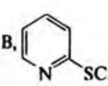
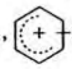
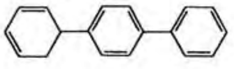
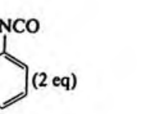
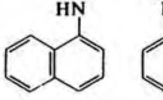
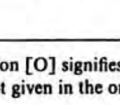
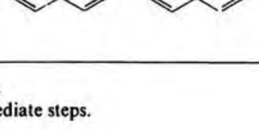
Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
13	$(C_2H_5)_3B$, , CH_3OSO_2F	—	NaOH, H_2O_2, reflux	 (63, --)	70
	", ", "	—	NaOH, H_2O_2	 (42, --)	70
	$(n\text{-}C_6H_{13})_3B$, $C_6H_5CH_2Br$	—	CH_3Li, CuBr; [O]	$C_6H_5C_7H_{15}$-*n* (64, --)	60
	", "	—	CH_3Li, CuCl; [O]	" (43, --)	60
	", "	—	CH_3Li, CuCN; [O]	" (63, --)	60
	", "	—	CH_3Li, CuI; [O]	" (45, --)	60
	", 	—	1. *n*-C_4H_9Li, −75° 2. Reflux; [O]	" (—, 70)	236
	", $C_6H_5SCH_2C_6H_5$	—	"	" (—, 75)	236
	", "	—	1. *n*-C_4H_9Li, −75° 2. CuI, reflux; [O]	" (—, 80)	236
	", "	—	1. *n*-C_4H_9Li, −75° 2. $(CH_3)_2SO_4$, reflux; [O]	" (—, 75)	236
	$CH_3CH{=}CHCH_2Li$ (2 eq), $C_6H_5CH{=}CHCH_2Cl$	*B*-*n*-C_4H_9-9-BBN (2 eq)	Ether, −78° to room temp	$C_6H_5CH{=}CHCH_2CH(CH_3)CH{=}CH_2$ (76, --)	379
	$CH_3CH{=}CHCH_2MgCl$ (2 eq), $C_6H_5CH{=}CHCH_2Cl$	" (2 eq)	"	" (74, --)	379
	$CH_3CH{=}CHCH_2CuCl$ (2 eq), $C_6H_5CH{=}CHCH_2Cl$	" (2 eq)	"	" (50, --)	379
	$CH_3CH{=}CHCH_2Li$ (2 eq), $C_6H_5CH{=}CHCH_2Cl$	$(n\text{-}C_4H_9)_3B$ (2 eq)	"	" (80, --)	379
	$C_6H_5CH{=}CHCH_2Li$, $CH_3CH{=}CHCH_2Cl$	$(n\text{-}C_4H_9)_3B$	"	$C_6H_5CH(CH{=}CH_2)CH_2CH{=}CHCH_3$ (--, 70)	379
	n-$C_4H_9C{\equiv}CH$, 	CATBH	1. $Pd[P(C_6H_5)_3]_4$, C_6H_6 2. $NaOC_2H_5$, C_2H_5OH, reflux; [O]	 (*E*)-(93, --)	364
	", 	"	"	 (*E*)-(81, --)	364
14	$C_6H_5CH_2Br$	BF_3-THF	1. Reflux 2. KOH, CH_3OH 3. $AgNO_3$	$C_6H_5(CH_2)_2C_6H_5$ (85, --)	235
	p-$CH_3C_6H_4Br$	"	"	*p*-$CH_3C_6H_4C_6H_4CH_3$-*p* (, 70)	235
	$C_6H_5CH_2I$	$(C_2H_5)_3B$	Air	$C_6H_5(CH_2)_2C_6H_5$ (90, 87)	366
	$(CH_2{=}CHCH_2)_3B$, $C_6H_5C{\equiv}CH$	—	1. CH_3OH, H_2, Pd-$SrCO_3$ 2. *n*-$C_{17}H_{35}CO_2H$	 (--, 60)[b]	
	$C_6H_5CH{=}CHCH_2Li$, $(CH_3)_2CH{=}CHCH_2Br$	$(n\text{-}C_4H_9)_3B$	Ether, −78° to room temp	$C_6H_5CH(CH{=}CH_2)CH_2CH{=}C(CH_3)_2$ (--, 82)	379
	n-$C_6H_{13}C{\equiv}CH$, C_6H_5Br	CATBH	1. $Pd[P(C_6H_5)_3]_4$, C_6H_6 2. $NaOC_2H_5$, C_2H_5OH, reflux; [O]	*n*-$C_6H_{13}CH{=}CHC_6H_5$ (*E*)-(98, --)	364
	$C_6H_5C{\equiv}CH$, C_6H_5Br	"	"	$C_6H_5CH{=}CHC_6H_5$ (*E*)-(50, --)	364
	n-$C_4H_9C{\equiv}CH$, 	"	"	 (*E*)-(87, --)	364

TABLE XII. ALKANES, CYCLOALKANES, AND ARENES (*Continued*)

Number of Carbon Atoms in Main Product	Reactant(s)	Borane Reagent	Reaction Conditions[a]	Product(s) and Yield(s) (GLC and Isolated, %)	Refs.
15	$(n\text{-}C_4H_9)_3B$, , CH_3OSO_2F	—	NaOH, H_2O_2, reflux	 (70, —)	70
	", ", "	—	NaOH, H_2O_2	 (56, —)	70
	$(n\text{-}C_8H_{17})_3B$,  $SCH_2C_6H_5$	—	1. $n\text{-}C_4H_9Li$, −75° 2. Reflux; [O]	$n\text{-}C_9H_{19}C_6H_5$ (—, 73)	236
	", $C_6H_5SCH_2C_6H_5$	—	"	" (—, 61)	236
	", "	—	1. $n\text{-}C_4H_9Li$, −75° 2. CuI, reflux; [O]	" (—, 69)	236
	", "	—	1. $n\text{-}C_4H_9Li$, −75° 2. $(CH_3)_2SO_4$, reflux; [O]	" (—, 63)	236
16	$n\text{-}C_6H_{13}CH{=}CH_2$	BH_3-THF	KOH, CH_3OH, e^-; [O]	$n\text{-}C_{16}H_{34}$ (69, —)	233
	", "	BH_3-DG	1. KOH, H_2O 2. $AgNO_3$	" (60-80, —)	232
	$n\text{-}C_8H_{17}Br$	BH_3-THF	1. Reflux 2. KOH, CH_3OH 3. $AgNO_3$	" (90, —)	235
	$(n\text{-}C_8H_{17})_3B$, $(n\text{-}C_6H_{13})_3B$	—	KOH, CH_3OH, e^-; [O]	" (33, —)	233
18	$NaB(C_6H_5)_4$,  $Fe(CO)_3BF_4^-$	—	1. H_2O, 90° 2. Ce^{4+}	 (—, 35-65)	381
19	$(n\text{-}C_4H_9)_3B$, , CH_3OSO_2F	—	$(CH_3)_3NO$ (2 eq), H_3PO_4, H_2O, reflux	 (75, —)	70
	$(C_6H_5)_3B$, NaCN	—	1. DG, 40° 2. TFAA, −78° to room temp; [O]	$(C_6H_5)_3CH$ (—, 45)	352
20	$n\text{-}C_4H_9C{\equiv}CB$  , C_6H_5NCO (2 eq)	—	Ether, 0° to room temp: EA, 0°	$C_6H_5NHCON(C_6H_5)COC{\equiv}CC_4H_9\text{-}n$ (—, 80)	362
	$t\text{-}C_4H_9C{\equiv}CB$  , " (2 eq)	—	" "	$C_6H_5NHCON(C_6H_5)COC{\equiv}CC_4H_9\text{-}t$ (—, 71)	362
28	",  (2 eq)	—	"	 (—, 68)	362

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[a] The abbreviation [O] signifies oxidation with alkaline hydrogen peroxide to decompose an intermediate organoborane.

[b] The yield is not given in the original paper. The yield in the table is determined by multiplication of the yields in intermediate steps.

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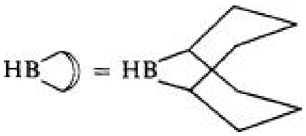
End Notes



*

* Thexyl is the 2,3-dimethyl-2-*n*-butyl group.

* Disiamyl = bis(2-methyl-2-*n*-butyl).

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The Vinylcyclopropane–Cyclopentene Rearrangement

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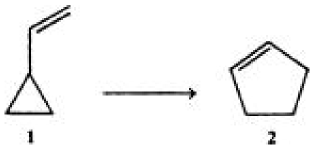
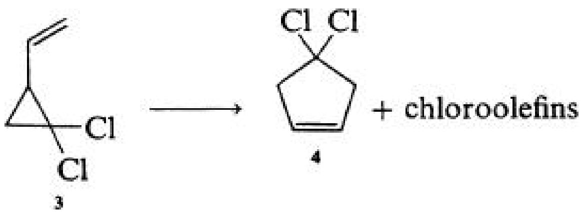
1. Introduction

The vinylcyclopropane-cyclopentene isomerization was discovered in 1959. After the mechanism was studied in detail, this rearrangement was incorporated into many useful synthetic schemes. Various heterocyclic permutations of the vinylcyclopropane system have also been investigated, yielding several synthetic methods based on the rearrangements of cyclopropyl ketones and cyclopropyl imines to dihydrofurans and dihydropyrroles, respectively. (1, 2) This review is concerned only with the rearrangements of vinylcyclopropanes to cyclopentenes (Eq. 1). Excluded are Cope rearrangements of divinylcyclopropanes and rearrangements of cyclopropyl compounds not leading to cyclopentenes. (3)



(1)

The isomerization of 2,2-dichlorovinylcyclopropane **3** was described in 1959. (4) The rearrangement of the parent hydrocarbon was reported independently by two laboratories a year later. (5, 6) Although no prior mention of this rearrangement exists in the literature, it appears likely that it occured unobserved as early as 1922 during the preparation of vinylcyclopropane by



drastic methods. (7) The presence of cyclopentene in the reaction mixtures resulting from the Hofmann elimination of a β -cyclopropylethylammonium salt is a likely possibility, considering the low temperature at which vinylcyclopropane rearranges. The detection and identification of reaction products by refractive indices only may have prevented recognition of the isomerization at that time.

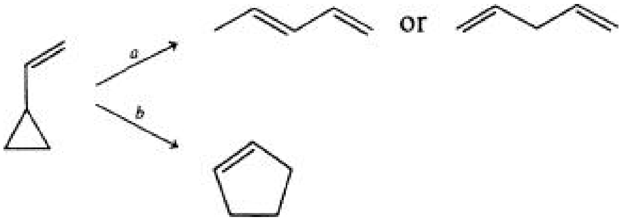
During the decade following the discovery of the rearrangement, virtually every simple vinylcyclopropane was studied in an attempt to settle the question of biradical versus concerted mechanism. The last decade, on the other hand, has witnessed intense activity in the applications of this rearrangement and many of its analogs to organic synthesis. Recent studies have also emphasized transition-metal-catalyzed rearrangements of vinylcyclopropanes.

2. Mechanisms

2.1. Thermal Rearrangements

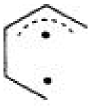
Several reviews offer summaries of mechanistic investigations. (8-12) No apparent settlement has been reached on the question of biradical (13-20) versus concerted (5, 21-24) nature of the rearrangement, although the accumulated experimental data appear to favor the former.

A vinylcyclopropane system may undergo two types of thermal reactions: (a) those involving only the cleavage of the cyclopropane ring and (b) those stemming from both the breaking of the cyclopropane ring and the involvement of the vinyl portion (Eq. 2).



(2)

The ring-opening process *a* is characteristic of the cyclopropane ring and occurs with energies of activation (E_{act}) of 59–66 kcal/mol. (8, 25, 26) The transformation to cyclopentene, on the other hand, takes place with E_{act} of 34–55 kcal/mol, and it was this observation that led to the original postulate of a concerted pathway for the rearrangement. (9) The allowed processes would involve a 1,3-suprafacial shift with inversion or a 1,3-antarafacial shift with retention of configuration at the migrating center. The energy difference between the two paths corresponds closely to the resonance stabilization energy of an allyl radical (12.6 kcal/mol). (18) The lower E_{act} in the isomerization to cyclopentene led to the proposal of a biradical mechanism involving an intermediate of type **5**, which takes full advantage of the resonance radical. Detailed kinetic studies are available in support of the biradical mechanism, (8, 9, 12, 27) but the data seem insufficient to rule out concerted pathways completely. (27)



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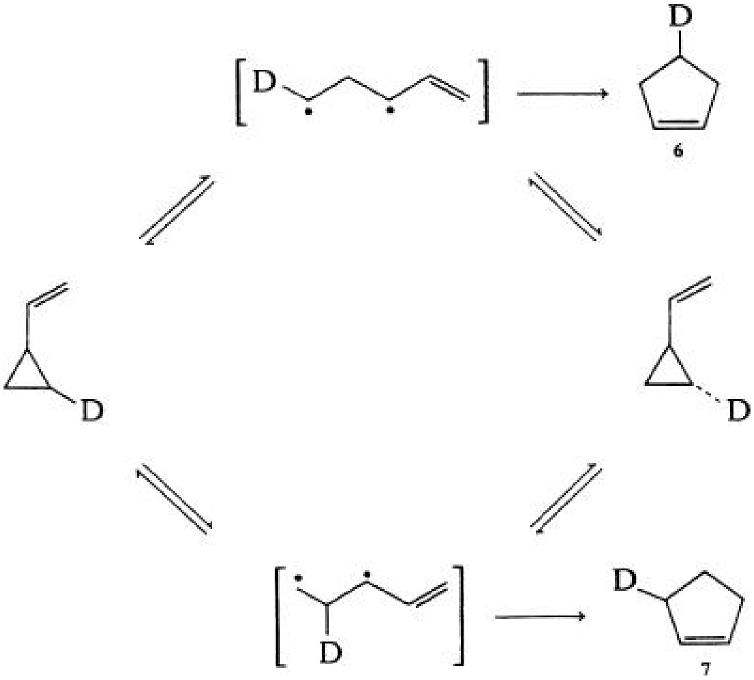
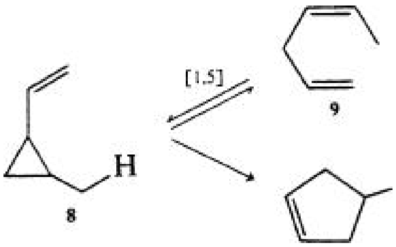
It has been demonstrated that the isomerization of substituents precedes the ring closure to cyclopentene. (28, 29) The ease with which a cyclopropane ring substituent isomerizes during the rearrangement contributes to the difficulties in kinetic studies, where scrambling of labels often takes place.

The simple vinylcyclopropanes are also subject to the regiochemically different modes of ring opening. Although the formation of a more stable radical often simplifies this problem, regioisomers such as **6** and **7** (Eq. 3) should be expected when the difference in stability between two incipient radicals is not pronounced. The presence of acyl groups, heteroatoms, or another olefin in the substrate eliminates this problem by activating only one bond toward cleavage. (30, 31)

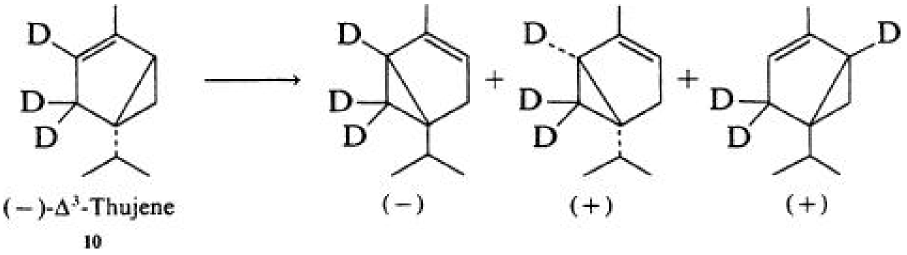


(3)

Alkyl vinylcyclopropanes in which a *cis*-oriented alkyl group contains at least one hydrogen can undergo another competing pathway, namely, the concerted suprafacial 1,5 shift (or retro-ene reaction). (32, 33) The retro-ene mode takes place at considerably lower temperatures (often about 200° lower) than the cyclopentene isomerization and has been shown to be reversible. (33-35) The E_{act} for the simplest reaction (**8** ® **9**) is 31.2 kcal/mol (15, 22, 32) and for most reactions is in the range of 30–35 kcal/mol. (5)



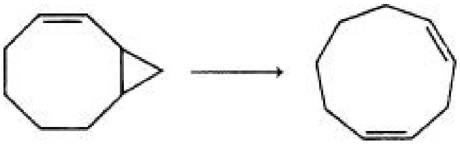
Vinylcyclopropanes contained in a rigid framework of other rings, such as bicyclo[3.1.0]hexenes, have also been investigated. (36, 37) The kinetics of racemization of thujene **10** indicate that the rearrangement is nonconcerted. (38, 39)



However, the endocyclic vinylcyclopropane rearrangement may proceed with enhanced stereoselectivity because of hindered rotation in biradical intermediates. (37) The slightly lower E_{act} (31–42 kcal/mol) in these rearrangements is interpreted in terms of temporary relief of ring strain. (40)

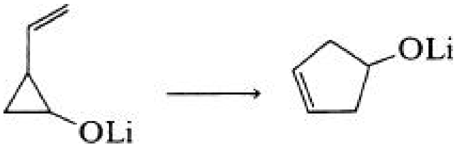
A serious side reaction in structurally suited endocyclic systems is the 1,5 shift leading, sometimes with ring enlargement, to 1,4-dienes (Eqs. 4 and 5). (41, 42)

(4)



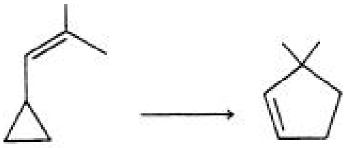
(5)

Studies of substituent effects on the rate of vinylcyclopropane rearrangement indicate that substitution on the vinyl portion of the system has little or no effect on the rearrangement, whereas radical-stabilizing groups (heteroatoms, olefins) on the cyclopropane ring tend to accelerate the reaction. (14, 20, 31, 43-46) A stereospecific vinylcyclopropane rearrangement that takes place at ambient temperature and probably involves anion–radical intermediates is shown in Eq. 6. (47)



(6)

Substitution on the double bond becomes important only in sterically congested systems. Vinylcyclopropanes of the type **11** rearrange to cyclopentenes only under forcing conditions. (14, 23, 43, 48) The rearrangement of the (*E*)



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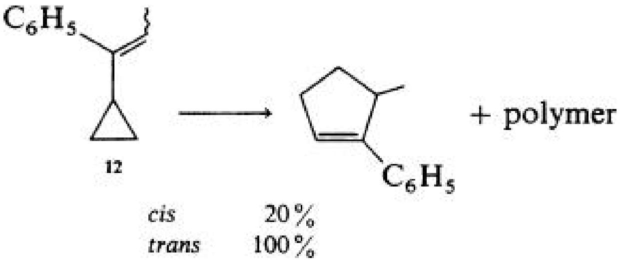
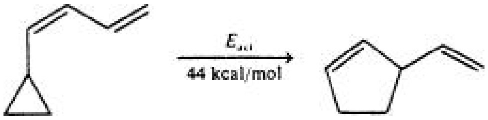
isomer **12** proceeds in only 20% yield, whereas the (*Z*) isomer rearranges smoothly. (43) The E_{act} for such systems is the largest measured for any vinylcyclopropane rearrangement (55 kcal/mol). (23) These findings are attributed



to the difficulties associated with reaching the necessary *cisoid* conformation of the biradical in the transition state. The less congested *transoid* form may predominate in severely hindered systems, leading to dienic products and eventually to polymers, instead of cyclopentenes. (49, 50)

The substitution of an additional olefinic moiety on either the ring or the vinyl group has a pronounced effect on the ease of rearrangement. For example, divinylcyclopropanes that are not capable of Cope rearrangement produce vinylcyclopentenes with substantially lower E_{act} (Eqs. 7, 8). This result can also be rationalized by the additional resonance stabilization of a dienyl radical compared with that of an allyl radical. (51, 52)

(7)



(8)

In summary, vinylcyclopropanes normally follow three avenues on pyrolysis: (a) isomerization to cyclopentenes, (b) diene formation, and (c) the reversible retro-ene reaction. In reactions where all three processes may compete, the 1,5-sigmatropic shift takes place exclusively and at the lowest temperature. At higher temperatures the vinylcyclopropanes are regenerated from 1,4-dienes and undergo fission to biradicals that either cyclize to cyclopentenes or eliminate to dienes. The competition between these two processes is dependent on the conformations that the biradical can assume. The outcome of such competitions may then be predicted by considering the structure of the vinylcyclopropane.

2.2. Photochemical Rearrangements

The formation of cyclopentene was observed in 1962 during the addition of a photochemically generated methylene diradical to butadiene, and for some time this observation led to speculation regarding the possibility of a direct 1,4 addition of a carbene to a diene. (19, 53) Such direct additions are involved only in sterically constricted dienes such as 1,2-dimethylenecycloheptane or norbornadiene. (54, 55)

Both direct and sensitized conditions have been investigated. The direct irradiation in simple $n - \pi^*$ systems produces fewer products and is useful from a preparative standpoint since the sensitized irradiation gives rise to triplet species with E_T = 80 kcal, which is far above the activation barrier for the vinylcyclopropane–cyclopentene isomerization. Consequently, the conversions and yields of those photochemical transformations conducted from the triplet manifold are low at the expense of other products.

It appears that a zwitterionic or biradical mechanism may be favored in systems containing strong chromophores such as acrylates and dienes. This rearrangement can occur from either the singlet or the triplet manifold, producing either biradicals of the type **5** or zwitterions of the type **13**, respectively.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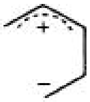
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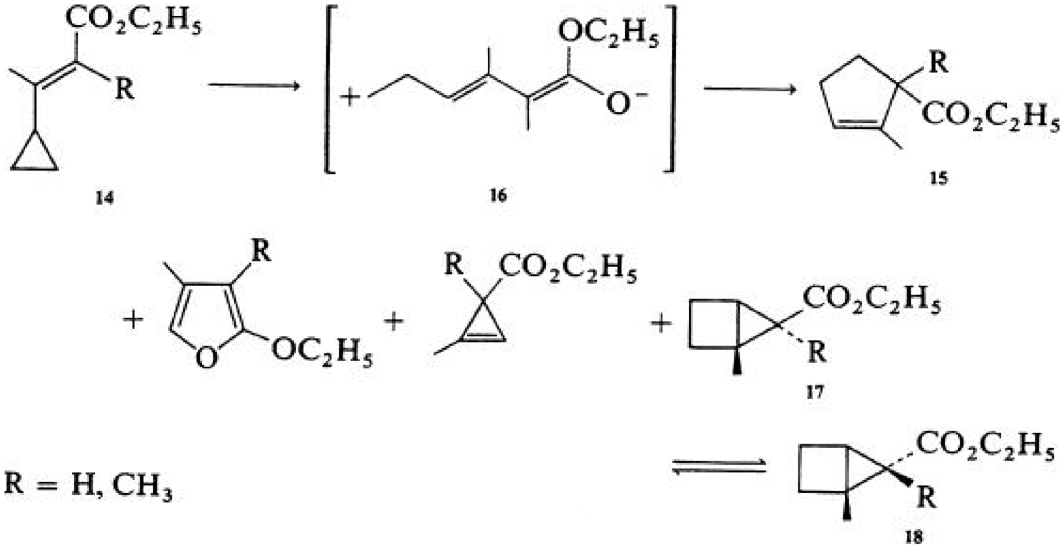
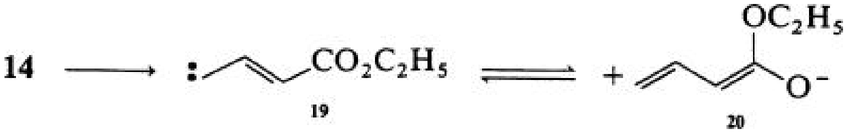
Both species can then undergo closure to cyclopentenes. A singlet-excited vinylcyclopropane may form a bicyclo[2.1.0]pentane that is itself photolabile and can isomerize to a cyclopentene. The rearrangement of simple alkyl vinylcyclopropanes can be rationalized in this way. A concerted 1,3-suprafacial shift can be postulated in some endocyclic vinylcyclopropanes, whereas a biradical (either triplet or singlet) mechanism seems to operate in others. In general, triplet-sensitized irradiation should favor zwitterionic intermediates. Finally, the rearrangement of vinylcyclopropenes to cyclopentadienes can be rationalized in terms of cyclopropenyl biradicals and their closure to the corresponding bicyclo[2.1.0]pentyl biradicals that then isomerize to cyclopentadienes.

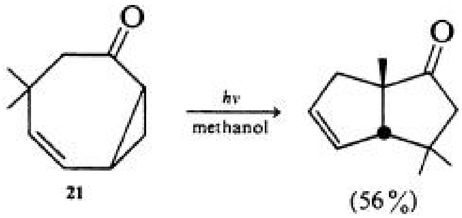
Vinylcyclopropanes of the type **14** rearrange to cyclopentenes **15** under direct irradiation. A zwitterionic mechanism involving the intermediate **16** has been advanced to explain the formation of furanoid products. (56, 57) A mechanism involving a cyclopropylcarbonyl system is postulated for the formation of bicyclo[2.1.0]pentanes **17** and **18**. (57)



An alternative to the proposed set of mechanisms involves, in addition to the zwitterion **16**, the dissociation of **14** to **19** and/or **20** to explain the formation of cyclopropenes and furans. (56)



Endocyclic vinylcyclopropanes have been studied under parallel photochemical and thermal conditions. Direct irradiation or pyrolysis of enones **21** and **22** leads to the corresponding bicyclic ketones, whereas sensitized conditions tend to produce polymers. (58-60)



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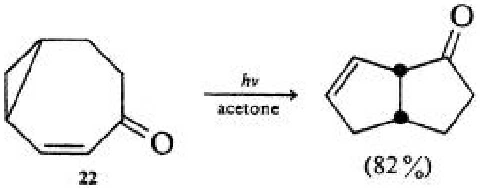

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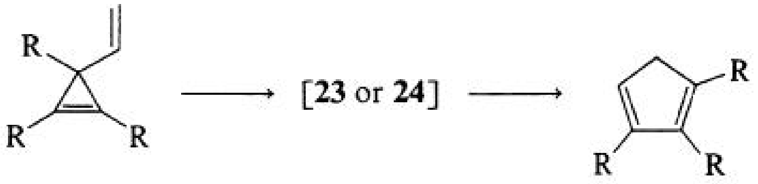
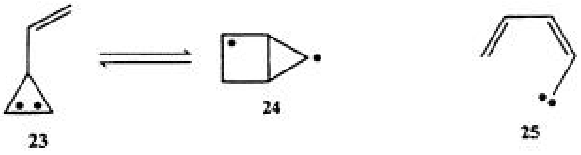
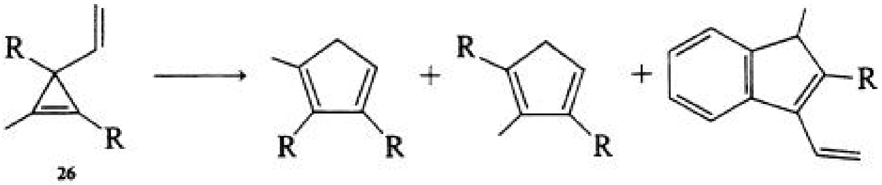
Most recently a new alternative to a photochemical vinylcyclopropane rearrangement has been reported. (61) The irradiation of vinylcyclopropane with a tunable CO_2 laser leads to the production of cyclopentene in up to 32% yield. The remaining portion of the reaction mixture consists of acyclic dienes and/or cyclopentadiene.

The photolytic rearrangements of vinylcyclopropanes give cyclopentadienes. Two different mechanisms are postulated: one involving a biradical **23** or **24** and the other a carbene **25**. (62) A similar mechanistic duality is believed to occur in the rearrangement of cyclopropene **26**. (63)







26

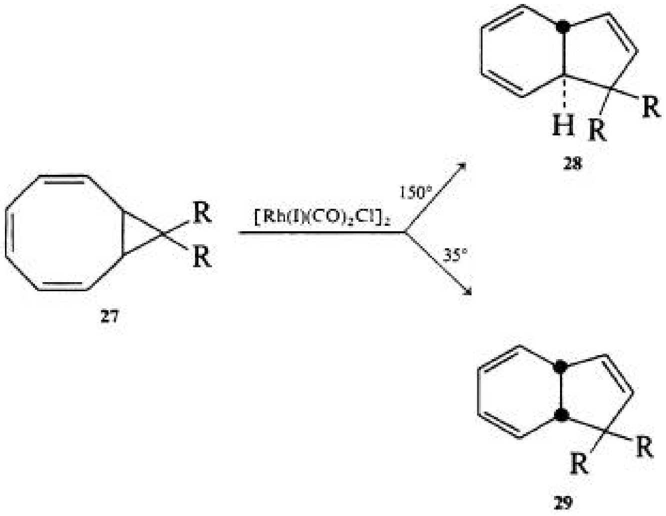
$R = C_6H_5$

In summary, photochemical initiation offers a wider variety of possible mechanisms for the vinylcyclopropane–cyclopentene rearrangement than thermolytic activation because of the higher energy content of the intermediates involved. For this reason, photochemical initiation, although theoretically interesting, is seldom utilized for preparative purposes.

2.3. Transition-Metal-Catalyzed Rearrangements

Vinylcyclopropanes are readily cleaved by a variety of transition-metal compounds. Most such interactions yield products derived from either a ligand insertion process or an elimination to dienes. Reactions of vinylcyclopropanes with metal carbonyls under thermal or photolytic conditions, as well as references to metal-induced rearrangements of simple cyclopropanes, have been reviewed. (64)

The endocyclic vinylcyclopropane **27** gives the *trans*-dihydroindene **28** at 150° in the presence of dicarbonylrhodium(I) dichloride dimer, $[Rh(I)\text{-}(CO)_2Cl]_2$, but only the *cis* isomer **29** when the reaction is carried out at 35°. (65)



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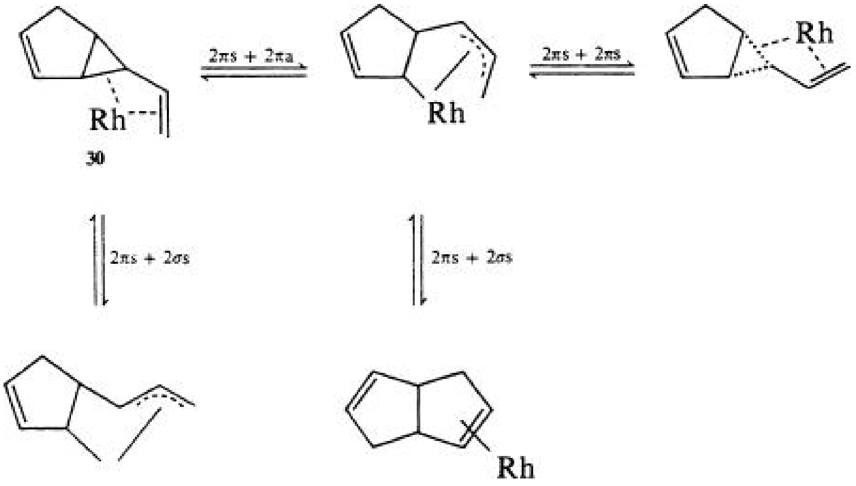
28

29

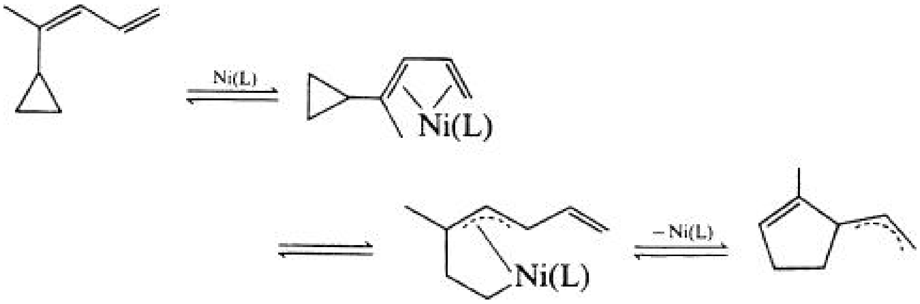
$R = H, CH_3$

Cleavage of vinylcyclopropanes to mixtures of dienes can be effected by Rh(I), Rh(III), or Ni(0). 66–68 The process **27** → **28** can be rationalized without invoking a vinylcyclopropane rearrangement. (66, 67) However, the presence of a metal complex drastically alters the orbital symmetry. Studies of Rh(I)-promoted rearrangements of vinylcyclopropane **30** indicate that a possible [2 π s + 2 σ a] pathway may compete with a metal-assisted biradical cleavage (Eq. 9). (68, 69) It appears superficially that unless an additional olefinic ligand is present these metal-catalyzed rearrangements yield dienes exclusively. (70) A study of Ni(0)-catalyzed rearrangements supports this hypothesis. Since both



(9)

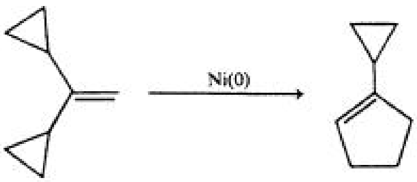
Rh(I) and Ni(0) have two sites of coordinative unsaturation, two potential ligands must be present within the vinylcyclopropane substrate. The mechanism has been postulated as depicted in Eq. 10. (70)



(10)

The Ni(0) process closely resembles the concerted Rh(I)-promoted rearrangement shown in Eq. 9. In both reactions the metal must first coordinate to the diene and thus be in proximity to the cyclopropane in order for the ring cleavage and σ -complexation to occur. The difference between the Rh(I) and Ni(0) reactions lies in the apparent catalytic mode of the latter.

There are very few examples of a simple vinylcyclopropane rearranging to a cyclopentene. Dicyclopropylethylene **31** and cyclopropyl ketones of the type **32** give cyclopentenes on treatment with Ni(0) and Rh(I)(C_2H_4)$_2$(AcAc) [acetylacetonates], respectively. (30, 70) It can be argued that in either **31** or **32**



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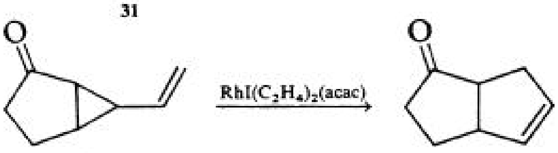

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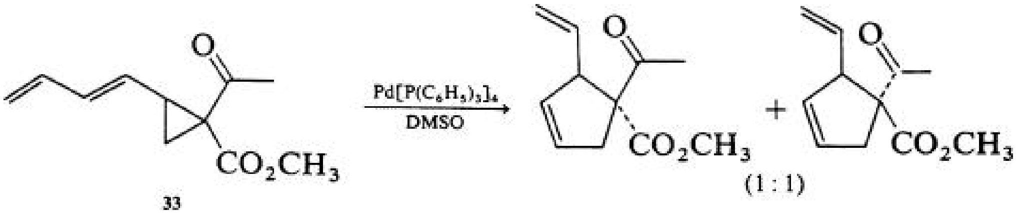
there is the necessary second functionality (other than the cyclopropane to be opened) to serve as a π donor. In the absence of this additional functionality, fragmentation to dienes takes place, indicating the possibility of a concerted process operating in these rearrangements.

A recent report describes a rearrangement of dienylcyclopropyl malonates of type **33** with the use of $Pd[P(C_6H_5)_3]_4$ in dimethyl sulfoxide (DMSO). However, this is not necessarily a true vinylcyclopropane rearrangement (biradical or concerted) but rather a nucleophilic type opening of an activated cyclopropane followed by a reclosure. (71)



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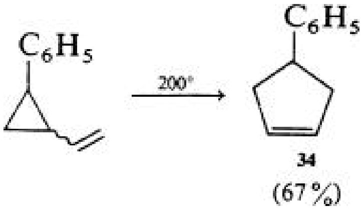
3. Scope and Limitations

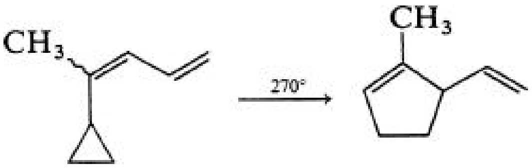
The vinylcyclopropane rearrangement has been used successfully in a number of synthetic schemes, ranging from the preparation of monofunctional cyclopentane compounds to annulation methods and natural product syntheses.

3.1. Simple Cyclopentenes

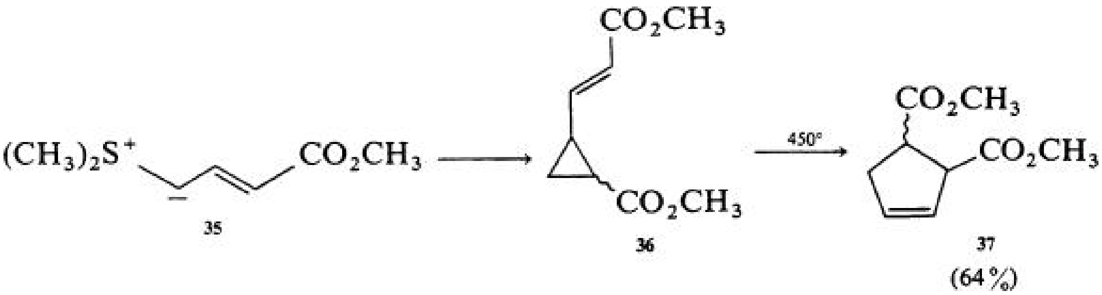
Both *cis*- and *trans*-phenylvinylcyclopropane give 4-phenylcyclopentene **34** in good yields. (72)

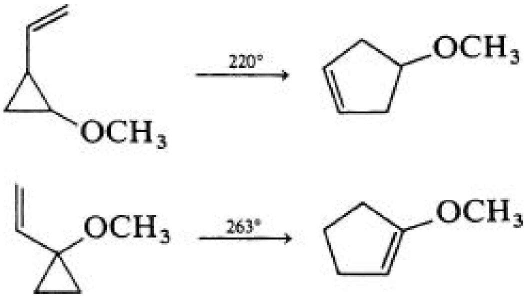


The best method of preparing alkylcyclopentenes relies on this rearrangement. In the preparation of dienes by the dehydration of homoallylic alcohols, cyclopropylbutadienes rearrange smoothly to vinylcyclopentenes at 270° (Eq. 11). (73) Addition of crotonylsulfonium ylide **35** to acrylates produces, under deprotonating conditions, a diastereomeric mixture of vinylcyclopropyl esters **36** that give cyclopentenes **37** (1 : 1 mixture of *cis* and *trans* isomers). (74)



(11)





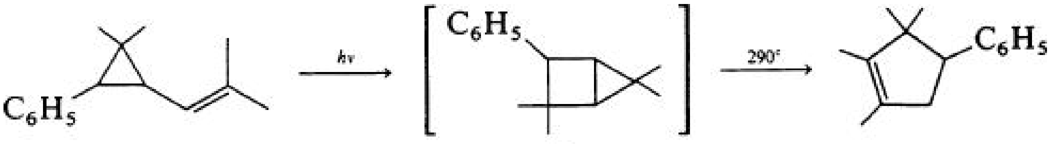
(12)

Heteroatom-substituted vinylcyclopropanes yield cyclopentenes under milder conditions than the corresponding carbocyclic compounds. Both 1-methoxy-2-vinyl- and 1-methoxy-1-vinylcyclopropane give the corresponding methoxycyclopentenes at 220° and 263°, respectively (Eq. 12). (75)

(13)

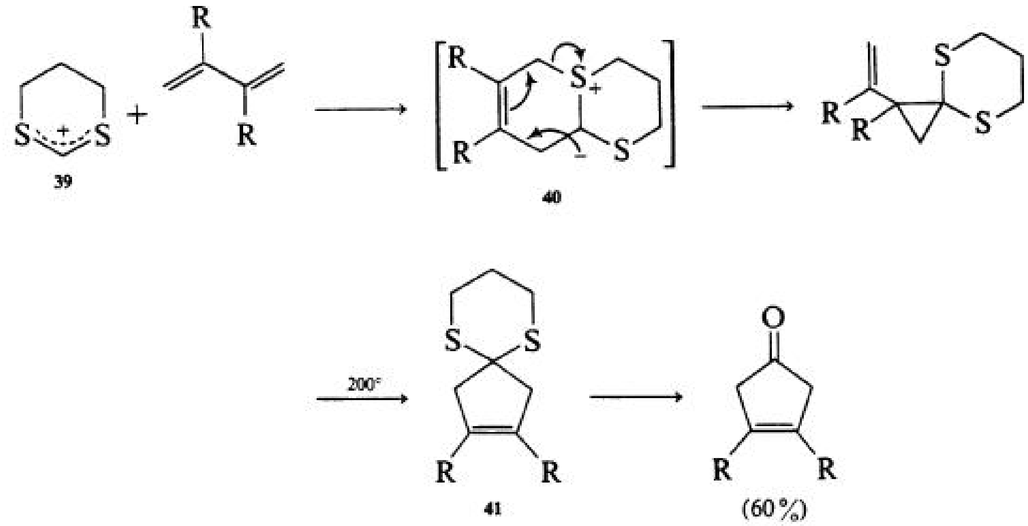
The formation of methylcyclopentene from 2-cyclopropylpropene via an excited singlet state of the vinylcyclopropane (Eq. 13) has been described. (76)

A bicyclo[2.1.0]pentane **38** is proposed as an intermediate in the following transformation. (77)



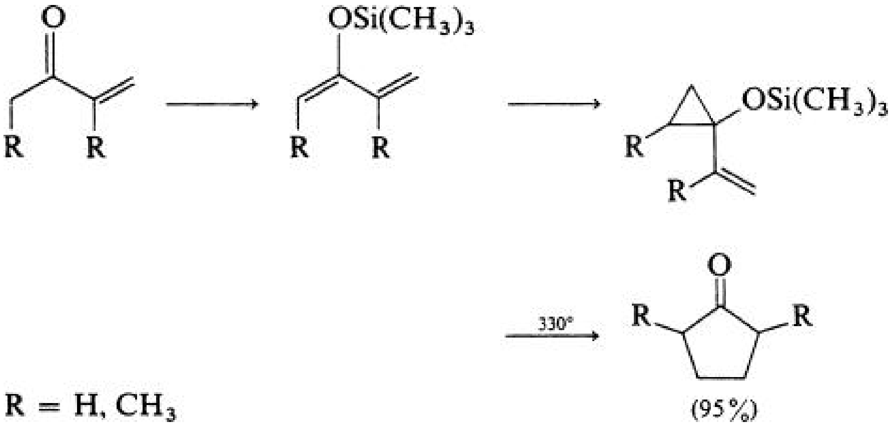
38

A useful synthetic equivalent is represented by the formal addition of carbon monoxide to a 1,3-diene in a four-step sequence involving an initial Diels-Alder reaction of dithianium ion **39** with a diene. The zwitterion **40** obtained on deprotonation with alkyllithium compounds undergoes a smooth sigmatropic rearrangement to a vinylcyclopropane, which gives the protected cyclopentenone **41** at 200°. The overall yields of this four-step scheme, exemplified on three representative dienes, are ~60%. (78)



R = H, CH_3

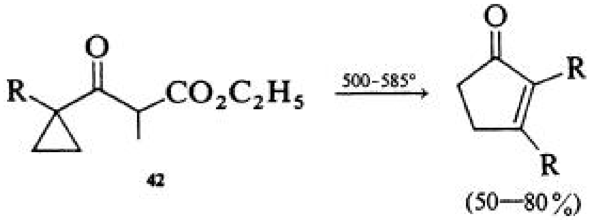
The enhanced regioselectivity in the Simmons-Smith cyclopropanation of trimethylsilyl dienol ethers has led to the synthesis of cyclopentanones from enones (Eq. 14). The yields of the regioselective cyclopropanation are ~50%, whereas 95% yields are obtained in the rearrangement step, which is performed at 330° in a sealed tube. (79)



(14)

R = H, CH_3

β -Cyclopropyl ketoesters of type **42** give cyclopentenones on flash vacuum pyrolysis at 500–585°; however, this transformation has been shown not to proceed by a vinylcyclopropyl rearrangement. (80)

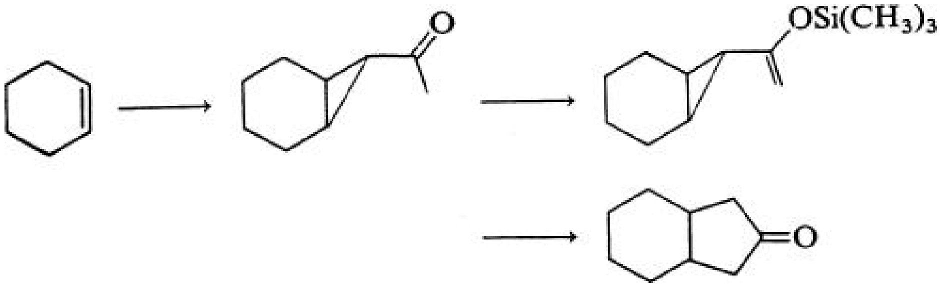


42

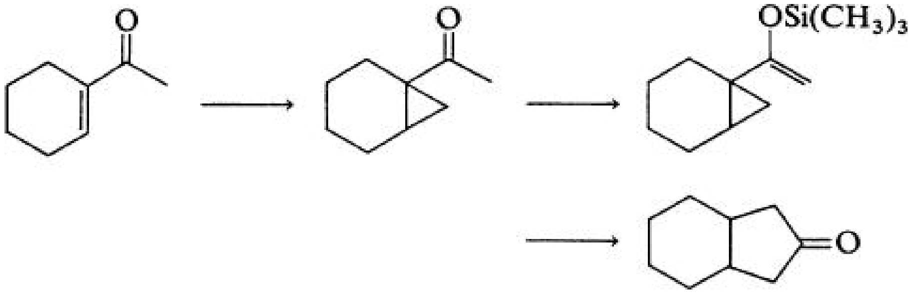
R = H, CH_3

3.2. Annulation Procedures

An elegant method of two regiochemically distinct cyclopentanone annulations combines the ease of rearrangement of heteroatom-substituted vinylcyclopropanes with the cyclopropanation of an olefin, giving the overall transformations in Eqs. 15 and 16.

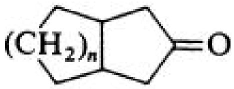


(15)



(16)

The rearrangements of several cyclic systems in the range 360–450° (either sealed tube or vapor-phase pyrolysis) give cyclopentanone annulated ring systems in yields ranging from 20% to 75%. A major side reaction is the 1,5 shift of the alkylvinylcyclopropanes, which leads to ketones such as **45** in yields of up to 80%. (81)



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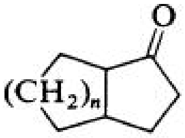

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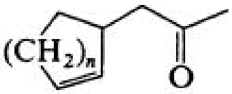
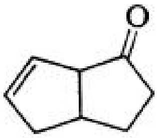


45

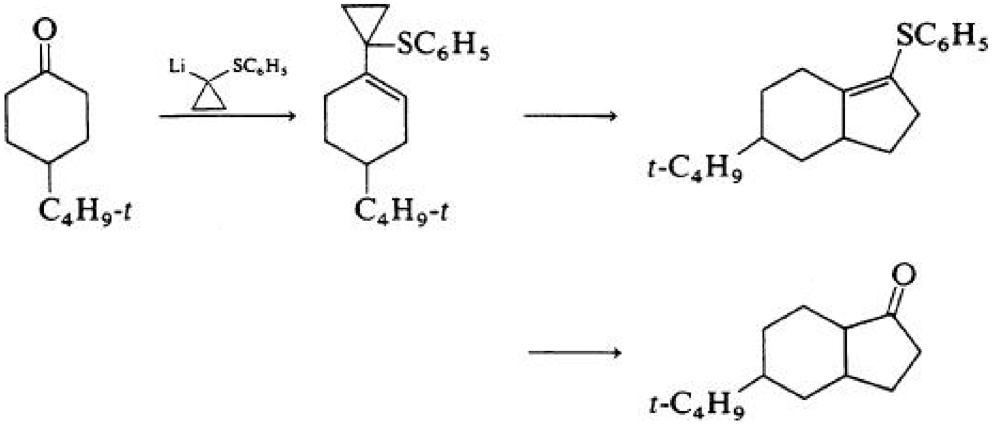
The addition of cyclopropyl organometallics to carbonyl compounds forms the basis of several annulation procedures that provide access to bicyclo[n.3.0] systems from cyclic ketones (Eq. 17). Bicyclo[3.3.0]octenone **46** is obtained by



46

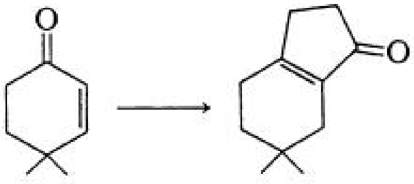
(65%)

the flash vacuum pyrolysis of the corresponding vinylcyclopropane. The latter compound is obtained from the addition of lithiocyclopropyl phenyl sulfide to

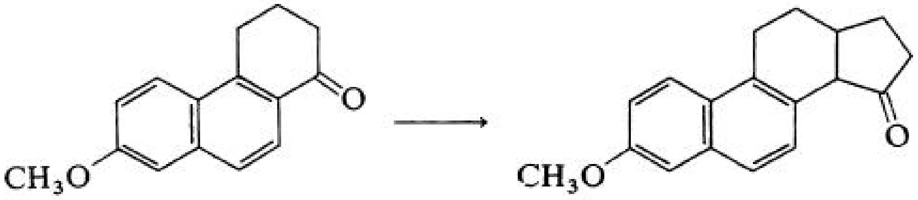


(17)

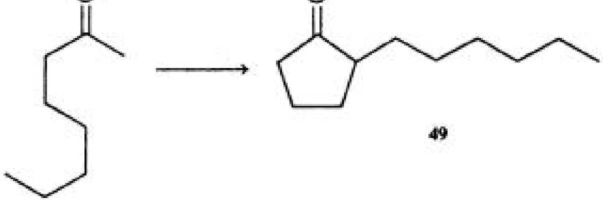
cyclopentenone. (82) An analogous procedure yields the ketones **47** and **48** and the enone **49** from corresponding carbonyl compounds. (83)



47

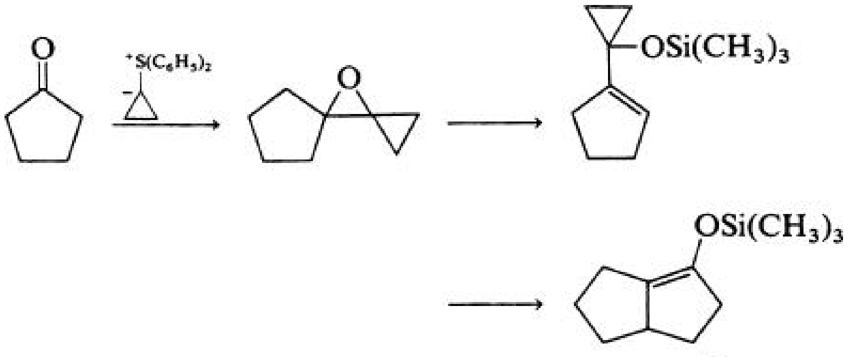


48



49

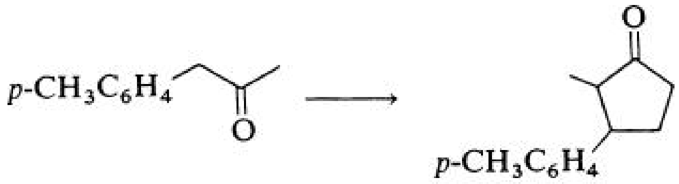
The base-induced opening of epoxides in oxaspiropentanes provides a useful alternative to the use of cyclopropyl organometallics. Equation 18 shows the conversion of a cyclic ketone to a bicyclo[n.3.0]system. The advantage of this



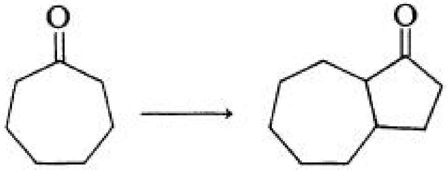
(18)

50

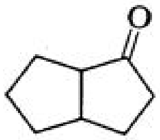
procedure over the aforementioned one lies in the brevity with which the requisite heteroatom-substituted vinylcyclopropane is generated. The use of the diphenylcyclopropylsulfonium ylide bypasses the preparation of an organometallic reagent. The rearrangement is performed by passing a hexane solution of a siloxyvinylcyclopropane under nitrogen through a silylated tube at 330°. Overall yields of 73–85% are obtained in the four-step sequence that generates cyclopentanones **51**, **52**, and **53** by hydrolysis of the silyl enol ethers of the type **50**. (84, 85) One disadvantage of this method stems from the resistance of tertiary



51



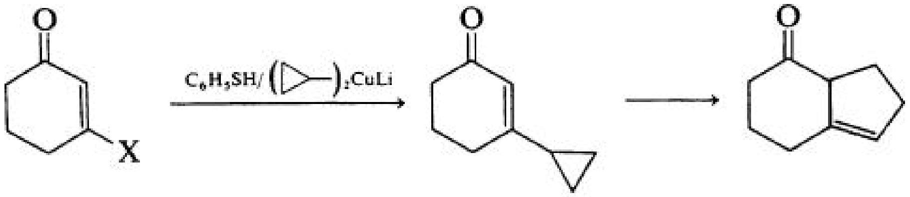
52



53

oxaspiropentanes to ring opening. Thus in accord with base-catalyzed epoxide cleavages, only primary and secondary hydrogens yield to abstraction. A detailed kinetic study of this vinylcyclopropane rearrangement, with the use of a microflow apparatus, confirms the accelerating effect of heteroatoms situated on the cyclopropane. (14, 20, 31, 43, 44, 86)

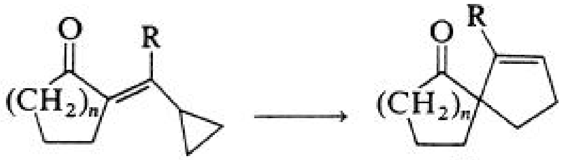
Another annulation procedure that involves the conjugate addition of lithium thiophenyl(cyclopropyl)cuprate to an enone of a suitable oxidation state provides access to annulated and spiroannulated bicyclic ketones (Eq. 19). Enones



(19)

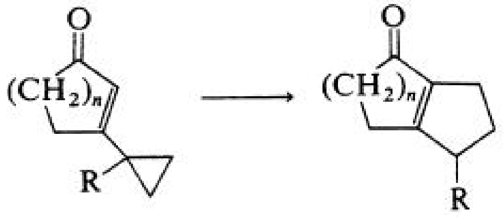
X = Br, I

54 and **55** are obtained in yields of 25–80%; in low-yield reactions dienone byproducts of type **56** are also isolated. (87) Exocyclic enones rearrange to spiroannulated products of type **54** in low yields.



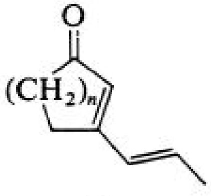
54

$n = 1, 2$
$R = H, CH_3$



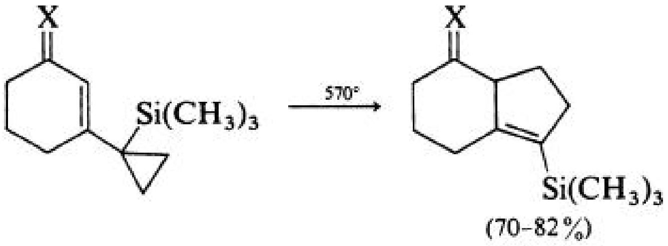
55

$n = 1, 2$
$R = H, CH_3$



56

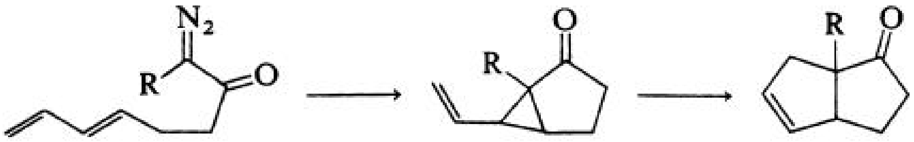
Cyclopropylsilanes are utilized in an extension of silyloxyvinylcyclopropane rearrangements in another annulation procedure (Eq. 20). (88) Although these rearrangements are quite facile, they require much higher temperatures than those involving heteroatom-substituted cyclopropanes.



(20)

$X = H_2, O$

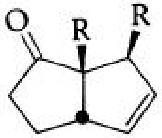
The intramolecular cyclopropanation of 1,3-dienes followed by a vinylcyclopropane rearrangement leads to bicyclic ketones, providing a topological equivalent to a formal 1,4 addition of a carbene to a conjugated diene (Eq. 21).



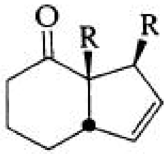
(21)

R = H, CH$_3$

Five- and six-membered ring closures proceed in excellent yields, whereas low yields and irreproducible cyclopropanations plague the higher homologs. (89) Bicyclooctanes **57** and bicyclononanes **58** are obtained by pyrolysis of corresponding vinylcyclopropanes over Vycor glass conditioned with lead carbonate. (30, 89-94)



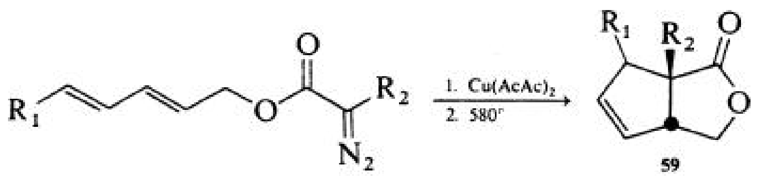
57



58

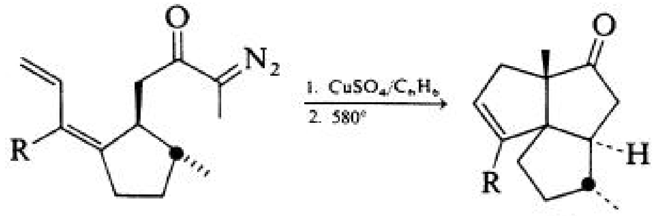
R = H, CH$_3$

The use of diazoethyl ketones provides access to angularly methylated cyclopentanones on rearrangement at 600° or by the action of Rh(C_2H_4)$_2$(AcAc) at 110°. (30) Since the 1,5 shift commonly encountered in thermolyses of *cis*-alkylvinylcyclopropanes is reversible, it is possible to control pyrolyses of such vinylcyclopropanes by selecting 400° for the production of 1,4-dienes or 600° for cyclopentenes. (35) This methodology has been extended to the synthesis of bicyclic lactones **59** and to the preparation of cyclopentene carboxylates of type **60** obtained by the cyclopropanation and rearrangement of exocyclic acrylates. (91, 93)



59

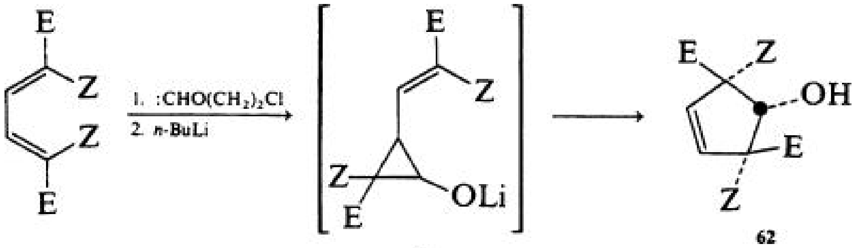
$R_1 = H, CH_3$
$R_2 = H, CH_3, CO_2CH_3$



60

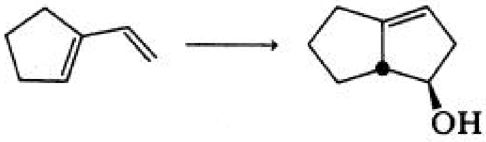
$R = CO_2CH_3, CO_2C_2H_5$

A cyclopentene annulation involving a vinylcyclopropane rearrangement that takes place at ambient temperature involves addition of an alkoxy carbene to a conjugated diene to produce a vinylcyclopropanol that is liberated *in situ* as the alkoxide **61** (Eq. 22).

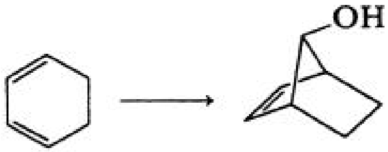


61 62 (22)

The high degree of stereoselectivity with which **61** produces cyclopentenols **62** has led to speculation concerning a concerted rearrangement of **61**. In addition to alkylcyclopentenols, several ring systems can be synthesized in high yields and under mild conditions. Bicyclic alkenols **63** and **64** are prepared from the corresponding dienes and chloromethyl β -chloroethyl ether in a highly stereoselective manner. (47, 95)

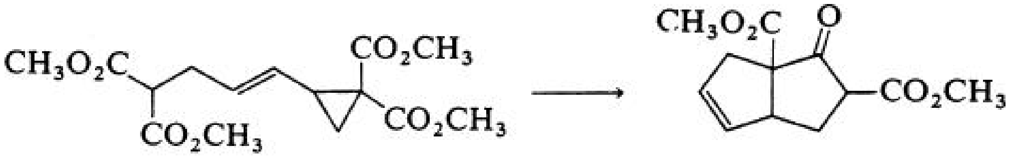


63



64

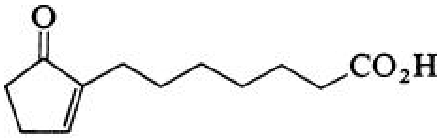
An equivalent of cyclopentene annulation is the transformation of the vinylcyclopropyl malonate **65**. Under deprotonating conditions the activated cyclopropane in **65** “equilibrates” in its position and eventually undergoes a ring opening that generates a cyclopentene ring. The bicyclic ketoester is then formed by Dieckmann condensation. (96)



65

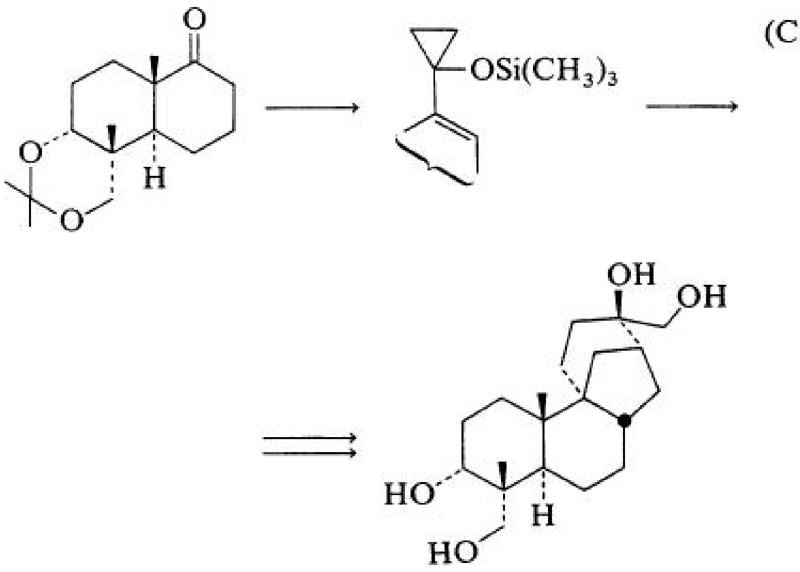
3.3. Natural Product Synthesis

Some of the preceding methodology has been useful in the synthesis of natural products. Prostaglandin precursor **66** is prepared in high yield by the oxaspiropentane annulation procedure followed by the introduction of the enone double bond at C-2/C-3 by oxidation. (97)



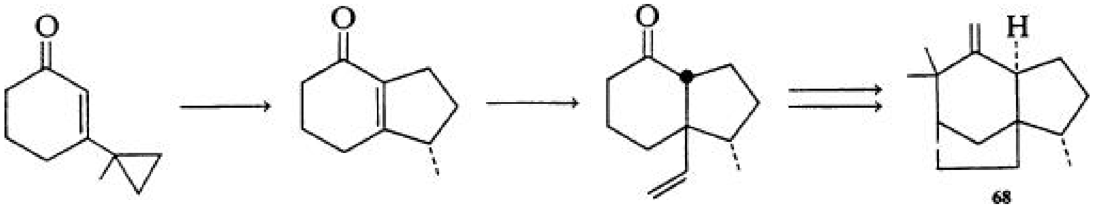
66

The total synthesis of the diterpene aphidicolin **67** (Eq. 23) involves the generation of the cyclopentane ring C by the same method. (98) The cyclopropyl enone rearrangement generates the perhydroindane nucleus of zizane **68** (Eq. 24). (99)



67

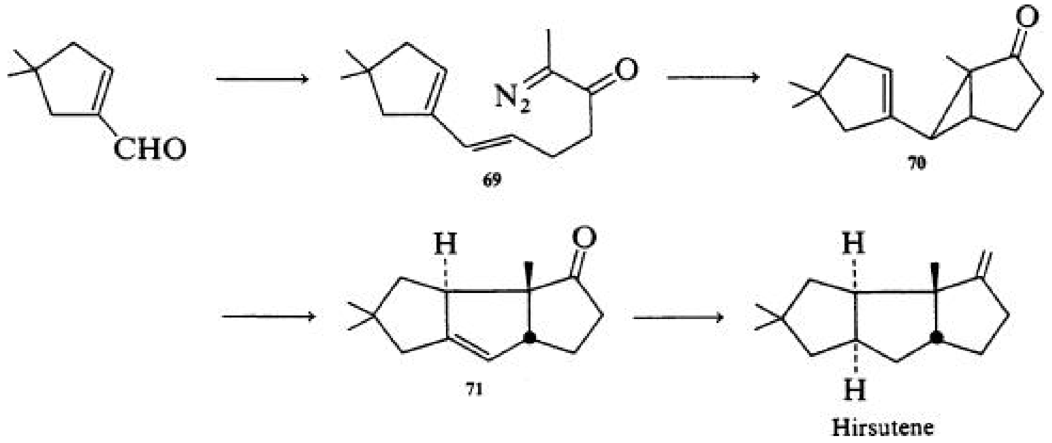
(23)



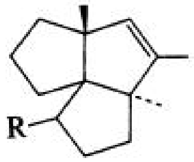
68

(24)

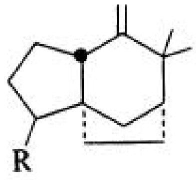
The sesquiterpene hirsutene is attained in a high-yield sequence by the intramolecular cyclopentene annulation of diene **69** followed by either pyrolysis of vinylcyclopropane **70** at 600° or by Rh-catalyzed rearrangement at 110°. The latter process is stereospecific. (30, 100)



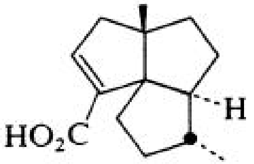
Among other natural products accessible by this type of cyclopentene annulation are triquinanes **72** of the isocomene family of sesquiterpenes, zizanes, and zizanoic acids **73** and the triquinane **74**, a subunit of retigeranic acid. (93, 101)



72



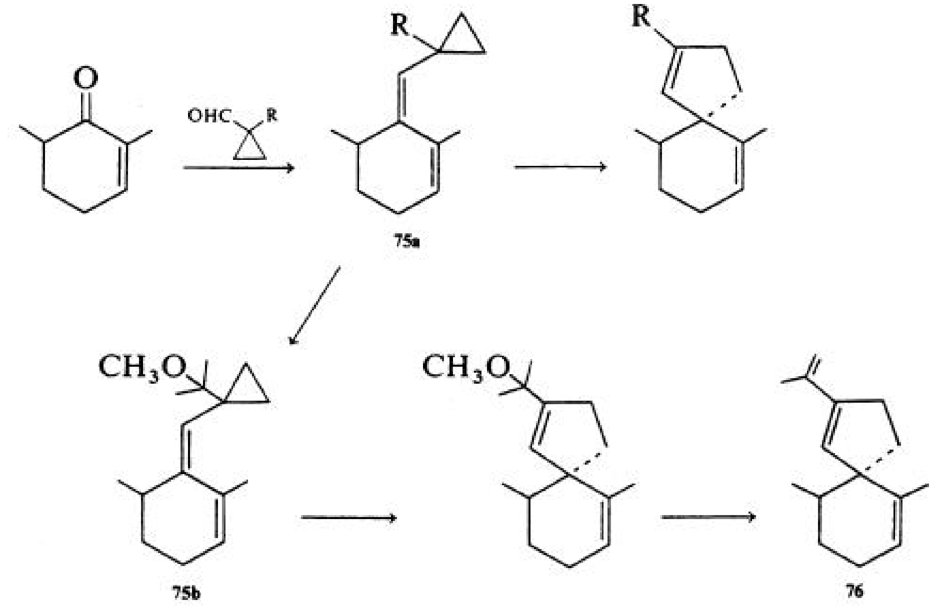
73



74

$R = CH_3, CO_2H$

α -Vetispirene **76** has been synthesized by the scheme shown in Eq. 25. The key step involves the thermolyses of vinylcyclopropanes **75a** and **75b**. (102)



75a

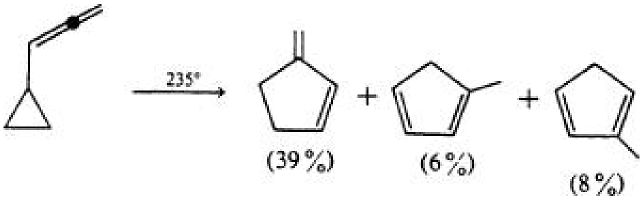
75b

76

R = Si(CH$_3$)$_3$

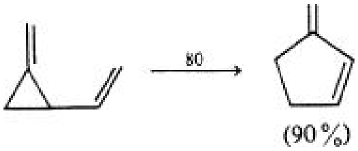
4. Miscellaneous Systems

Vinylcyclopropanes of higher oxidation states undergo the corresponding bond reorganization to appropriate five-membered rings. Thus cyclopropylallene rearranges to a mixture of methylenecyclopentene and cyclopentadienes (Eq. 26). (103, 104)



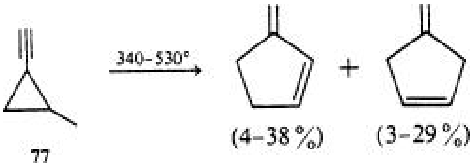
(26)

On the other hand, methylenevinylcyclopropane undergoes rearrangement to methylenecyclopentene at 80° in high yield (Eq. 27). (105)

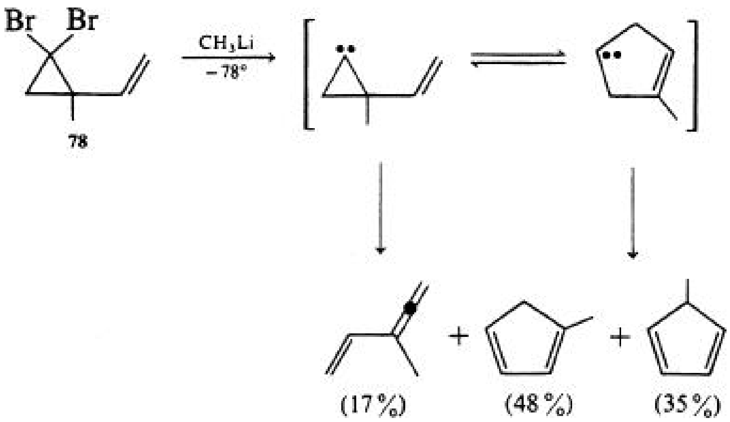


(27)

Cyclopropylacetylenes of type **77** require moderate temperature for rearrangement to methylenecyclopentenes. (106) Vinylcyclopropane carbenes rearrange to

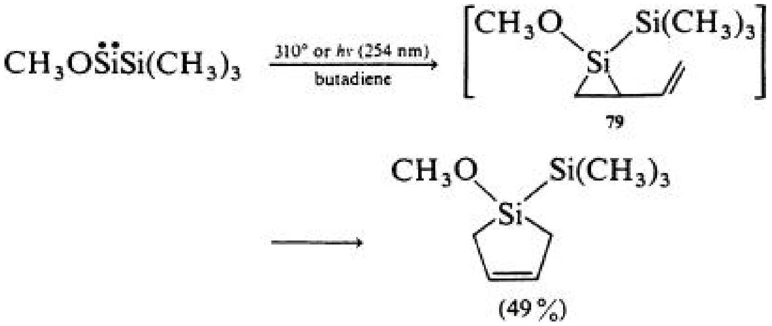


cyclopentene carbenes, which insert into a carbon — hydrogen bond to yield cyclopentadienes (Eq. 28). The intermediate carbenes are commonly generated from geminal cyclopropyl halides of type **78**. (107)



(28)

A divalent silicon equivalent to a carbene adds to conjugated dienes to produce silacyclopentenes directly. Occasionally it may be possible to isolate the corresponding vinylsilacyclopropanes of type **79**. These vinylcyclopropanes can be rearranged to five-membered rings either photochemically or thermally (Eq. 29). (108, 109)



(29)

5. Experimental Procedures

5.1.1.1. 3,4-Dimethylcyclopent-3-enone (78) (Sealed-Tube Thermolysis)

Two milliliters of a 10–20% solution of 2-methyl-2-(2-propenyl)cyclopropanone dithiopropyl ketal in dry benzene was sealed in a heavy-walled Pyrex tube (previously treated with concentrated NH_4OH for 3 days) under vacuum. The sealed tube was heated at 200° in a rapidly stirred silicone oil bath for 5 hours. The tube was cooled to room temperature, chilled in liquid nitrogen, and opened. The crude oil was distilled (in a Kugelrohr apparatus) to give the pure dithiopropyl ketal of the title compound in 95% yield. The thioketal was then hydrolyzed quantitatively to the cyclopentenone in acetone-water (8 : 1) containing excess $HgCl_2$ and $CaCO_3$ for 16 hours at room temperature.

5.1.1.2. 2-Methyl-3-(p-tolyl)cyclopentanone (97) (Flow Pyrolysis)

A solution of 900 mg of crude 1-(*p*-tolyl)-2-(trimethylsilyloxycyclopropyl)propene in 7 mL of hexane was passed dropwise through a Pyrex column heated to 330–350° under nitrogen flow (15 mL/sec) over a 20-minute period. Collection of the effluent in a trap at –78° resulted in 945 mg of crude product, which was treated with 7 mL of THF and 10 drops of 6 *N* HCl for 15 minutes at room temperature. The reaction mixture was diluted with 100 mL of hexane and 75 mL of water. The organic layer was separated and the aqueous layer was extracted three times with 50-mL portions of hexane. The combined hexane extracts were washed once with water, dried, and evaporated to give 785 mg of crude ketone. Purification by preparative thin-layer chromatography (silica/hexane-ether, 8:2) gave 284 mg (66%) of pure product, IR (neat) 1735 cm^{-1}. This yield represents the overall yield from *p*-tolylacetone.

5.1.1.3. 7-Methylbicyclo[4.3.0]non-6-en-2-one (87) (Flow Pyrolysis)

A vertically held Pyrex tube (1.2 × 40 cm), filled with glass helices, was washed successively with saturated aqueous sodium bicarbonate, water, acetone, and *n*-hexane. The tube was heated to 450° and thoroughly purged with a stream of nitrogen. A solution of 3-(1-methylcyclopropyl)-2-cyclohexen-1-one (12.3 g) in 30 mL of *n*-hexane was added dropwise to the column. During the thermolysis a slow stream of nitrogen was passed through the column and the thermolysate was trapped in a flask cooled by a dry ice-acetone bath. Gas-liquid chromatographic analysis of the oil obtained by removal of the solvent from the thermolysate indicated that it consisted of a mixture of the title compound and its β , γ -unsaturated isomer in a ratio of 3 : 7. This mixture was dissolved in 100 mL of methanol containing a small amount of sodium methoxide, and the resultant solution was stirred at 0° for 1 hour. The methanol was removed under reduced pressure and the residue was taken up in ether. The ether solution was washed with brine and dried over anhydrous magnesium sulfate. Removal of ether followed by distillation of the residual material gave 10.7 g (87%) of the title compound, bp 55–58° (0.3 torr); UV λ_{max} (CH_3OH) 247 nm (ε = 12,100); IR (film) 1670, 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (d, 3*H*, *J* = 6.5 Hz), 1.1–1.7 (m, 2*H*), 1.7–3.0 (diffuse m, 9*H*).

5.1.1.4. 2-Trimethylsilylbicyclo[3.3.0]octene (88) (Flash Pyrolysis–Inert Atmosphere)

1(1-Cyclopentenyl)-1-trimethylsilylcyclopropane (314 mg) was vaporized in a stream of nitrogen (6 mL/min) through a 300-cm quartz tube packed with chips of quartz at 570°. The pyrolysate was collected in a trap immersed in a dry-ice– 2-propanol bath giving 280 mg (89%) of the title compound, which was purified by preparative GC (3.65 m × 6.4 mm, 5% SE-30). Mass spectrum, *m/e* calcd.: 180.1334; observed: 180.1338.

*5.1.1.5. Bicyclo[3.3.0]oct-4-en-4-ol (**63**) (95) (Oxyanion-Accelerated Rearrangement)*

To a mixture of 0.157 g of 1-vinyl-2-chloroethoxybicyclo[3.1.0]hexane and 1-(1-cyclopentenyl)-2-(β -chloroethoxy)cyclopropane in 3 mL of dry THF at 0° was added 1.68 mL of 2.5 *M n*-butyllithium solution in hexane. After 10 minutes, 3 mL of hexamethylphosphoramide was added and the resulting solution was heated for 1.5 hours at 50°. The reaction mixture was cooled and worked up with ether and saturated NH_4Cl solution. Distillation gave 0.077 g of pure title compound (73%) as a colorless oil, IR (neat) 3320 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.3 (m, 1*H*), 1.8–2.1 (m, 6*H*), 2.5–2.6 (m, 1*H*), 2.7–2.8 (m, 2*H*), 4.1–4.2 (m, 1*H*), 5.14 (dd, 1*H*, *J* = 2.7, 4.3); ^{13}C NMR ($CDCl_3$) δ 24.7, 28.3, 29.4, 45.8, 58.3, 81.2, 115.3, 152.1; mass spectrum (70 eV), *m/e* 122 (M^+); calcd. for $C_8H_{12}O$: 124.0888, found: 124.0888.

*5.1.1.6. [(4,4a,4b,5,6,6a,7,8,9b,10,11,11a - Dodecahydro - 2,2,4a,9b - tetramethylcyclopenta[5,6]naphtho[2,1-D] - 1,3 - dioxin - 9 - yl)oxy]trimethylsilane (4a α ,4b β ,6a β,9b α ,11a α) (**67**) (98) (Flash Vacuum Pyrolysis)*

The trimethylsilyloxyvinylcyclopropane precursor of the title compound (1.1 g) was distilled at 0.5 torr through a hot tube heated to 610°. The distillate was collected in a trap cooled to –78°, transferred to a flask, and evaporated to give 1.06 g (96%) of crude condensate. Neutral alumina chromatography (activity grade III) with hexane as solvent gave the pure title compound as a mixture of C-8 isomers (8 α /8 β ,2:1), ^1H NMR ($CDCl_3$) δ 0.13 (s, 9*H*), 0.6 and 0.65 (s each, 3*H*), 1.00 and 1.06 (s each, 3*H*), 1.28 (s, 6*H*), 3.04 and 3.45 (ABq, 2*H*, *J* = 12 Hz), 3.5 (d, 1*H*, *J* = 3 Hz).

*5.1.1.7. 1,9,9-Trimethyl-6,7-dehydro-cis, anti, cis-tricyclo[6.3.0.0^{2,6}]undecan-2-one and its cis, syn, cis Epimer (**71**) (30, 100) (Flash Vacuum Pyrolysis)*

A sample of vinylcyclopropane (**70**) (204 mg, 1 mmol) was evaporated at 580° through a Vycor tube that had been previously washed with a slurry of lead carbonate in water and dried. The crude condensate (200 mg, 98%) was chromatographed to obtain 134 mg (65.5%) of the title compound, 24 mg (11.2%) of its epimer, and 30 mg of a bicyclic enone byproduct that was not further identified. IR (neat) 1740, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 3*H*), 1.05 (s, 3*H*), 1.07 (s, 3*H*), 1.2–2.8 (m, 8*H*), 3.0–3.2 (m, 2*H*), 5.2 (m, 1*H*); ^{13}C NMR ($CDCl_3$) δ 17.7 (q), 26.3 (t), 30.5 (q), 31.0 (q), 38.9 (t), 39.9 (t), 40.2 (t), 42.3 (s), 55.9 (d), 56.8 (s), 59.8 (d), 120.9 (d), 151.3 (s), 223.9 (s); mass spectrum (70 eV), *m/e* (relative intensity) 204 (M^+, 25), 189 (10), 176 (b, 100), 161 (35), 105 (32), 91 (60), 77 (30); calcd. for $C_{14}H_{20}O$: *m/e* 204.1514; found: *m/e* 204.1517.

*5.1.1.8. Rhodium-Promoted Rearrangement of **70** (30) (Transition-Metal-Promoted Rearrangement)*

A mixture of 20 mg of vinylcyclopropane **70** and 40 mg of $(C_2H_4)_2$ Rh(acac) (0.1 mmol) in 20 mL of benzene (degassed with argon prior to use) was refluxed under argon for 48 hours. The product was isolated by washing the mixture with 20% potassium cyanide solution followed by removal of solvents. The reaction times were considerably shortened by performing the reaction in a sealed tube. In this way the title compound was obtained as one diastereomer (*cis, anti, cis*) in ~80% yield.

5.1.1.9. (4 β ,8 α) - 1 α - Methyl - 5 β - methyl - 9 - (carboethoxy)tricyclo[6.3.0.0^{4,8}]undec-9-en-2-one (93) (Flash Vacuum Pyrolysis)

The precursory vinylcyclopropane (2.47 g, 9 mmol) was vaporized [120° (0.1 torr)] through a horizontally situated hot tube (Vycor or Pyrex, 580–600°) and condensed in a liquid-nitrogen-cooled trap. The glass tubes were conditioned prior to use with a slurry of lead carbonate in water and dried *in vacuo* at ~300°. The total distillation time was approximately 10 minutes.

The crude condensate was chromatographed on silica gel (3:1 hexanediethyl ether) to give 1.6 g (60%) of the title compound as one diastereomer, IR (neat) 1710, 1735, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (d, 3*H*, *J* = 7 Hz), 1.05 (s, 3*H*), 1.2 (t, 3*H*, *J* = 7 Hz), 1.4–2.8 (m, 10*H*), 4.1 (q, 2*H*, *J* = 7 Hz), 6.6 (t, 1*H*, *J* = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 18.4 (q), 21.2 (q), 30.7 (t), 34.6 (t), 40.0 (t), 42.3 (d), 44.8 (t), 57.3 (s), 60.0 (t), 66.7 (s), 141.0 (s), 161.4 (d), 164.2 (s), 224.6 (s); mass spectrum (70 eV), *m/e* (relative intensity) 262 (M, 15), 244 (10), 216 (30), 188 (30), 166 (35), 146 (40), 118 (52), 104 (65), 91 (B), 76 (74), 54 (85). Calcd for $C_{16}H_{22}O_3$: 262.1569; found: 262.1572.

5.1.1.10. 1,4,4-Trimethylbicyclo[3.3.0]oct-6-en-2-one (59) (Photolysis)

A solution of 2 g of 1,4,4-trimethylbicyclo[5.1.0]oct-5-en-2-one in 450 mL of reagent-grade acetone was irradiated with a 450-W Hanovia mercury vapor lamp in a quartz immersion well fitted with a Corex filter. The progress of the reaction was followed by withdrawal of aliquots at intervals and by analysis of these by GC. After 5 hours the solvent was evaporated and the nonpolymeric residue (1.9 g) was purified by preparative GC. The title compound was isolated in 10% yield as a colorless oil: IR (neat) 1745, 1680 cm^{-1}; semicarbazone, mp 202 204°.

5.1.1.11. 1,1-Dicarbomethoxy-2-vinylcyclopent-3-ene (71) (Transition-Metal-Promoted Rearrangement)

A solution of 0.24 g of 1-(2,2-dicarbomethoxycyclopropyl)butadiene in 3 mL of dimethyl sulfoxide containing 30 mg of $Pd[P(C_6H_5)_3]_4$ was heated at 50° under an argon atmosphere for 15 minutes. The resulting yellow solution was diluted with 5 mL of ether and washed with brine. The aqueous layer was extracted twice with 5 mL of ether, and the organic layers were combined, dried, and evaporated to yield a residue that was chromatographed (silica, hexane/ethyl acetate, 10:1) to give 0.21 g of pure title compound (87%) as an oil.

6. Tabular Survey

The following four tables contain reported examples of reactions discussed in this chapter. Tables I, II, and III list examples of the rearrangements of vinylcyclopropanes in thermal, photochemical, and transition-metal-catalyzed modes, respectively. Table IV contains examples of rearrangements of vinylcyclopropanes that have a carbon or silicon skeleton but a higher degree of unsaturation than vinylcyclopropane (vinylcyclopropylallene, etc.). Vinylcyclopropene rearrangements, although discussed from the mechanistic point of view, are excluded from the tabular survey. Most of the reported examples represent very few structural types; nevertheless, there are hundreds of examples that differ only in substituents. In addition to previously mentioned references (Refs, 62 and 63), a number of leading references in this field are supplied at the end of the chapter (Refs. 223-228).

The examples are arranged in the tables according to increasing carbon number. Structures appearing in brackets represent intermediates that were not isolated. Reaction conditions and yields have been summarized wherever possible, as have product ratios; a dash indicates that no yield was given in the reference. Numbers in parentheses represent yields, whereas numbers without parentheses indicate ratios of products. When more than one reference appears for a particular structure, the first reference gives (in the author's opinion) the most complete experimental description. The literature has been reviewed through March 1983.

The following abbreviations are used in the tables:

acac	acetylacetonate
COD	1,5-cyclooctadiene
DMSO	dimethyl sulfoxide
Et_2O	diethyl ether
HMPA	hexamethylphosphoramide
tetralin	tetrahydronaphthalene
THF	tetrahydrofuran

Table I. Thermal Rearrangements of Vinylcyclopropanes

View PDF

Table II. Photochemical Rearrangements of Vinylcyclopropanes

View PDF

Table III. Transition-Metal-Catalyzed Rearrangements of Vinylcyclopropanes

View PDF

Table IV. Miscellaneous Rearrangements

View PDF

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES

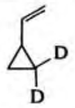
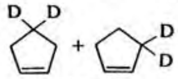
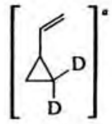
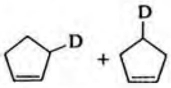
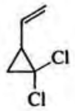
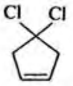
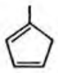
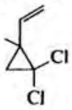
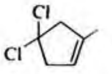
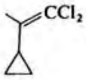
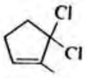
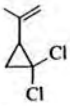
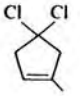
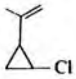
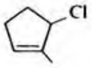
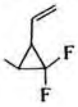
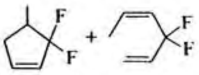
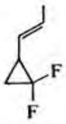
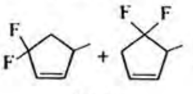
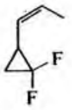
	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_5	Bicyclo[2.1.0]pent-2-ene	25°, 2 hr quartz vessel	Cyclopentadiene (−)	110,111
		Gas phase, 186°	 (--) 44 : 56	112
	 [a]	186°	" (−)	112
		Sealed tube, 360°, 10 min	 (6)	28,113
		400–500[c]	 (10) +  (30)	4
		Vycor, glass wool, N_2 flow, 500°	" (−)	4
		Glass wool, 200–275°	" (90)	4,11,14
		N_2 flow, 275–300°	" (88–93)	20
	1,1-Difluoro-2-vinylcyclopropane	Sealed tube, 258°, 45 min	1,1-Difluoro-3-cyclopentene 4, 1,1-difluoro-2-cyclopentene 96 (85)	45,114
	1-Vinylcyclopropane	Sealed tube, 339–391°	Cyclopentene 99, *cis* and *trans* 1,3-pentadiene, 2-methyl-1,3-butadiene, 1,4-pentadiene 1 (−)	5,19
		400–470°	Cyclopentene + cyclopentadiene (−)	115
		Glass chips, N_2 flow, 500–520°	Cyclopentene 95, 1,4-pentadiene 5 (−)	6
		Sealed tube, 325–390°	Cyclopentene 96, 1,4-pentadiene 1.6, *cis*-1,3-pentadiene 1.1, *trans*-1,3-pentadiene 1.2 (−)	21,116
		Gas phase, 435–507°	Cyclopentene (−)	117
	[2-Acetoxy-1-cyclopropylethane]	N_2 flow	Cyclopentene (69)	6
	Octafluorovinylcyclopropane	131–183°, Monel cylinder	Octafluorocyclopentene (--)	118
	 [a]	135°	Vinylcyclopropane 99, cyclopentene 1 (−)	112
C_6		Gas phase, five passes, N_2 flow, 250°	 (84)	14,86
		400°	 (--)	14
		300°	 (−)	14,86
		400°	 (--)	14
	 *trans*-	275°, 5 min, gas phase	 66 : 34	45,119
	cis-	150°, 20 min	" (100)	45,119
		275°, 1 hr	 (−) 97 : 3	45
		293°, 3.75 hr	" 49 : 12 " (--) *cis*-5,5-difluoro-1,3-hexadiene 24, *cis*-piperylene 15	45

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

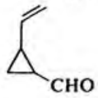
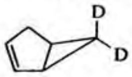
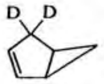
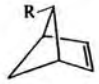
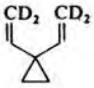
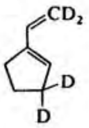
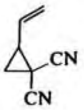
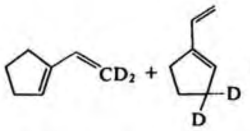
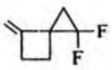
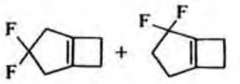
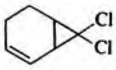
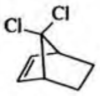
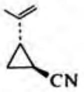
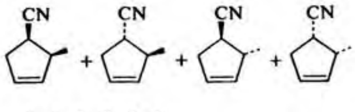
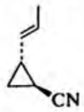
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
2-Cyclopropylpropene	332–386°	1-Methylcyclopentene (63)	16
1-Methyl-1-vinylcyclopropane	313–357°	" (—)	17
cis-1-Methyl-2-vinylcyclopropane	296–328°	1-Methylcyclopent-3-ene, (7) *cis*-1,4-hexadiene (84)	15
	166–220°, Pyrex vessel	*cis*-1,4-Hexadiene (—)	34,15
trans-1-Methyl-2-vinylcyclopropane	296–328°	1-Methylcyclopent-3-ene, (7) *cis*-1,4-hexadiene (84)	34,15
1-Methoxy-1-vinylcyclopropane	263–287°, gas phase	1-Methoxycyclopentene (—)	14,75
1-Methoxy-2-vinycyclopropane (*cis*- and *trans*-)	220–250°	4-Methoxycyclopentene (—)	75
1-Cyclopropyl-1-methoxyethylene	Pyrex, glass wool, N_2 flow, 535°	1-Methoxycyclopentene (30)	80,120
 (*cis* and *trans*)	400°, gas phase	Cyclopent-3-ene carboxaldehyde (—)	121
	255°	 (—)	122
 R = H, NO, N_2, N_3, NH_2HCl	150–200°	 (—)	44
	148–190°	 (100)	123
C_7 	242°	 (—)	52
	Sealed tube, toluene, 170°, 12 hr	 (17)	124
	242°	 (—)	52
	Pyrex, gas phase, 231°	 (90)	114
	275°, 18 passes	 (—)	14
	Sealed tube, 217°, 7.25 hr	 (3) + epimerized starting material *cis/trans*: 53/43	125
	Sealed tube, 217°, 10.5 hr	" (2.5) " 19/78	125,126
	Sealed tube, 218°		126
	387°, flow system	" " " " (—)	126
"	Gas phase, 218°	" (—)	126

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

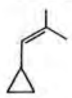
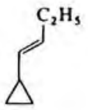
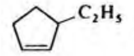
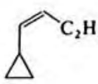
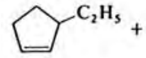
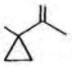
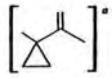
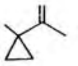
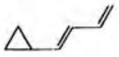
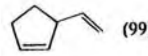
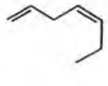
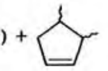
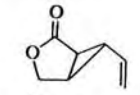
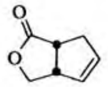
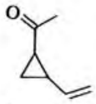
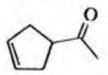
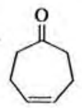
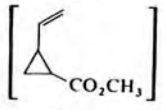
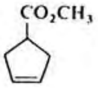
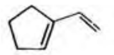
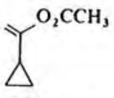
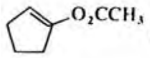
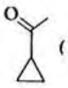
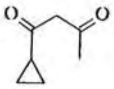
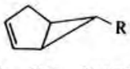
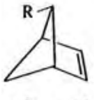
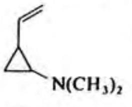
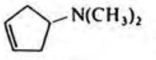
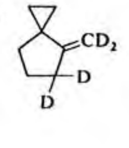
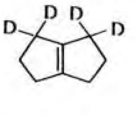
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	370°, 2 hr	 (−)	23,116
	332–374°	 (−)	23,116,127,128
	380–390°	" (−)	127,128
	380–390°	 + (mostly polymer)	127,128
	325–368°, aged vessel	 (−)	10,17,116
	145°	" 3 +  97 (−)	112
	Gas phase, 271–316°	 (99)	51,122
 (1*S*,2*S*)–	Sealed tube, 296°, 1–2 hr	 65 +  8 +  22 +  5 (−)	129.130
	Gas phase, 300°	 (major) +  (−)	131
	Gas phase, 300°	" " (−)	131
	580°, Vycor tube conditioned with $PbCO_3$, 10 min	 (55)	92
	300–380°, 3–10 min	 (30–75) +  (50–25)	132
	Distillation, 90°	 (4)	133
	Sealed tube, 233–257°	 (100)	52
	415°	 (4) +  (12) +  (70)	120
 R = CH_3, $NHCONH_2$, OCH_3	150–200°	 (−)	44
 (*cis*- and *trans*-)	Gas phase, 178–203°	 (24) + *cis/trans* starting material (54)	134,31
C_8 	350°	 (−)	130

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

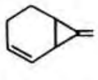
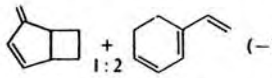
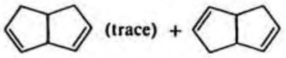
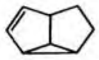
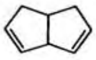
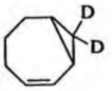
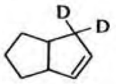
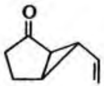
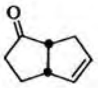
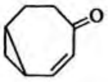
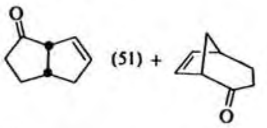
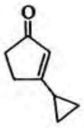
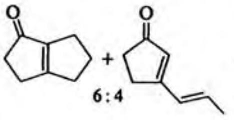
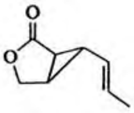
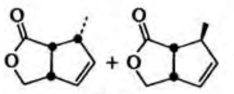
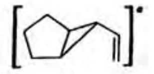
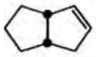
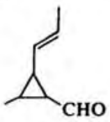
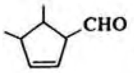
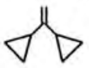
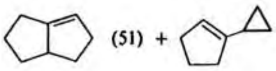
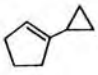
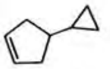
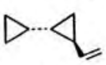
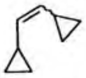
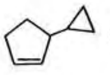
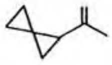
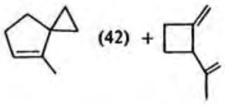
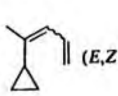
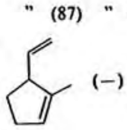
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	N$_2$ flow, 110°	 + 1:2 (−)	8,135,136
	305°, 24 hr	 (trace) + (85)	50,122
	140–178°	 (−)	123
	325°	 (50)	137
	Vycor, conditioned with PbCO$_3$, 580°	 (65)	30,89,94
	Hexane solution, N$_2$ flow, 600°	 (51) + (24)	60
	Glass helices, 450°	 + 6:4 (80)	87a,87
	Vycor, PbCO$_3$ conditioned, 620°, 10 min	 + 72:28 (42)	92
	300°	 (5)	138
	313–357°	 (−)	139
	Vycor, 400°	 (51) + (40)	20,43,140,141
	342–389^b	" (53)	141
	Vycor, 480°	" (100)	141
	300°	 (−)	122
	300°	" (−)	122
	300°	 (−)	122
	Sealed tube, 245°, 70 min	 (42) + (2)	142,143
	285°, 2.5 hr	" (87) " (5)	173,204
 (*E,Z*)	270°	 (−)	73

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

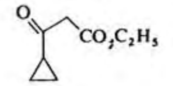
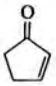
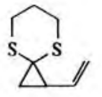
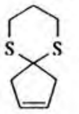
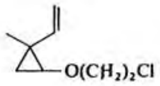
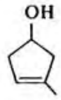
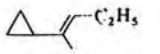
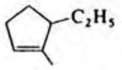
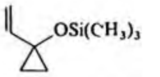
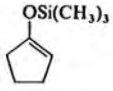
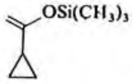
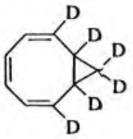
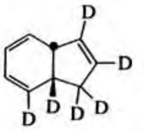
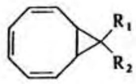
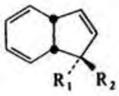
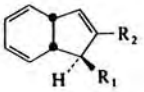
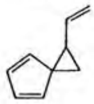
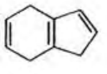
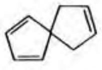
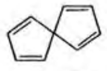
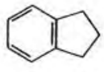
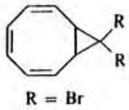
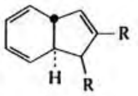
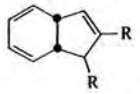
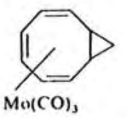
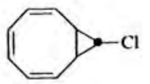
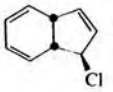
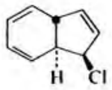
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Vycor, glass wool, 565°	 (51) +  (7)	80,120
	540°	" (47) + " (2)	80,120
	Sealed tube, C_6H_6, 200°, 16 hr	 (97)	78
	n-C_4H_9Li (5 eq), Et_2O/hexane, 25°	 (69)	47
	390°	 (—)	127
	Sealed tube, 350°, 1 hr	 (95) (as ketone)	79
	Gas phase, 330°, 0.5 hr	" (—)	79
	Base-washed ampoule, 360°, 2 hr	" (73)	81
	Conditioned quartz reactor, 350°, 2 hr	" (—)	144
	Glass helices, 520°	" (—)	86
C_9 	Base-washed sealed tube, 120°	 (—)	145
 $R_1 = R_2 = D$	(—)	 + 	146
$R_1 = D, R_2 = Cl$	--	" (—) " (—)	147
$R_1 = Cl, R_2 = D$	—		147
	140–150°	 (90) +  (8)	148
	260–320°, flow system	" (50)	149
	350°	 +  + 	150
 R = Br Cl	80–90°	  (100) (100)	151,1 1
	90	(80)	151-153,146,121
	Sealed tube, 90°, 24 hr		154
	125°	 (–)	146
	90°	 (9) +  (1)	153
	75°, CCl_4		147
	70°, 3 hr		150,154,147

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

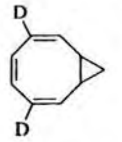
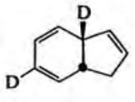
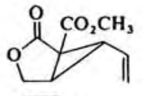
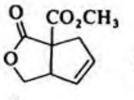
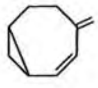
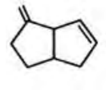
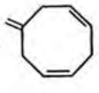
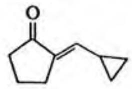
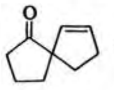
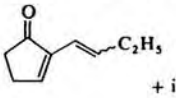
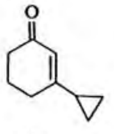
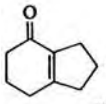
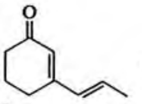
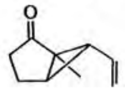
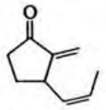
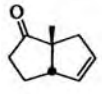
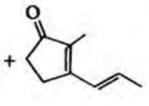
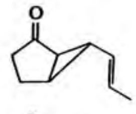
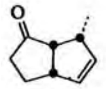
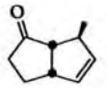
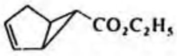
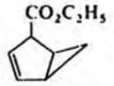
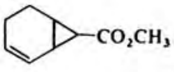
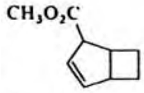
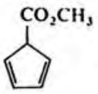
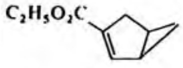
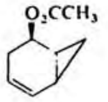
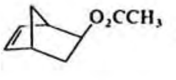
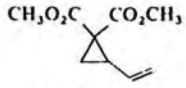
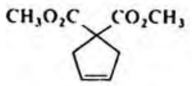
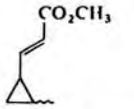
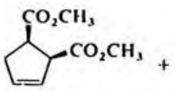
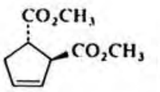
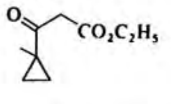
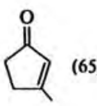
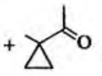
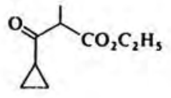
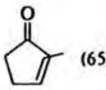
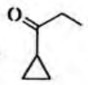
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Base-washed sealed tube, 120°	 (–)	145
	Vycor, $PbCO_3$ conditioned, 580°	 (60)	92
	N_2 flow, 575°	 (54) +  (3) +  (40)	60
	Glass helices, 450°, *n*-hexane, N_2 flow	 (26) +  (44) + indane (11)	155,87
	Glass helices, 450°	 +  (83) 92 : 8	155,87,87a
	Pyrex, 400°, 10 min	 (91)	30,35
	Vycor, $PbCO_3$, 580°	 (70) +  (23)	30
	Vycor, $PbCO_3$, 580°	 (48) +  (18)	30
	260°, 24 hr, gas phase	 (15) + isomerized starting material (85)	30
	420–425°, Pyrex tube	 +  (–)	156,14
	220	 (30)	157
	–	 (–)	158
	Pyrex chips, 400–425°	 (96)	159
	N_2 flow, Pyrex, 450°	 +  (–) 49 : 51	74,160
	Vycor, glass wool, 500°	 (65) +  (9)	80,120,161
	Vycor, glass wool, 585°	 (65) +  (2)	80,120,161

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

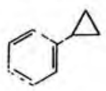
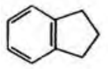
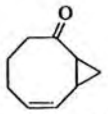
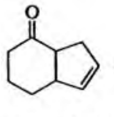
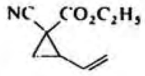
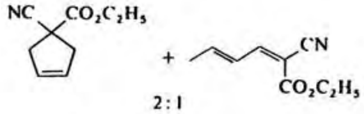
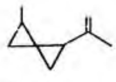
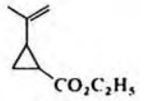
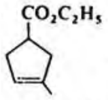
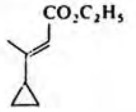
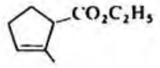
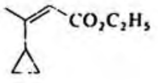
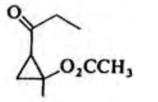
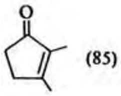
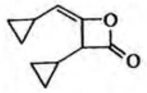
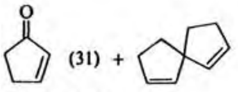
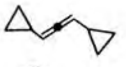
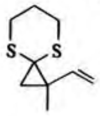
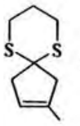
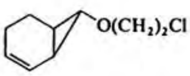
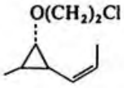
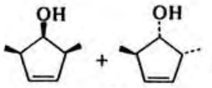
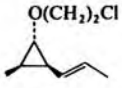
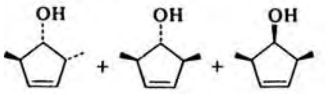
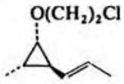
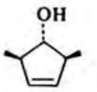
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
		 ( )	14
	Hexane, N_2 flow, 650°	 (24)	60
	Sealed tube, toluene, 220°, 7 hr	 (80) 2 : 1	124
	Sealed tube, 245°, 1.25 hr	 (33)	142
	500°	 (74)	56,162
	Sealed tube 375°, 30 min	 (95)	56,163
	Sealed tube, 350°, 20 min with hydroquinone	" (—)	56,163
	Sealed tube, 70 min, 350°	" (68)	56,163
	Sealed tube, 350°, 70 min	" (34)	163
	Reflux, 4% NaOH/MeOH, 1 hr	 (85)	164
	Pyrex, glass wool, 560°	 (31) + (14)	161
	Pyrex, glass wool, 560°	" " (—)	161
	200°, C_6H_6, 4 hr	 (97)	78
	n-C_4H_9Li, Et_2O, 25°	 (45)	47,95
	n-C_4H_9Li, THF/HMPA, 50°, 1–2 hr	 (37) 16 : 84	47,95
	n-C_4H_9Li, THF/HMPA, 50°, 1–2 hr	 (59) 79 : 15 : 6	95
	n-C_4H_9Li, THF/HMPA, 50°, 1–2 hr	 (74)	95

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

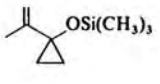
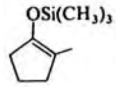
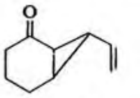
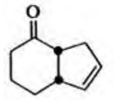
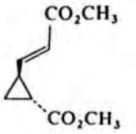
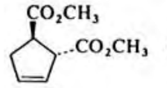
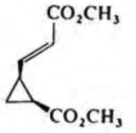
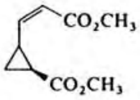
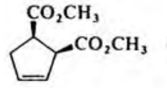
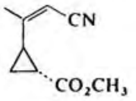
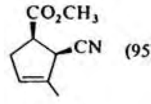
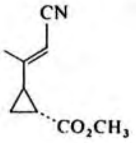
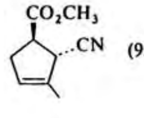
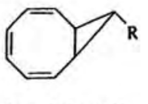
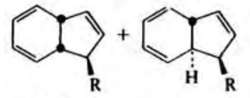
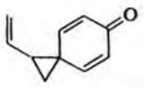
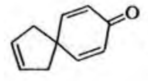
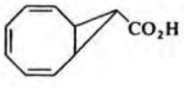
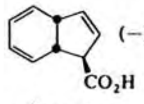
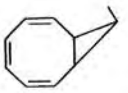
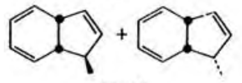
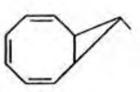
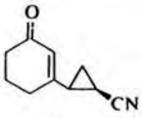
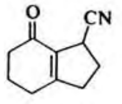
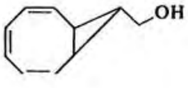
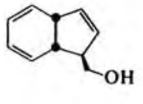
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Sealed tube 330°, 0.5 hr	 (as ketone) (95)	79
	Vycor, $PbCO_3$, 580°	 (72)	89,90,94
	320°, 1 hr	 (86)	160
	340°, 1 hr	" (86)	160
	450°, 1 hr	 (86)	160
	320°, 2 hr	 (95)	160
	320°, 2 hr	 (95)	160
C_{10} 	90°	 (−)	153
R = CN, OCH_3	70°, 20 hr	" " (−)	154
	$CDCl_3$	 (100)	165,166
	70°, 17 hr; 95°,1.5 hr	 (55)	167
		 (−)	168
	Vapor phase, 170°, 5 min	 (95) 83 : 17	169
	Vapor phase, 200°, 30 min	" 79 : 21 " (−)	169
	340°	 (50)	160
	Sealed tube, 120°, 20 min	 (95)	170,171

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

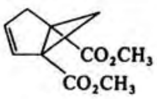
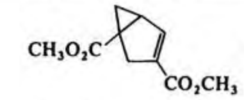
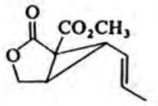
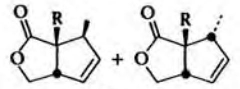
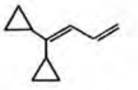
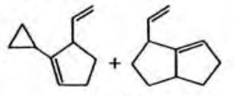
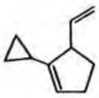
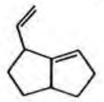
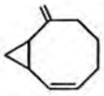
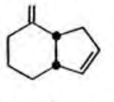
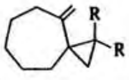
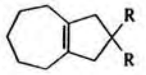
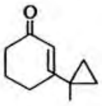
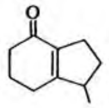
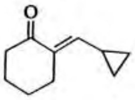
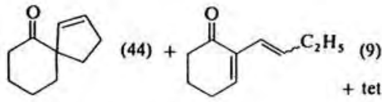
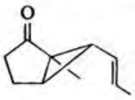
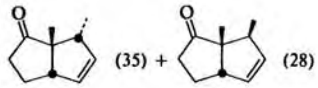
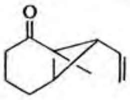
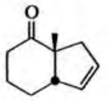
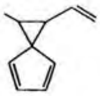
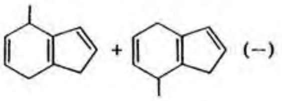
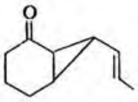
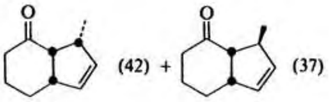
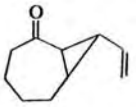
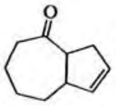
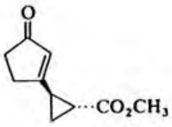
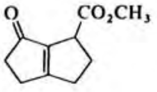
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	130–140°, 5 hr	 (64)	40,157,172
	Vycor, $PbCO_3$, 580°	 (52) 83 : 17 R = CO_2CH_3	92
	Vycor, 3 passes, 400°, glass wool	 (−) 85 : 15	24,25
	400°	 (33)	24,25
	600°	 (95)	60
 R = Br, Cl	N_2 flow, 285°	 (—)	54
	Glass helices, 450°	 (87)	155,87,87a,99
	Glass helices, 450°	 (44) + (9) + tetralin (33)	155,87
	Vycor, $PbCO_3$, 600°	 (35) + (28)	30
	Vycor, $PbCO_3$, 580°	 (74)	90
		 (−)	149
	Vycor, $PbCO_3$, 580°	 (42) + (37)	90
	Vycor, $PbCO_3$, 580°	 *cis* : *trans* (45 : 55) (71)	89
	340°, 2 hr	 (50)	160

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

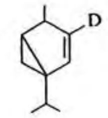
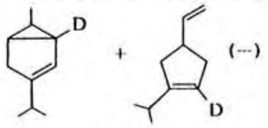
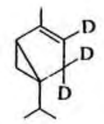
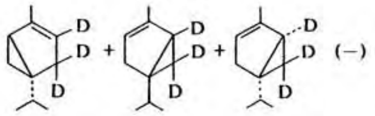
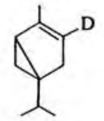
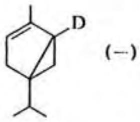
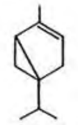
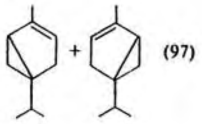
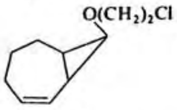
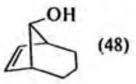
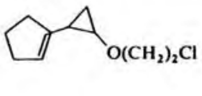
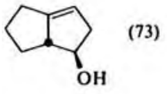
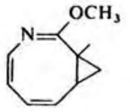
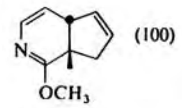
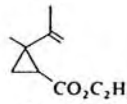
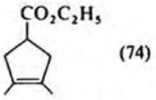
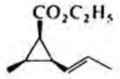
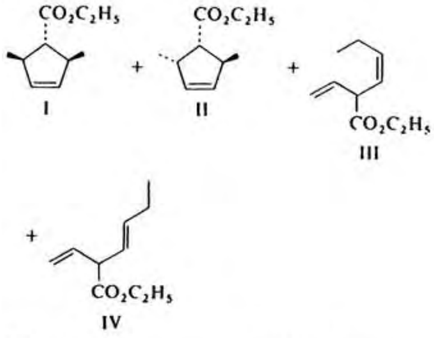
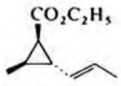
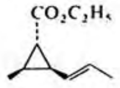
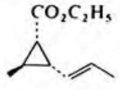
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Sealed tube, 250°, 20 hr	 1 : 1	39
	Sealed tube, 300°, 20 hr	" (100)	39
	485°		38,171
	250°, 20 hr		39,37,122,113
 (−)-	200–275°, Pyrex or 403–501°, Pyrex		38,39,113, 122,172
	n-C_4H_9Li (5 eq), THF/HMPA, 50°, 1–2 hr		95
	"		95
	Sealed tube, $C_2H_2Cl_4$, 100°, 6 hr		172
	N_2 flow, neat, 500°, 1 hr		162
	N_2 flow, 480°, 30 min, 2–5% cyclohexane solution	 I : II : III : IV 1.3 : 1.0 : 8.8 : 0	27,173,174 27
	480° 285°	I : II : III : IV 1.3 : 1.0 : 5.6 : 0 I : II : III : IV 1.4 : 1.0 : 0 : 11	27 27
	480°	I : II : III : IV 1.7 : 1.0 : 11.7 : 0	27
	480° 285°	I : II : III : IV 1.6 : 1.0 : 5.3 : 0 I : II : III : IV 1.7 : 1.0 : 0 : 0.5	27 27

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

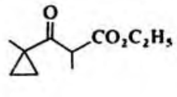
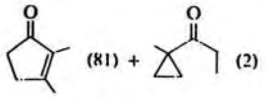
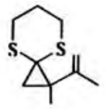
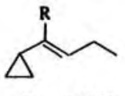
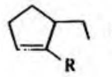
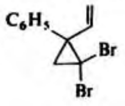
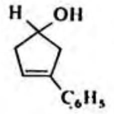
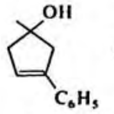
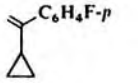
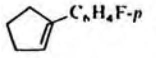
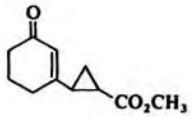
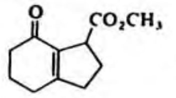
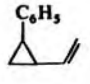
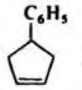
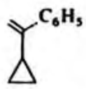
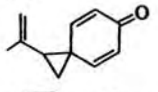
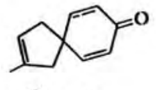
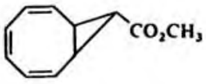
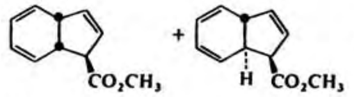
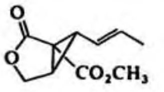
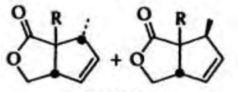
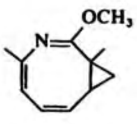
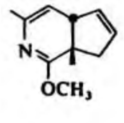
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Vycor, glass wool, 535°	 (81) + (2)	80
	570	" (68)	80
	200°, C$_6$H$_6$, 5 hr	 (95)	78
 R = n-C$_3$H$_7$, i-C$_3$H$_7$	390°	 (·)	127
C$_{11}$ 	1. n-C$_4$H$_9$Li, −100° 2. CH$_3$OH 3. n-C$_4$H$_9$Li, 2 eq 4. O$_2$, −78° 5. 25°, 2 hr	 (45)	47
	As above, except step 2: CH$_3$I	 (40)	47
	Vycor, glass helices, 400°	 (92)	20,140,175
	340°, 2 hr	 (100)	160
	220–250°, gas phase	 (--)	75,14
cis/trans	Sealed tube, 240–270°	" (100)	13,72,75,176
	224°, 24 hr, sealed tube, methylcyclohexane	" (67)	72
	400°, glass wool	"	20,43,140,175
	70°, 17 hr; 95°, 1.5 hr	 (55)	167
		 (--)	152,146,153
	Vycor, PbCO$_3$, 580°	 (52) 17 : 83 R = CO$_2$CH$_3$	92
	C$_2$H$_2$Cl$_4$, 70–91°	 (—)	177

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

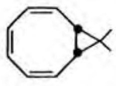
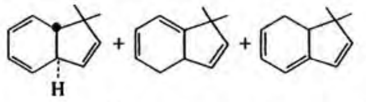
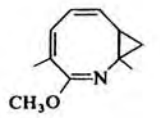
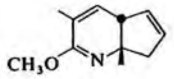
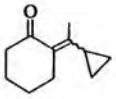
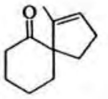
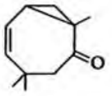
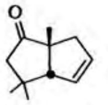
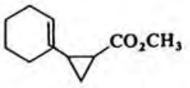
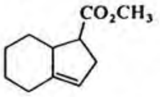
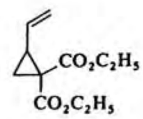
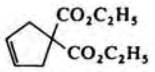
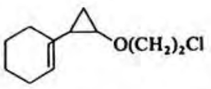
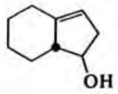
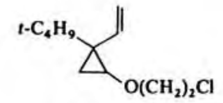
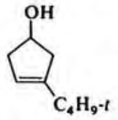
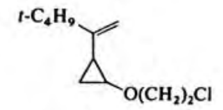
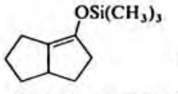
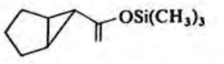
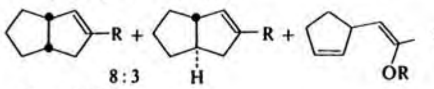
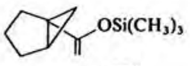
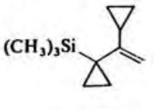
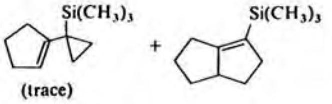
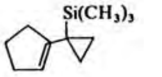
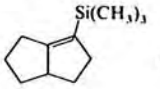
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	151°, refluxing nonane		178
	15 min	(12) (–) (–)	
	65 min	(25) (8) (13)	178
	Sealed tube, $C_2H_2Cl_4$, 100°, 6 hr	 (–)	177,172
	Glass helices, 450°	 (25)	87
	550°	 (80)	60
	360°	 (–)	127,128,112
	Sealed tube, xylene, 280°, 11 hr	 (10)	124
	Pyrex, glass helices, 400–425°	" (95)	159
	n-C_4H_9Li (5 eq), THF/HMPA, 50°, 1–2 hr	 (70)	95
	n-C_4H_9Li, Et_2O/hexane, 250°	 (95)	47
	"	" (–)	47
	Glass helices, 330°, hexane, N_2 flow	 (89)	79,84,86
	Sealed tube, 350°, 1 hr	" (–) (as ketone) (95)	79
	Sealed tube, C_6H_6, 360°, 2–3 hr	 (71) R = $OSi(CH_3)_3$	81,144
	Sealed tube, C_6H_6, 360°, 2–3 hr	" (21)	81,144
	N_2 flow, quartz chips, 570°	 (trace) (80)	179,88
	570°, N_2 flow system, quartz chips	 (82)	179,88

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

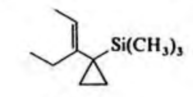
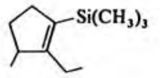
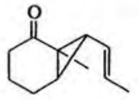
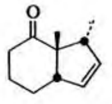
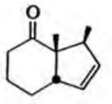
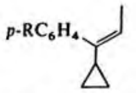
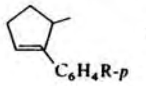
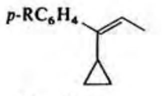
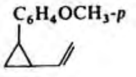
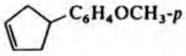
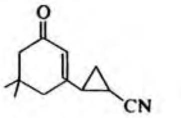
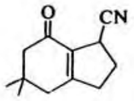
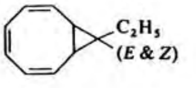
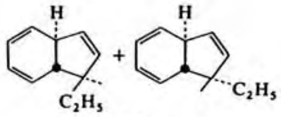
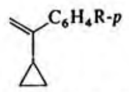
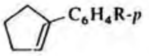
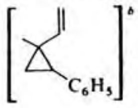
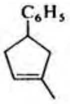
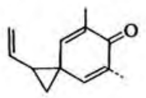
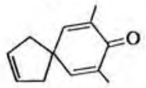
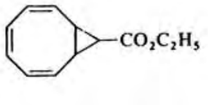
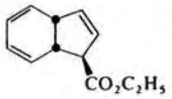
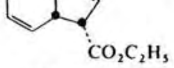
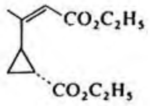
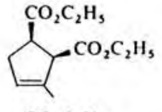
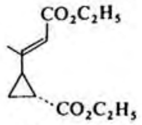
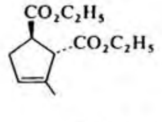
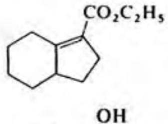
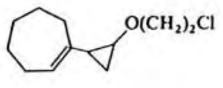
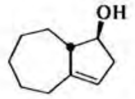
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	N$_2$ flow, 570°	 (71)	179,88
	Vycor, PbCO$_3$ conditioned, 580°, 10 min	 (34) +  (26)	90
C$_{12}$ 	N$_2$ flow, 400°	 (100)	42
 R = H, F	N$_2$ flow, 400°	" (20) + polymer	42
	Sealed tube, 222°, 2 hr	 (44)	134
	340°, 2 hr	 (—)	160
	170°, 5 min	 (—) 1.8 : 1	180
 R = CH$_3$, OCH$_3$	400°, Vycor, glass wool	 (95)	20,140,175
	Gas phase, 700°	 (25)	181
	70°, 17 hr; 95°, 1.5 hr	 (50)	167
	150°, 10 min	 +  (75) 4 : 1	182,146
	370°, 2 hr	 (80)	160
	370°, 2 hr	 (80)	160
	360°	 (—)	127,128
	n-C$_4$H$_9$Li (5 eq), THF/HMPA, 50°, 1–2 hr	 (61)	95

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

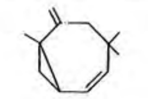
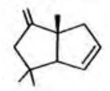
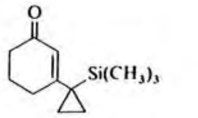
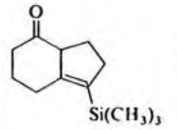
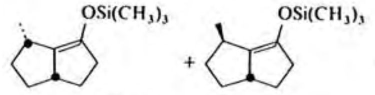
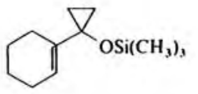
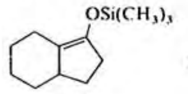
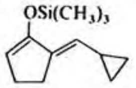
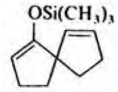
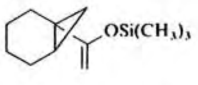
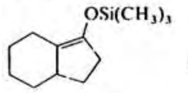
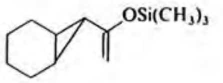
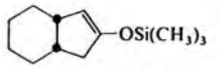
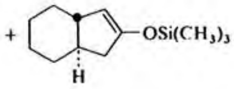
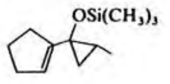
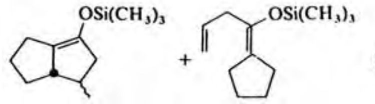
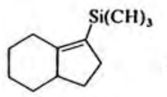
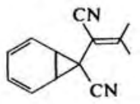
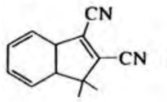
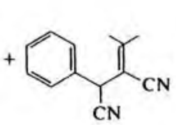
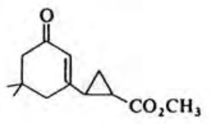
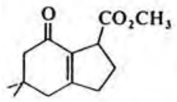
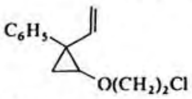
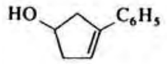
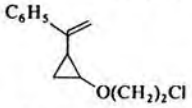
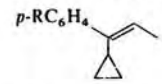
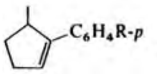
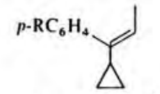
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	550°	 (70)	60
	N$_2$ flow, 600°	 (75)	88
	350°, 2 hr	 (--)	86,183
		 (−)	183
	Sealed tube, 350°, 1 hr	" (95)	79
	425°	 (56)	155
	Sealed tube, 360–450°, C$_6$H$_6$, 2 hr	 (as ketone) (99)	81,144
	Sealed tube, 360°, 2 hr	 (17) +  (35)	81,144
	Conditioned quartz vessel, 350°, 2 hr	 (--)	86
	570°	 (80)	179,89
C_{13} 	180°, *o*-C$_6$H$_4$Cl$_2$, 1 hr	 (2) +  (56)	184
	340°, 2 hr	 (50)	160
	*n*-C$_4$H$_9$Li, Et$_2$O, 25°	 (90)	47
	"	" (−)	47
	400°, glass-wool-packed column	 (10–12)	43,48
 R = CH$_3$, OCH$_3$	400°, glass wool packing	" (100)	43,48

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

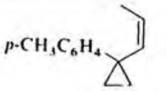
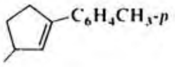
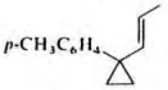
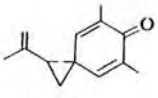
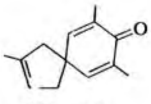
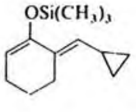
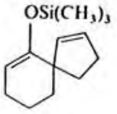
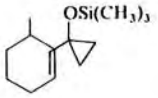
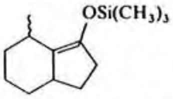
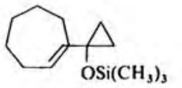
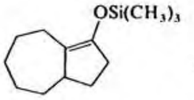
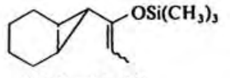
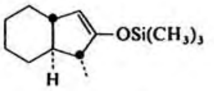
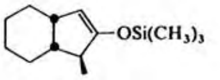
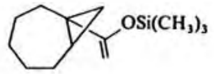
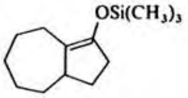
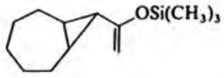
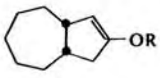
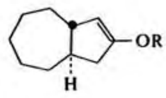
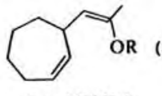
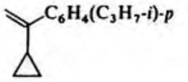
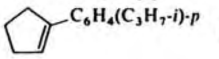
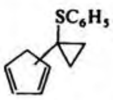
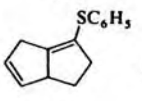
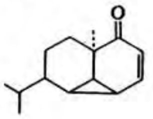
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	450°	 ( )	48
	400°	" (–)	48
	70°, 17 hr; 95°, 1.5 hr	 (55)	167
	Glass helices, 450°	 (50)	87
	425°, N_2 flow	" (89)	155
	280°, 2 hr	 (—)	86,183
	Pyrex, N_2 flow, 4 sec, 330°	 (99)	84
 (Z:E = 62:38)	360°, 2 hr, base-washed ampoule	 (64) +  (7)	81,144
	360°, 2 hr, base-washed ampoule, C_6H_6	 (85)	81,144
	"	 +  (5, combined)  (80) R = $Si(CH_3)_3$	81,144
C_{14}			
	325°, sealed tube	 (—)	20,140,175
	400° glass-wool-packed Vycor column	" (95)	20,140,175
	Pyrex beads, 500°	 (80)	82
	N_2 flow, quartz chips, 450°	 (90)	185

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

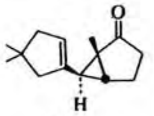
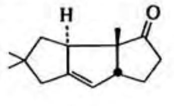
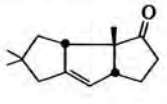
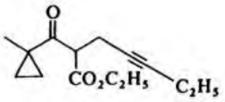
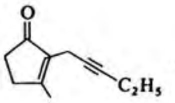
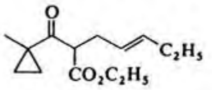
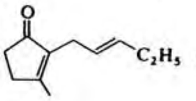
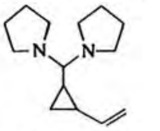
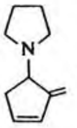
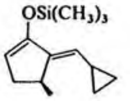
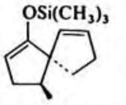
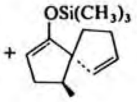
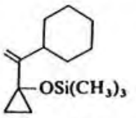
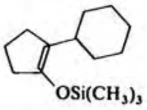
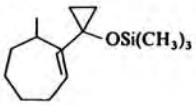
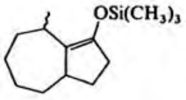
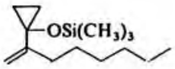
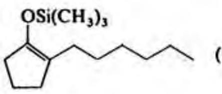
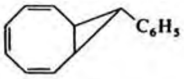
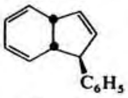
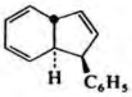
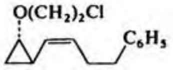
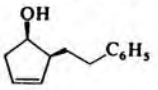
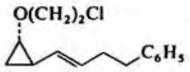
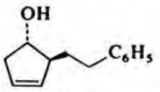
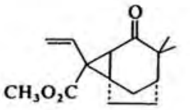
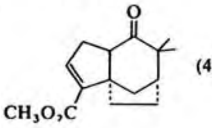
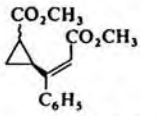
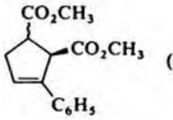
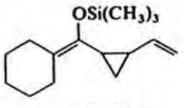
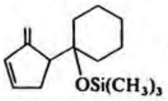
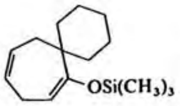
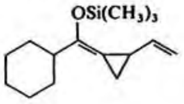
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Vycor, $PbCO_3$, 580°, 10 min	 (65) +  (10)	30
	Glass wool, N_2 flow, 540°	 (53)	186
	Glass wool, N_2 flow, 515°	 (57)	186
	Sealed tube, toluene, 110°, 21 hr	 (28)	187
	380°	 (35) +  (14)	155
	N_2 flow, 280°	 (—)	84
	N_2 flow, 300°	 (—)	183
	Pyrex, glass helices, 330°	 (97)	84
C_{15} 	90°	 +  (—)	153
	n-C_4H_9Li (5 eq), 25°, 1 hr	 (78)	95
	n-C_4H_9Li, THF/HMPA, 25°, 1 hr	 + " (77–82) 99 : 1	95
	580°, Vycor, $PbCO_3$ conditioned, 10 min	 (48)	188
	320°	 (66–76)	160
	150°, 30 min	 +  (—)	189
	150°, 30 min	" " (—)	189

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

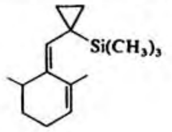
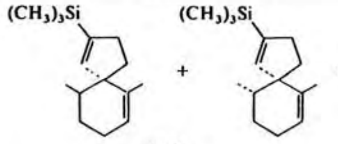
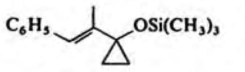
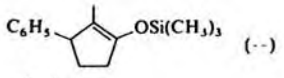
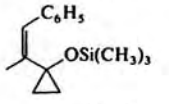
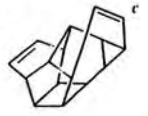
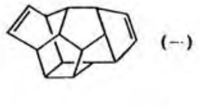
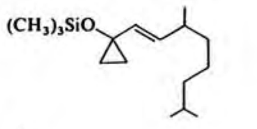
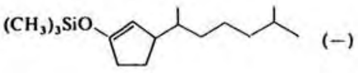
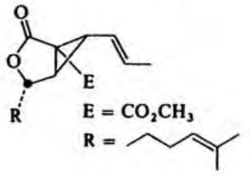
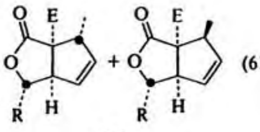
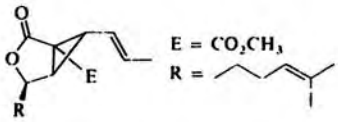
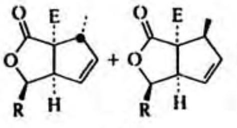
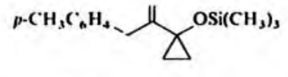
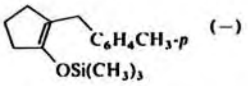
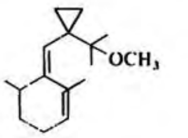
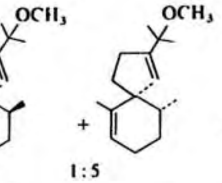
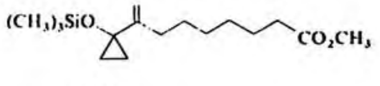
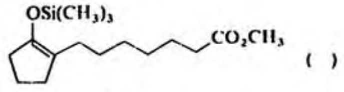
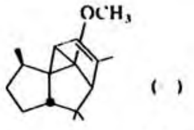
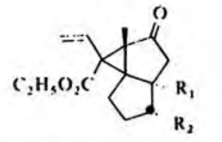
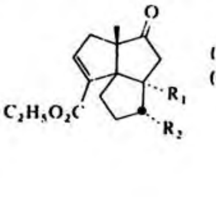
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	560°	 1:4 (—)	102
	330°		97
	330°	" (—)	97
C_{16} 	100		122,190
	330°		183
 E = CO_2CH_3 R =	580°, Vycor, $PbCO_3$ conditioned,10 min	 (61) 3:1	191
 E = CO_2CH_3 R =		 (60) 1:3	191
	330°		97
	435–440°	 (100) 1:5	102
	330		97
	205–230°		192
 R_1 = H, R_2 = CH_3 R_1 = CH_3, R_2 = H	Vycor, $PbCO_3$, 580°	 (60) (65)	93 101

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

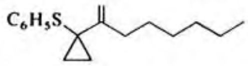
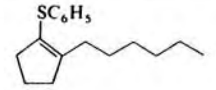
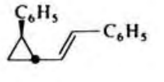
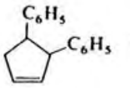
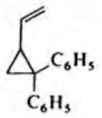
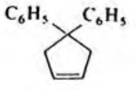
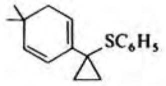
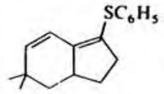
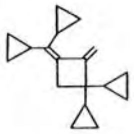
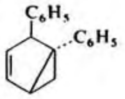
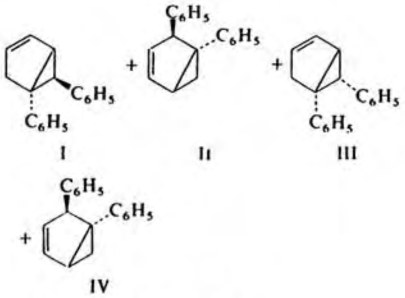
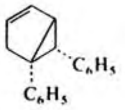
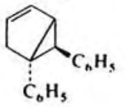
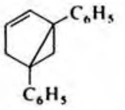
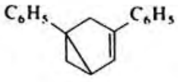
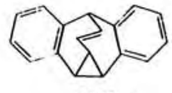
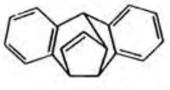
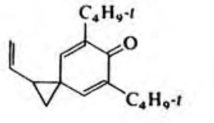
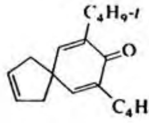
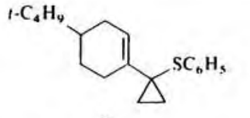
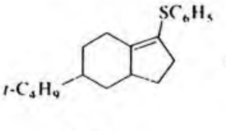
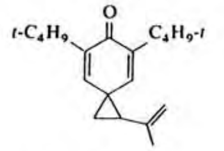
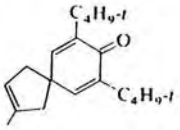
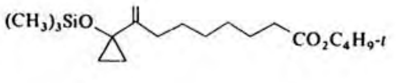
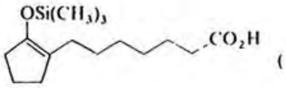
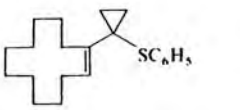
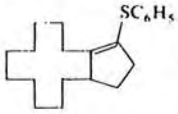
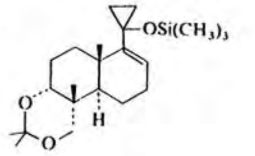
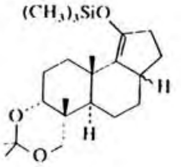
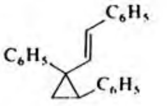
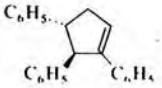
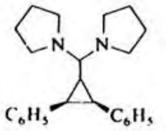
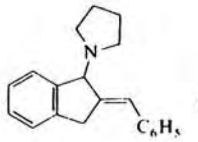
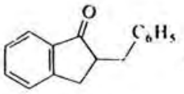
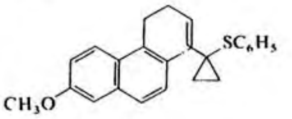
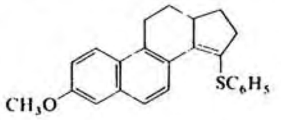
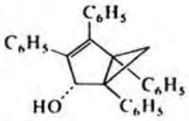
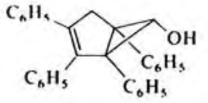
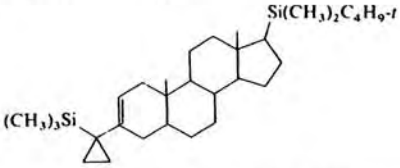
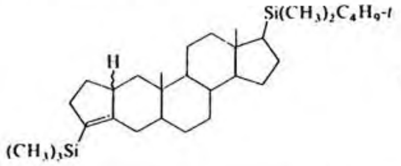
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	N_2 flow, hexane solution, 350°, 12 sec	 (95)	83
C_{17} 	Sealed tube, 240–270°	 (100)	13
	250°, 8 hr	 (100)	124
	Conditioned hot tube packed with glass helices, N_2 flow, 350°, 12 sec	 (92)	83
C_{18} 	200°, C_6H_6, 32 hr	 (56)	193
	Cyclohexane solution, 130°, 24 hr; 170°, 24 hr	 I : II : III : IV 58 : 40 : 1 : 1	37
	180–212°	I : II : III : IV 32 : 20 : 40 : 7	37
	170°, 2 hr; 130°, 46 hr	I : II : III : IV 58 : 40 : 1 : 1 I : II : III : IV 59 : 40 : 1 : 1	37 37
	Cyclohexane solution, reflux, 1 hr	 (—)	194
	N_2 flow, 450°	 (25)	195
	70°, 17 hr; 95°, 1.5 hr	 (50)	167

TABLE I. THERMAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_{19}		Conditioned hot tube, glass helices, N_2 flow, 350°, 12 sec	 (95)	83
		70°, 17 hr; 95°, 1.5 hr	 (92)	167
		330°	 ( )	97
C_{21}		Conditioned hot tube, glass helices, 350°, N_2 flow	 (92)	83
C_{22}		Flash vacuum pyrolysis, 610°	 (97)	98
C_{23}			 ( )	126
C_{24}		Toluene, reflux, 45 hr	 (80) +  (7)	187
C_{25}		Sealed tube, toluene, 250°, 2 hr	 (94)	83
C_{30}		205°, tetralin	 (83)	196
C_{31}		660°	 ( )	155

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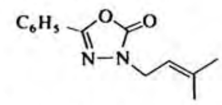
[a] The starting material was generated *in situ* from the corresponding pyrazoline.

[b] The starting material was generated *in situ* from:



[c] The starting material was generated from cyclooctatetraene on photolysis.

TABLE II. PHOTOCHEMICAL REARRANGEMENTS OF VINYLCYCLOPROPANES

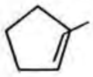
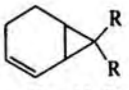
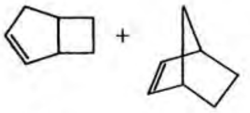
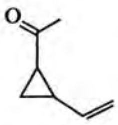
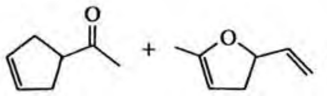
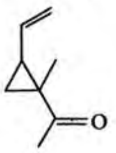
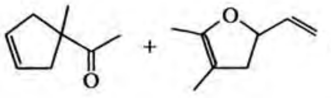
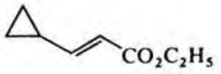
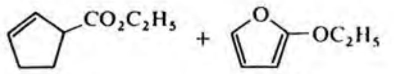
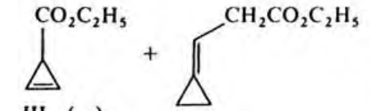
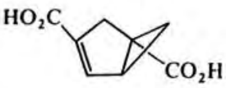
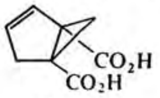
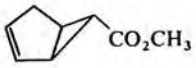
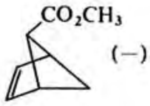
	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_5	Vinylcyclopropane	Hg arc Hanovia, Pyrex vessel, 65°, 366 nm	Cyclopentene, *trans*-1,3-pentadiene, isoprene, *cis*-1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene (—)	19,53
	[Vinylcyclopropane][a]	200 W, Hg lamp, 436 nm, Pyrex, 3 hr, 25°	Cyclopentene (—)	19,21
		"	Cyclopentene, vinylcyclopropane, pentadienes (—)	197,117
	Vinylcyclopropane	CO_2 laser, 5 J/cm², 940 cm^{-1}/0.2 mm	Cyclopentene 32 cyclopentadiene 52 *trans*-1,3-pentadiene 4 (–) *cis*-1,3-pentadiene 4 1,4-pentadiene 1	61
C_6		Hexane solution, 450 W, Hanovia, quartz	 (55)	76
C_7	 R = CO_2H, CH_2OH (*exo* and *endo*)	Hexane 0.5% solution, 253.7 nm	 (—)	198
	 R = H, D		 + dienes	
		Pentane, 214 nm *hν*, sensitized	11 10 79 (75)	199
			55 — 45 (50)	200
	 (*cis* and *trans*)	450 W, Hanovia, ether, 16 hr	 (–)	201
C_8	 (*cis* and *trans*)	450 W, Hanovia, ether, 16 hr	 (–)	201
		Ether solution, 450 W, Hanovia, Vycor,		163,56,57
		7 hr	I (50) II (19)	
		9 days	(23) (–)	
			 III (—) (62) IV	
		Hexane solution, 9 days, Hanovia	I : II : III : IV 23 : 0 : 0 : 62	163
		Hanovia Q81 lamp, Vycor filter	 (23)	157
		*hν*, hexane	 (—)	198

TABLE II. PHOTOCHEMICAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

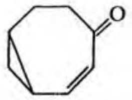
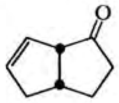
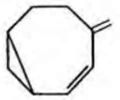
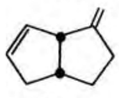
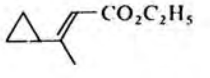
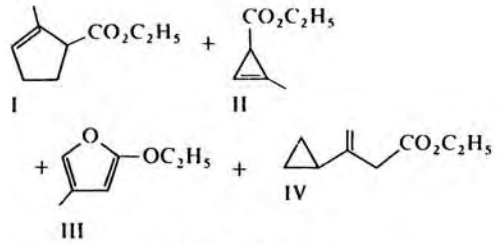
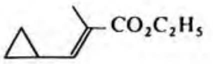
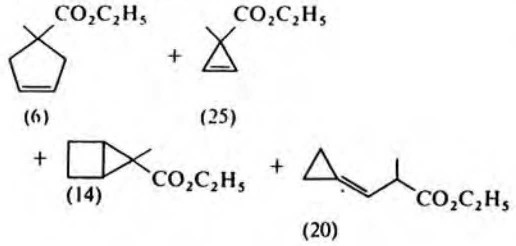
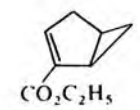
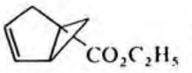
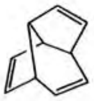
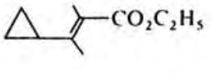
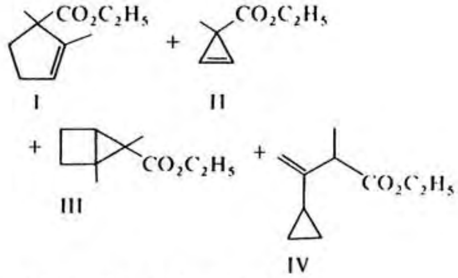
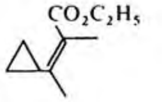
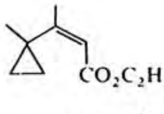
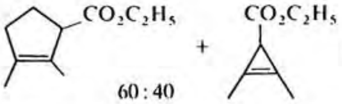
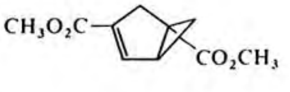
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pentane, N_2, 200 W Hanovia, Pyrex filter, 2.5 hr	 (39)	59,58
	Acetone, *hv*, Pyrex	" (82)	58
C_9 	Acetone, 450 W Hanovia, 3.25 hr	 (40)	59,58
	Pentane, Vycor filter	(53)	58
			
	450 W Hanovia, Vycor	I : II : III : IV 42 : 5 : 1.5 : 5 (—)	56
	hv, 216 hr	I : II : III : IV 70 : 8 : 2.6 : 17 (60)	163
	*hv*, 216 hr		163
	Hanovia Q81 lamp, Vycor filter, 0°	 (—)	157
C_{10} 	*hv*, Hanovia, Vycor	 (—)	190
	450 W, Hanovia, Vycor filter *hv*, 10 days		56,163
		I : II : III : IV 6 : 13 : 0 : 0 (—)	56
	"	I : II : III : IV 10 : 24 : 48 : 10 (48)	163
	450 W. Hanovia	I : II : III : IV 6 : 0 : 20 : 0 ( )	57
	*hv*, ether solution, 23 hr	 60 : 40 (60)	163
	*hv*, Hanovia Q81, Vycor filter	 (80)	157,40

TABLE II. PHOTOCHEMICAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

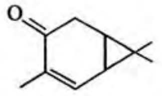
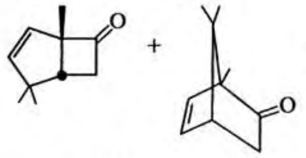
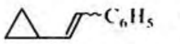
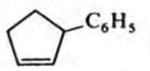
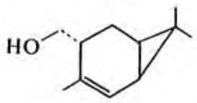
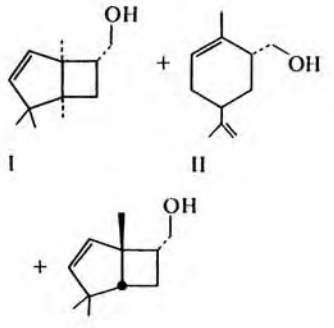
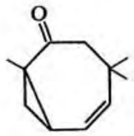
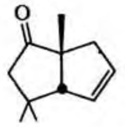
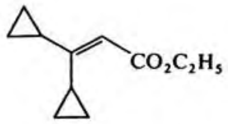
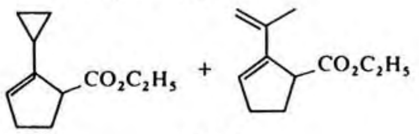
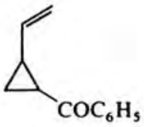
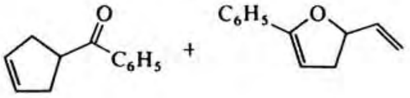
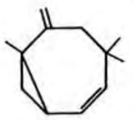
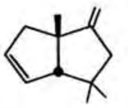
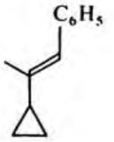
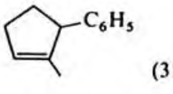
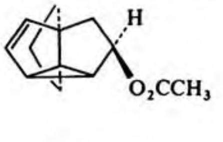
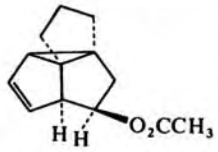
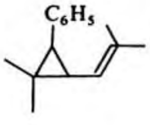
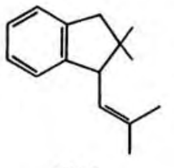
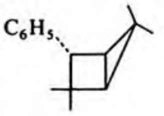
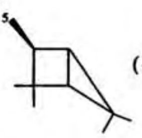
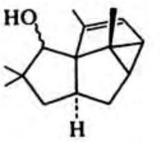
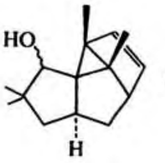
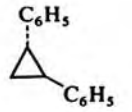
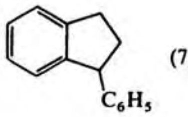
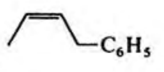
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	Hanovia 450, Pyrex, CF_3CO_2H, 6 hr	 (−)	200
C_{11}  (*cis* and *trans*)	*hν*, hexane	 (40)	202
	450 W. Hanovia, C_6H_6, 14 hr	 I, II, III	
		I : II : III 65 : 0 : 11 (−)	203
	hexane, 16 hr, 210 nm	I : II : III 21 : 19 : 3 (−)	203
	methanol, 7 hr, 210 nm	I : II : III 12 : 35 : 2 (−)	203
	t-C_4H_9OH, 6 hr, 210 nm	I : II : III 6 : 26 : 1 (−)	203
	450 W, Hanovia, acetone, Corex, 5 hr	 + polymer (10)	59,58
	250 nm, ether, Corex, 5 hr	" + polymer (8)	58
	*hν*, ether solution, Vycor, 9 days	 (69) 88 : 12	163
C_{12}  (*cis* and *trans*)	*hν*, ether solution 16 hr, 450 Hanovia, quartz	 (−)	201
	450 W, Hanovia, CH_3OH, 10 hr	 (56)	59,58
	220 nm, Vycor or Pyrex, acetone solution	" (−)	58
	*hν*, hexane	 (31)	202

TABLE II. PHOTOCHEMICAL REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_{13}		*hν*, Vycor filter, cyclohexane, 35 hr	 (−)	204
C_{15}		Hg lamp, 253.7 nm	 (11) +  (50) +  (−)	77
		450 W, Hanovia, Vycor, cyclohexane	 (−)	205
		Solution in C_6H_6, 253.7 nm, 8.5 hr	 (7) +  (7) +  (16)	206
		Hanovia, 450 W, Vycor, cyclohexane, 195 min	 (−)	207
		"	 (−)	207

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[a] The starting material was generated *in situ* from diazomethane and butadiene.

TABLE III. TRANSITION-METAL-CATALYZED REARRANGEMENTS OF VINYLCYCLOPROPANES

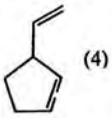
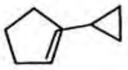
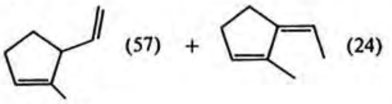
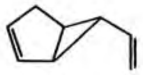
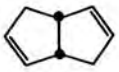
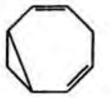
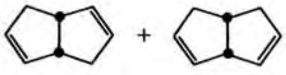
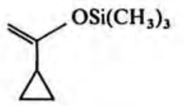
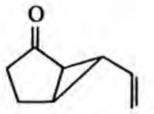
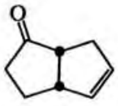
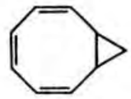
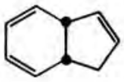
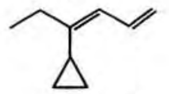
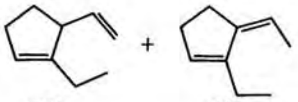
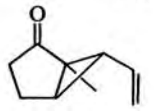
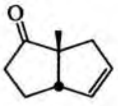
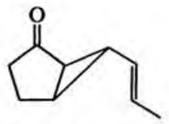
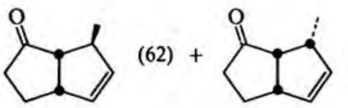
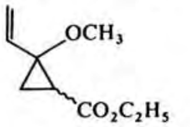
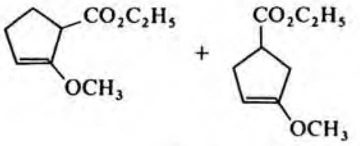
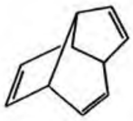
	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_5	Vinylcyclopropane	Ni(COD)$_2$, (*n*-C_4H_9)$_3$P, C_6H_6, 70°	No rearrangement	70
C_6	2-Propenylcyclopropane	"	No rearrangement	70
C_7	1-Cyclopropylbutadiene (*E*/*Z* = 87/13)	"	 (4)	70
C_8	1,1-Dicyclopropylethylene	"	 (99)	70
	1-Methyl-1-cyclopropylbutadiene (*E*/*Z* = 67/33)	"	 (57) + (24)	70
		(C_2H_4)$_2$Rh(acac), 80°, 36hr	 (31)	68,69
		270°, Ni(NO$_3$)$_2$·6H_2O, silica conditioned, 2.5 min	 + (—)	50
		305°, "	" + " (—) 42 : 58	50
		Ni(COD)$_2$, (*n*-C_4H_9)$_3$P, C_6H_6, 70°	No rearrangement	70
		(C_2H_4)$_2$Rh(acac), C_6H_6, 48 hr	 (70)	30
C_9		(CO)$_4$Rh$_2$Cl$_2$. 350°, 2 hr	 (100)	65,66
	 (*E*/*Z* = 99/1) (*E*/*Z* = 60/40) (*E*/*Z* = 1/99)	Ni(COD)$_2$, (*n*-C_4H_9)$_3$P, C_6H_6, 70°, 40 hr	 (79) + (18) (64) + (24) (80) + (3)	70
		(C_2H_4)$_2$Rh(acac), 48 hr, C_6H_6	 (75)	30
		"	 (62) + (5)	30
				
		Copper–bronze (10 mol %), 2 hr	1.1 : 1 (41)	208
		CuCl (10 mol %), 4 hr, 135°	1.6 : 1 (22)	208
C_{10}		Fe$_2$(CO)$_9$	 (—)	209

TABLE III. TRANSITION-METAL-CATALYZED REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

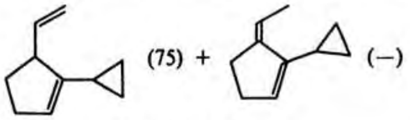
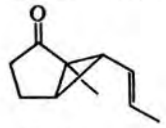
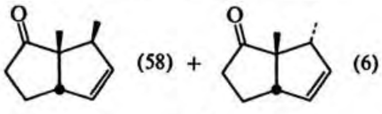
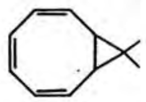
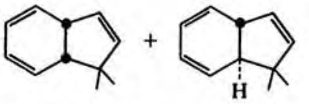
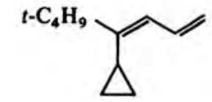
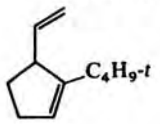
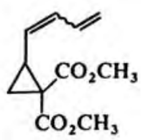
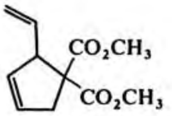
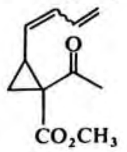
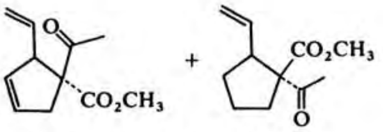
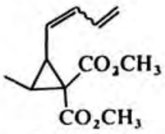
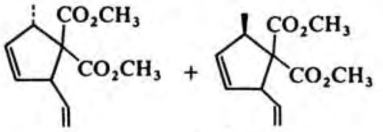
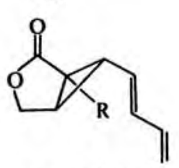
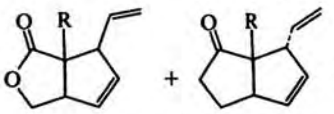
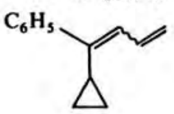
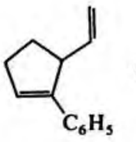
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
1,1-Dicyclopropylbutadiene	No catalyst, sealed tube, C_6H_6, 70°	 (75) + (—)	70
	Ni(COD)$_2$, $(C_6H_5O)_3P$ (0.9 eq), C_6H_6, 70°	(50) (—)	70
	Ni(COD)$_2$, $(C_6H_6)_3P$ (1 eq), C_6H_6, 70°	(61) (19)	70
	Ni(COD)$_2$, $(n\text{-}C_4H_9)_3P$ (0.9 eq), C_6H_6, 70°	(68) (20)	70
	$(n\text{-}C_4H_9)_3P$ (2 eq), C_6H_6, 70°	(22) (—)	70
1,1-Dicyclopropylbutadiene (*E*/*Z* = 1 : 1)	Ni(COD)$_2$, $(n\text{-}C_4H_9)_3P$ (1 eq), C_6H_6, 70°	(93) (6)	70
	$(C_2H_4)_2$Rh(acac), C_6H_6, 48 hr	 (58) + (6)	30
C_{11} 		 +	
	$(CO)_4Rh_2Cl_2$, 140°, 30 min	(80) (2)	65,66
	$(CO)_4Rh_2Cl_2$, 150°	(—) (100)	65,66
	Ni(COD)$_2$, $(n\text{-}C_4H_9)_3P$, 70°	 (31)	70
	$Pd[(C_6H_6)_3P]_4$, DMSO, 50°	 (87)	71
	"	 +	
1*R*,2*S*		1 : 1 (96)	71
1*S*,2*R*		1 : 1 (88)	71
C_{12} 	"	 +	
E/*Z* = 7 : 3		3 : 1 (84)	71
E		3 : 1 (85)	71
Z		3 : 1 (70)	71
 R = $CO_2C_2H_5$	"	 + (82) 1 : 1	71
C_{13} 	Ni(COD)$_2$, $(n\text{-}C_4H_9)_3P$, C_6H_6, 70°	 (75)	70

TABLE III. TRANSITION-METAL-CATALYZED REARRANGEMENTS OF VINYLCYCLOPROPANES (*Continued*)

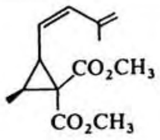
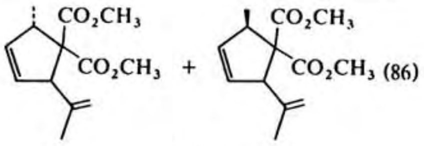
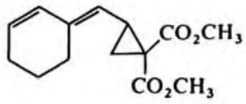
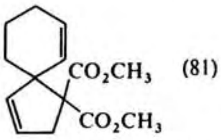
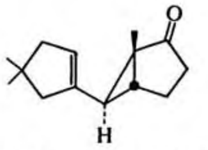
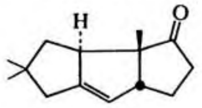
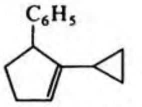
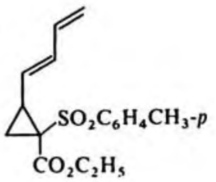
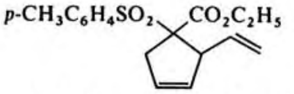
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	$Pd[C_6H_6)_3P)]_4$, DMSO, 60°	 (86) 3 : 1	71
C_{14} 	"	 (81)	71
	$(C_2H_4)_2Rh(acac)$, 48 hr, C_6H_6	 (68)	30
1,1-Dicyclopropyl-2-phenylethylene	$Ni(COD)_2$, $(n\text{-}C_4H_9)_3P$, C_6H_6, 70°	 (77)	70
C_{17} 	$Pd[(C_6H_6)_3P)]_4$, DMSO, 25°	 (89) (1 : 1 mixture of *cis* and *trans*)	71

TABLE IV. MISCELLANEOUS REARRANGEMENTS

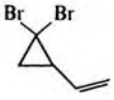
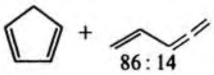
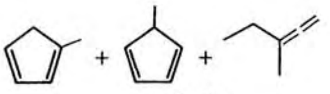
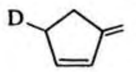
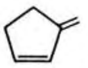
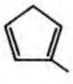
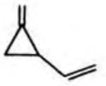
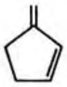
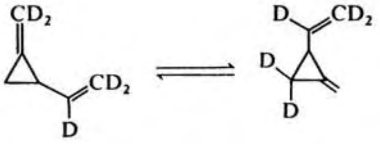
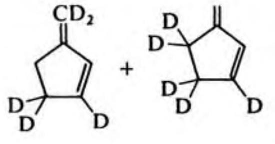
	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_5		CH_3Li, −78°	 86 : 14 (−)	107,210,211
	"	CH_3Li, −78°	 48 : 35 : 17 (−)	107
C_6		313°, 40 min	 (−)	104
		235°, 40 min	 (39) +  (6) +  (8)	104,103
		80°, sealed tube, dil. pentane solution, 13 hr	 (90)	105,212
		80°	" (−)	213
		80°	 (−)	213

TABLE IV. MISCELLANEOUS REARRANGEMENTS (*Continued*)

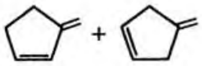
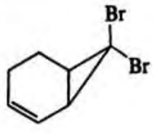
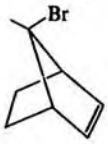
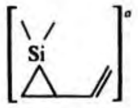
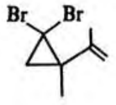
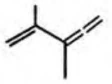
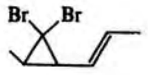
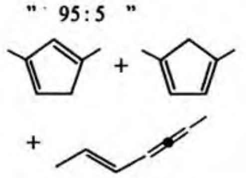
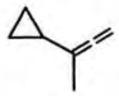
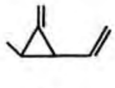
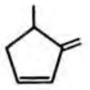
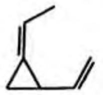
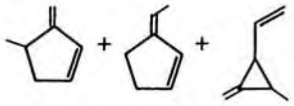
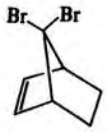
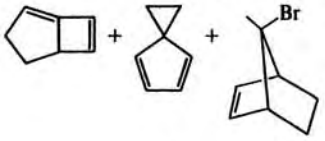
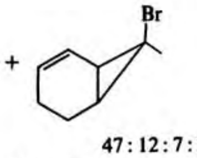
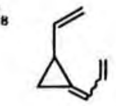
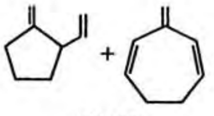
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
			
	340°	4:3	106
	370°	" 9:5 "	106
	530°	" (38) " (29)	106
C$_7$ 	CH_3Li, −78°, ether	 (80)	107
 [a]	225°, sealed tube, 18 hr	 (15)	214
	CH_3Li, 0°	 (98)  (—)	107
	CH_3Li, 0°	" 95:5 "	211
	CH_3Li, 0°	 (—) 48:20:32	107
	280–300°, hexane, sealed tube	 (—)	103
	—	 (—)	212,215
	80°	 (—)	216.213
	CH_3Li, 100°	  (90) 47:12:7:20	217
$NNLi(O_2SC_6H_4CH_3\text{-}p)$ 	CH_3Li, 275°	62:5:0:0 (70)	217
C$_8$ 	61°	 (73) 20:80	215

TABLE IV. MISCELLANEOUS REARRANGEMENTS (*Continued*)

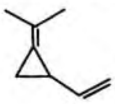
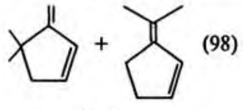
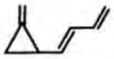
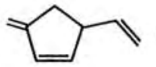
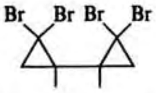
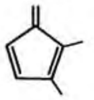
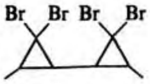
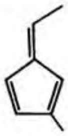
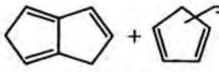
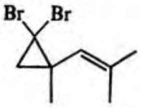
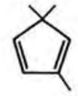
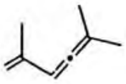
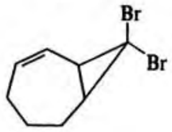
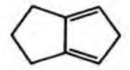
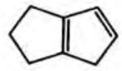
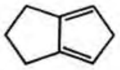
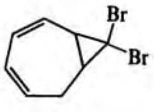
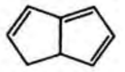
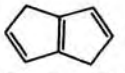
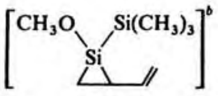
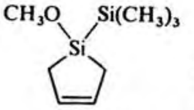
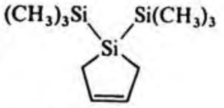
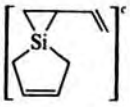
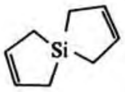
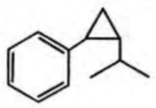
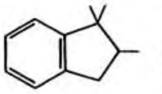
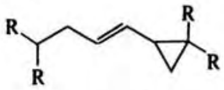
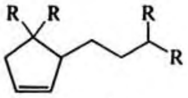
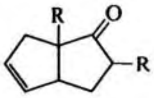
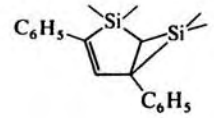
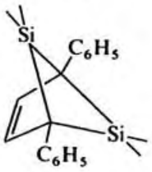
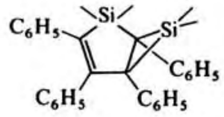
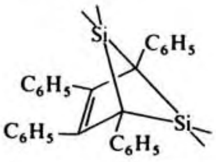
Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
	118°	 (98) 33 : 67	213,218
	190°	" " (—)	105
	56°	 (—)	215
	CH_3Li, −78°	 (—)	107
	CH_3Li, −78°	 (—)	107
	CH_3Li, 2.5 eq, −40°, ether	 + allenes (32) 59 : 39 : 7	219
	CH_3Li, −78°	 (70) +  (7)	107,210
	CH_3Li, −30 to −40°	 (94)	210,220
	CH_3Li, −30°	" (65)	221
	CH_3Li, 25°	 +  (70) 4 : 1	221
	CH_3Li, −30°	 (—)	221,219
	CH_3Li, 25°	 (—)	
	hν, 254 nm, 310°	 (49) +  (23)	108
	1. hν, 254 nm, 6 hr 2. 310°, 2.5 hr	 (32)	108

TABLE IV. MISCELLANEOUS REARRANGEMENTS (*Continued*)

	Starting Material	Conditions	Product(s) and Yield(s)(%)	Refs.
C_{12}		90% H_2SO_4, 35°, 1.5 hr	 (22)	222
C_{15}		DMSO, Na, 50°, 2 hr	 (58)	96
	R = CO_2CH_3	DMSO, Na, 90°, 21 hr	 (71)	96
C_{20}		C_6D_6 solution, 450-W Hg lamp, 105°, 3 hr	 (—)	109
C_{32}		"	 (100)	109

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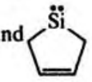
[a] The starting material was generated *in situ* from butadiene and $(CH_3)_2\ddot{Si}$.

[b] The starting material was generated *in situ* from butadiene and $CH_3O\ddot{Si}Si(CH_3)_3$.

[c] The starting material was generated *in situ* by thermolysis of butadiene and 

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