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The Reaction of Organoboranes with *d*-Carvone and *l*-Perillaldehyde in the Presence of Oxygen. Evidence for a Coordination between Organoboranes and α,β-Unsaturated Carbonyl Oxygens in Their Oxygen-Induced Free Radical Reaction Process

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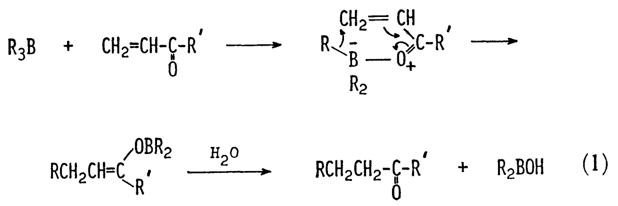
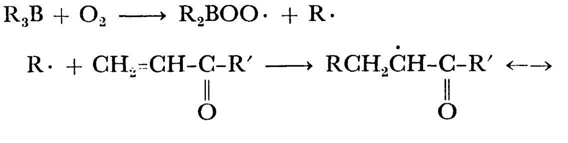
Oxygen-induced 1,4-addition reactions of trialkylboranes with cyclic α,β-unsaturated carbonyl compounds were studied. Stereoselective 1,4-additions of the alkyl groups of trialkylboranes were observed in the reactions of *d*-carvone and L-perillaldehyde. Namely, it was shown that the alkyl group adds to *d*-carvone from the *trans* side with respect to isopropenyl group to give the corresponding saturated ketones. The same type of one side attack of the alkyl group to *l*-perillaldehyde was also observed. The evidence seems to strongly support the hypothesis that coordination of boron atoms of trialkylboranes to carbonyl oxygens plays an important role, even in the oxygen-induced free radical chain reaction of organoboranes with α,β-unsaturated carbonyl compounds.

It has been previously reported by us that trialkylboranes undergo rapid 1,4-addition reactions with methyl vinyl ketone[1] to give vinyloxyboranes, which undergo hydrolysis on treatment with water to form corresponding saturated ketones (Eq. 1).


(1)

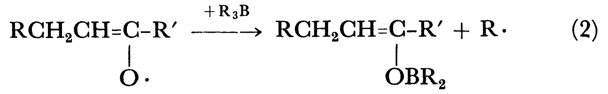
The reaction was initially considered to proceed *via* a cyclic transition state,[1] (co-ordination mechanism). The same type of reaction was shown to occur readily with other α,β-unsaturated carbonyl compounds, such as acrylaldehyde,[2] methacrylaldelyde,[3] α-bromoacrylaldelyde,[3] 2-methylcycloalkanones,[3] and isopropenyl methyl ketone.[4] However, the reaction failed when an alkyl substituent is present in the 3-position as in the cases of *trans*-crotonaldehyde and *trans*-3-penten-2-one.[4] Furthermore, it was discovered that galvinoxyl inhibits the reaction between trialkylboranes and acrylaldehyde or methyl vinyl ketone,[4] and that the reaction with 3-substituted enone systems is effectively promoted by an addition of acyl peroxide[5] or air,[6] or by photochemical means.[5] These reactions therefore were concluded to proceed by a radical chain mechanism as shown in Eq. 2.[4]

The nature of the chain propapagation step may be associated with the formation of the strong boron–oxygen bond in the vinyloxyborane, and is similar to the reaction of alkoxy radicals with trialkylboranes.[7] The failure of the reaction of 3-substituted enone systems in the absence of air or radical initiators may possibly be the result of the relatively short chain length of radical addition to these systems compared to the addition to unsubstituted systems.



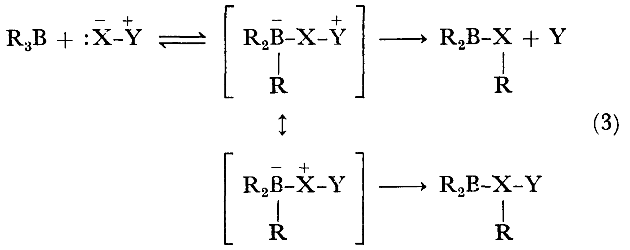
$$R_3B + O_2 \longrightarrow R_2BOO\cdot + R\cdot$$

$$R\cdot + CH_2{=}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}R' \longrightarrow RCH_2\dot{C}H\text{-}\underset{\underset{O}{\|}}{C}\text{-}R' \longleftrightarrow$$



$$RCH_2CH{=}\underset{\underset{O\cdot}{|}}{C}\text{-}R' \xrightarrow{+R_3B} RCH_2CH{=}\underset{\underset{OBR_2}{|}}{C}\text{-}R' + R\cdot \quad (2)$$

On the other hand, there are many examples which suggest that reactions of organoboranes seem to proceed *via* co-ordination mechanisms, including carbonylation reactions,[8] and reactions between organoboranes and α-halocarbanions,[9] ylids,[10] diazo compounds,[11] carbenes,[12] 2-furyllithium,[13] alkyl azides,[14] and α-azidostyrene.[15] The reaction which is considered to proceed by a coordination mechanism usually involves initial Lewis acid–Lewis base interaction between the organoborane and the substrate to form an adduct, which subsequently undergoes rearrangement with migration of an alkyl group from boron to carbon (Eq. 3).



$$R_3B + :\overset{-}{X}\text{-}\overset{+}{Y} \rightleftarrows \left[\underset{\underset{R}{|}}{R_2\overset{-}{B}}\text{-}X\text{-}\overset{+}{Y}\right] \longrightarrow R_2B\text{-}X + \underset{\underset{R}{|}}{Y}$$

$$\updownarrow \qquad (3)$$

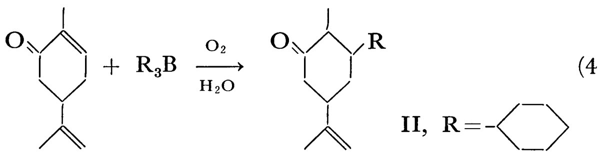
$$\left[\underset{\underset{R}{|}}{R_2\overset{-}{B}}\text{-}\overset{+}{X}\text{-}Y\right] \longrightarrow R_2B\text{-}X\text{-}\underset{\underset{R}{|}}{Y}$$

In order to know if such a Lewis acid–Lewis base interaction is involved even in the radical chain process, we conducted the reaction of trialkylboranes with *d*-carvone and *l*-perillaldehyde in the presence of oxygen.

Results and Discussion

The reaction of *d*-carvone (I) with tricyclohexylborane was carried out in aqueous tetrahydrofuran solution. During the initial stage of the reaction, a 50 mol % oxygen for tricyclohexylborane was bubbled into the solution for 1 h. Although two products, A and B, were detected by GLPC, these were not isolated by preparative GLPC or by preparative TLC. Consequently, the products, A and B, were collected as a mixture by preparative GLPC.

The elemental analysis of the mixture consisting of A and B, coincided with $C_{16}H_{26}O$. The IR spectrum showed an absorption band at 1700 cm^{-1} due to saturated carbonyl group and the PMR spectrum in carbon tetrachloride indicated the following absorptions: 0.93 (d, J=7.0 Hz, $-CH_3$), 0.97 (d, J=7.0 Hz, $-CH_3$), 0.80—2.70 ($-CH_2-$ and $-\overset{|}{C}H$), 1.68 ($CH_3-\overset{|}{C}=$), and 4.76 ($CH_2=\overset{|}{C}-$). The mass spectra, obtained by GC-mass spectrometry, included the following peaks: m/e (relative intensity) 234 (29), 151 (32), 137 (100), 95 (52), 69 (32), and 55 (38) for the product A, and 234 (30), 151 (32), 137 (100), 95 (46), 69 (30), and 55 (34) for the product B. These data suggest that the products are 2-methyl-5-isopropenyl-3-cyclohexyl-1-cyclohexanones (II). The composition of the mixture was estimated by GLPC and the major product, A and the minor one, B, were 63 and 37%, respectively.



I

II, R=

III, R=C_2H_5
IV, R=n-C_3H_7

(4)

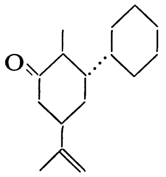
Similarly, 2-methyl-5-isopropenyl-3-ethyl-1-cyclo hexanone (III) and 2-methyl-5-isopropenyl-3-propyl-1-cyclohexanone (IV) were obtained from corresponding trialkylboranes under the same reaction conditions. The results are shown in Table 1.

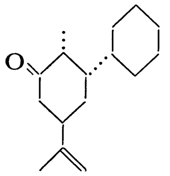
Table 1. Reaction of cyclic α,β-unsaturated carbonyl compounds with trialkylboranes in the presence of oxygen

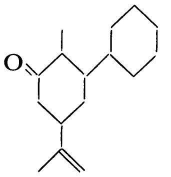
α,β-Unsaturated carbonyl compound	Trialkylborane R_3B	Product	Yield,[a] %
I	Triethylborane	III	55
I	Tripropylborane	IV	60
I	Tricyclohexylborane	II	82
VII	Tricyclohexylborane	VIII	70

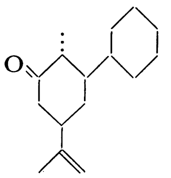
a) Based on the trialkylborane used.

Four stereoisomers, IIa, IIb, IIc, and IId, are considered for II. Namely, the introduction of the cyclohexyl group from the *trans* side against the isopropenyl group affords IIa or IIb, whereas the attack of the cyclohexyl group frcm *cis* side gives IIc or IId.


IIa


IIb


IIc


IId

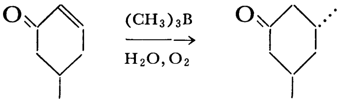
In an attempt to determine the stereochemistry, an epimerization reaction was carried out on the mixture of A and B. Thus, a mixture of A (63%) and B (37%) was treated with sodium methoxide in tetrahydrofuran at 40 °C. The reaction mixture was sampled periodically and analyzed by GLPC. The results are summarized in Table 2.

Table 2. Epimerization of IIa and IIb in the presence of sodium methoxide at 40 °C

Reaction time, h	Percent composition of IIa	and IIb	Total amount of IIa and IIb
0	63	37	100
1	72	28	100
2	74	26	99
3	74	26	100
4	74	26	99

The equilibrium distribution, 74% A to 26% B, was obtained after 2 h, and the total amount of the compounds A and B was not changed during the reaction, demonstrating that they are epimers with one another. Consequently, it was concluded that the cyclohexyl group was introduced from one side to the cyclohexenone ring of d-carvone.

In order to clarify whether the attack of alkyl group of organoboranes occurs *trans* or *cis* to 5-alkyl group of cyclohexenone derivatives, the reaction of 5-methyl-2-cyclohexen-1-one (V) with trimethylborane was examined as a model case of the reaction. From the experimental evidence that the reaction gave only *trans*-3,5-dimethyl-1-cyclohexanone (VI) which was identified by direct comparison of its 2,4-dinitrophenylhydrazone with that of the authentic sample prepared by House and Fischer,[16] it was decided that the methyl group of trimethylborane attacked exclusively from *trans* side to 5-methyl group (Eq. 5).



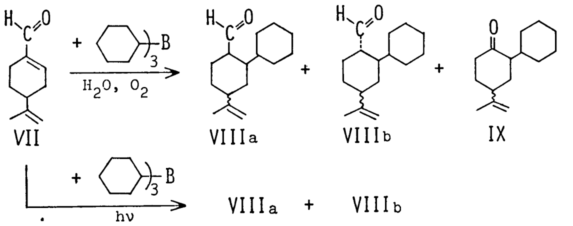
V VI

(5)

From the analogy of the above reaction and the epimerization reaction, reasonable structures for the products, A and B in the reaction of tricyclohexylborane with d-carvone, are assigned to IIa and IIb, respectively. These facts seem to indicate that the cyclohexyl attack occurs *trans* to isopropenyl group in d-carvone.

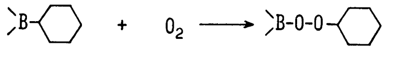
The stereoselective addition of the alkyl group of trialkylborane to 5-alkyl-2-cyclohexen-1-one derivatives mentioned above led us to examine the stereochemistry in the reaction of trialkylborane with other types of cyclic α,β-unsaturated carbonyl compounds. Thus the reaction between tricyclohexylborane and l-perillaldehyde (VII) was carried out under the same conditions. In the reaction, three compounds, C, D, and E were obtained. Although by preparative GLPC and by preparative TLC, the compounds C and D could not be isolated purely, the IR spectrum of the mixture consisting of 60% C and 40% D, collected by preparative

GLPC showed absorptions at 2700 and 1730 cm^{-1} due to saturated aldehyde structure. The PMR spectrum in carbon tetrachloride solution showed the following absorptions in ppm: 0.70—2.50 ($-CH_2-$ and $-\overset{|}{\underset{|}{C}}-H$); 1.73 ($CH_3-\overset{|}{C}=$); 4.71 ($CH_2=\overset{|}{C}-$); 9.70 (s, -CHO); 9.73 (S, -CHO). The mass spectra, obtained by GC-mass spectrometry, included the following peaks: m/e (relative intensity) 234 (41), 216 (12), 151 (64), 109 (100), and 83 (50) for the product C, and 234 (67), 216 (23), 151 (67), 109 (100), and 83 (99) for the product D. The elemental analysis of the mixture coincided with $C_{16}H_{26}O$. These data were all consistent with 2-cyclohexyl-4-isopropenyl-1-cyclohexanecarbaldehydes (VIIIa and VIIIb). On the other hand, the product, E, was determined from its spectroscopic data and its elemental analysis to be 2-cyclohexyl-4-isopropenyl-1-cyclohexanone (IX). Namely, it has an IR absorption peak at 1710 cm^{-1} caused by ketonic carbonyl and PMR peaks in carbon tetrachloride at 0.70—2.60 ($-CH_2-$ and $-\overset{|}{\underset{|}{C}}-H$), 1.70 ($CH_3-\overset{|}{C}=$), and 4.71 ppm ($CH_2=\underset{|}{C}-$). Addition to these data, it gave the following mass peaks: *m/e* (relative intensity) 220 (2), 138 (100), 97 (67), and 95 (46).



(6)

Since our efforts were mainly directed toward learning if a Lewis acid–Lewis base interaction is involved even in the radical chain process of organoborane reaction, a detailed discussion on formation of the abnormal product (IX) was not a main purpose in this paper. The reaction, however, should be considered to proceed through the following path. It is well known that alkyldioxydialkylborane is formed by air-oxidation of trialkylborane.[17]



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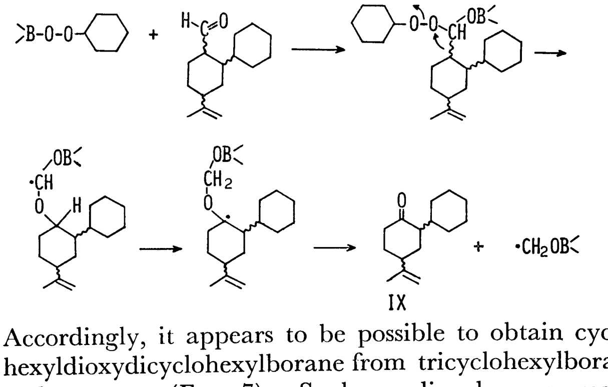


(8)

Accordingly, it appears to be possible to obtain cyclohexyldioxydicyclohexylborane from tricyclohexylborane and oxygen (Eq. 7). Such a dioxyborane reacts with *l*-perillaldehyde in a similar manner which is postulated in Baeyer-Villiger reaction as depicted in Eq. 8.[18]

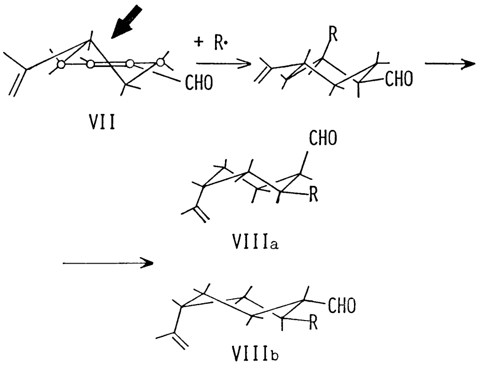
If the above-mentioned mechanism is correct, the formation of such a cyclohexanone derivative (IX) should be excluded by the photochemically induced reaction[5] of tricyclohexylborane with perillaldehyde, because oxygen is not used as a radical initiator. As expected, when the reaction was carried out under UV irradiation in the absence of air, the products were shown to be VIIIa and VIIIb, and no unusual product (IX) was detected.

Table 3. Epimerization of VIIIa and VIIIb in the presence of sodium methoxide at 40 °C

Reaction time, h	Percent composition of VIIIa	and VIIIb	Total amount of VIIIa and VIIIb
0	40	60	100
1	41	59	94
3.5	46	54	97
15	46	54	97

In an attempt to know the structure relationship between VIIIa and VIIIb, epimerization reaction was carried out. Thus, after a mixture of VIIIa (40%) and VIIIb (60%) was treated with sodium methoxide in tetrahydrofuran under the same reaction conditions conducted in a mixture of IIa and IIb, the reaction products were analyzed by GLPC. The results are summarized in Table 3. This evidence shows that VIIIa and VIIIb are epimers with one another, and the equilibrium ratio is 46 : 54. It is reasonable to consider that in both VIIIa and VIIIb, cyclohexyl group, the most bulky substituent on the parent cyclohexane ring, is located in the equatorial position, and that VIIIa in which the aldehyde group is in axial, is less stable than VIIIb having an aldehyde group in the equatorial position. On the other hand, it is known that protons situated in equatorial of cyclohexane ring give rise to resonances downfield from their axial counterparts.[19] In the PMR spectrum of the mixture, 40% VIIIa and 60% VIIIb, two singlet peaks due to the aldehydic protons are observed at $\delta=9.70$ and 9.73 ppm, and their peak ratio is 2 : 3. This fact supports the structures assigned to VIIIa and VIIIb.

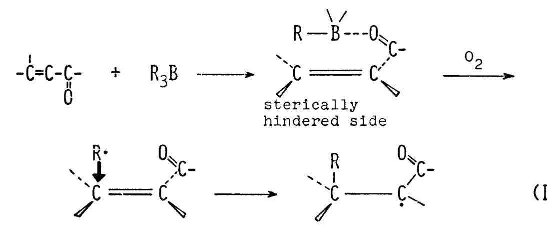
Although the stereochemistry of the isopropenyl group has not been fully clarified, it is considered that the cyclohexyl group of tricyclohexylborane was introduced from one side of cyclohexene ring of *l*-perillaldehyde (Eq. 9).



(9)

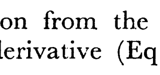
According to an analogous consideration for *d*-carvone mentioned above, it is tentatively concluded that in the products, VIIIa and VIIIb, the cyclohexyl group is located in *trans* with respect to 4-isopropenyl group (Eq. 9).

The highly stereoselective results obtained in this work seem to suggest that even when the reaction of organoboranes with α,β-unsaturated carbonyl compounds proceeds *via* a radical chain process, such a trialkylborane first approaches the carbonyl oxygen from the less hindered side of the molecule because of a Lewis acid–Lewis base intraction, and then the alkyl radical formed from the trialkylborane attacks the β-carbon from the same side of the unsaturated carbonyl derivative (Eq. 10).

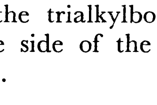


(10)

There are reports which show Lewis base–Lewis acid interactions between boron and oxygen atoms in hydroboration of olefins. For example, in the hydroboration of 7,7-dimethylnorbornene (X)[20], *endo*-attack is favored, 22% *exo*- and 78% *endo*-, while *exo*-attack is predominant in the 7,7-dimethoxy derivative (XI).[21] This result is not explained by means of steric hindrance in hydroboration, but may be rationalized in terms of a more predominant approach of borane to the methoxy side. Consequently, the present proposal is not singular.



X



XI

Recently, there has been an increased interest in methods for effecting 1,4-addition to α,β-unsaturated carbonyl compounds using organometallic compounds.[22–29] Although in such cases of reactions with cyclic α,β-unsaturated carbonyl compounds with substituent, mixtures containing major *trans*-1,4-addition products and minor *cis*-isomers have been reported to be obtained.[22,28,29] We did not detect corresponding *cis*-1,4-addition products in the present experiment.

Experimental

Instruments. Analytical GLPC and preparative GLPC were performed using a Hitachi Model K-53 Gaschromatograph and Varian Aerograph Model-920, respectively. PMR spectra were obtained on Hitachi Model R-20A spectrometer. Chemical shifts are reported in δ unit using TMS as the internal standard. Infra red spectra were recorded on Shimadzu 27G spectrometer. Mass spectra were obtained on Hitachi Model M-52 mass spectrometer. The light source of UV irradiation was 400W Rikosha High Pressure Mercury Lamp.

Materials. *d*-Carvone and 1-perillaldehyde were distilled before use.

Reaction of Tricyclohexylborane with d*-Carvone.* Into a 25-ml round bottomed flask, equipped with a gas inlet, a septum inlet, a reflux condenser and a magnetic stirring bar, 4 mmol of tricyclohexylborane in 4 ml of THF, prepared by hydroboration of cyclohexene, under nitrogen atmosphere and 1 ml of water were charged. To the stirred solution 0.6 g (4 mmol) of *d*-carvone was added at 40 °C, and then 224 ml of air (2 mmol of oxygen) was bubbled for 1 h. After stirring for 12 h at the same temperature, the solution was saturated with sodium chloride, and the upper organic layer was analysed by GLPC. A column, packed with PEG 20 M (15%) on Diasolid M was used at 200 °C. It was indicated that the cyclohexylated products had been obtained in an 82% yield in a ratio of IIa : IIb=63 : 37. In the preparative experiment, the scale of the reaction was enlarged 10 times. After completion of the reaction, the organic layer was separated by decantation and then the lower layer was extracted with ethyl ether several times. The combined organic layer and extracts were dried over anhydrous magnesium sulfate. After removal of the solvent, the products were collected by preparative GLPC.

Anal. Found: C, 81.70; H, 11.40%. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18%.

Reaction of Triethylborane with d*-Carvone.* The reaction was carried out under the same conditions described above. The product, III, (yield, 55%) was collected. The IR spectrum showed an absorption at 1708 cm^{-1}. The PMR (CCl_4) spectrum showed the following absorptions: 0.80—1.05 ($-CH_3$), 1.05—2.70 ($-CH_2-$ and $-\overset{|}{\underset{|}{C}}H$), 1.72 ($CH_3-\overset{|}{C}=$), and 4.76 ($CH_2=\overset{|}{C}-$). The mass spectra (70 eV) included the following peaks: *m/e* (relative intensity) 180 (43), 151 (18), 97 (73), 95 (73), 83 (100), 69 (75), and 55 (50) for the major product, and 180 (38), 151 (8), 97 (44), 95 (64), 83 (100), 69 (56), and 55 (40) for the minor product.

Anal. Found: C, 80.10; H 11.21%. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%.

Reaction of Tripropylborane with d*-Carvone.* A small scale reaction and preparative scale reaction were carried out in the same manner with that of tricyclohexylborane with *d*-carvone. The product IV (yield, 60%) was collected by GLPC. The IR spectrum showed an absorption at 1710 cm^{-1}. PMR (CCl_4) spectrum: 0.85—1.15 ($-CH_3$), 1.15—2.70 ($-CH_2-$ and $-\overset{|}{\underset{|}{C}}H$), 1.75 ($CH_3-\overset{|}{C}=$), and 4.70 ($CH_2=\overset{|}{C}-$). The mass spectra (70 eV) included the following peaks: *m/e* (relative intensity) 194 (24), 151 (14), 97 (100), 95 (56), 69 (46), and 55 (44) for the major product, and 194 (28), 151 (13), 97 (100), 95 (60), 69 (34), and 55 (48) for the minor product.

Anal. Found: C, 80.72; H, 11.63%. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

Epimerization of IIa and IIb. The mixture (47 mg) of IIa (63%) and IIb (37%), and 0.1 ml of 0.1M-sodium methoxide in THF and diphenyl ether (internal standard for GLPC) were added into 1.9 ml of THF. The solution was stirred at 40 °C and 0.1 ml portions of the solution were periodically sampled. They were neutralized with 0.01 M-HCl, saturated with sodium chloride and then extracted with petroleum ether. The extracts were analysed by GLPC. PEG 20 M (15%) supported on Diasolid M was used as the packing materials for GLPC.

Reaction of Trimethylborane with 5-Methyl-2-cyclohexen-1-one. The reaction appratus was composed essentially of two parts. flask A and flask B. The flask A was a 100 ml-three necked flask fitted with a magnetic stirring bar, a gas inlet glass tube, a septum inlet and an efficient condenser. Flask B was a 25 ml-flask equipped with a septum inlet and a condenser. The top of the condenser of a flask A was connected with a Tygon tube which had a syringe needle at the end. The needle was inserted into the bottom of flask B through the septum inlet.

In the flask A 1.62 g (60 mmol) of magnesium turning was placed. The entire reaction apparatus was flushed with nitrogen, and then 8.52 g (60 mmol) of methyl iodide in 20 ml of ethyl ether was added slowly to maintain a gentle reflux. After addition of methyl iodide, the mixture was stirred at 25 °C for 1 h. On the other hand, in flask B were charged 0.66 g (6 mmol) of 5-methyl-2-cyclohexen-1-one prepared by the Crossley's procedure[30] and 2 ml of THF, and the flask was cooled down to -25 °C. Then 8.5 g of boron trifluoride etherate was added dropwise to the Grignard reagent solution in flask A, and the resulting trimethylborane was introduced into flask B. A smooth dissolution of trimethylborane was observed. After generation of the trimethylborane ceased, flask A was flushed with nitrogen to sweep the remained trimethylborane in the flask into the flask B. Then the colling bath was removed, and 1 ml of water was added to the reaction mixture in B. Into the solution in flask B, 400 ml of air was bubbled slowly. After 12 h, the reaction mixture was saturated with sodium chloride, and the organic layer separated was dried over anhydrous magnesium sulfate. Thus, *trans*-3,5-dimethyl-1-cyclohexanone was isolated in a yield of 51% by GLPC at 150 °C (PEG 20 M(15%) supported on Diasolid M). 2,4-Dinitrophenylhydrazone of the ketone, recrystallized twice from ethyl alcohol, melts at 108.0—109.5 °C (literature,[16] 108.4—110 °C).

Reaction of Tricyclohexylborane with l-*Perillaldehyde.* A small scale and preparative scale experiments were carried out in the same manner as described in the reaction of tricyclohexylborane with *d*-carvone. GLPC analysis (Apiezon glease L (15%) on Diasolid M at 180 °C) indicated that the products, VIII and IX, had been obtained in yields of 70% and 18%, respectively.

Anal. Found: C, 81.80; H, 11.38%. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18%.

Spectroscopic data of IX were as follows: IR, 1710 cm^{-1}; PMR (CCl_4), 0.70—2.60 ($-\underset{|}{C}H_2-$ and $-\overset{|}{\underset{|}{C}}H$), 1.70 ($CH_3-\overset{|}{C}=$), and 4.71 ($CH_2=\overset{|}{C}-$); mass spectrum (70 eV), m/e (relative intensity) 220 (2), 138 (100), 97 (67), and 95 (46).

Anal. Found: C, 81.80; H, 11.18%. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98%.

Epimerization Reaction of VIIIa and VIIIb. A reaction was carried out under the same conditions as mentioned in the epimerization of IIa and IIb.

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