m.p. 155.5–156.5°; $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 242 (log ε 4.05), 270 (log ε 3.02), 280 mμ (log ε 2.72).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; neut. equiv., 266. Found: C, 81.10; H, 7.03; neut. equiv., 267.

1,2,3,4-Dibenzcyclohepta-1,3-diene-5-one.—A sample[113] (44.3 mg.) was purified by chromatography on neutral alumina (grade I). Elution with 1:1 ether–benzene gave a colorless, crystalline solid, m.p. 86–87° (lit. m.p. 85–86°,[114] 85–86°,[35] yellow prisms); $\lambda\lambda_{\max}^{\text{isoöctane}}$ 255.5 (log ε 4.03), 283 (log ε 3.30), 295 mμ (log ε 3.32).

1,2,3,4-Dibenzcyclohepta-1,3-diene-6-one was prepared by hydrolysis[115] of 5-cyano-1,2,3,4-dibenzcyclohepta-1,3-diene-6-imine[116] (m.p. 191.5–193°) as described for the 4′,1″-dimethyl derivative. The product, purified by elution with 1:1 hexane–benzene on neutral alumina (grade III) and recrystallization from aq. methanol, had m.p. 78–79.5°; lit. m.p. 78–79°,[116] 78–79.8°.[65]

1,3-Diphenyl-2-propanone (Eastman Kodak Co.) was recrystallized three times from chloroform–ligroin to constant m.p. 34.5–35.5°, lit.[80] m.p. 36–37°.

2-Benznorbornenone was freshly prepared by Oppenauer oxidation of *endo*-benznorbornenol[117] as described[92] for the *exo* isomer. The product was purified by elution with 30% benzene–ether on neutral alumina (grade I) followed by distillation (bath temp. 40–60°, 0.02 mm.). The infrared spectrum was identical in all respects with that reported[92] for the ketone.

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.75. H, 6.76.

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[113] Kindly provided by Prof. H. Rapoport.

[114] H. Rapoport and A. R. Williams, *J. Am. Chem. Soc.*, **71**, 1774 (1949).

[115] T. Sakan and M. Nakagazi, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 2, 23 (1950); *C. A.*, **46**., 5036 (1952).

[116] J. Kenner and E. G. Turner, *J. Chem. Soc.*, 2101 (1911).

[117] Kindly provided by Prof. P. D. Bartlett.

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydroboration. XIV. Rates and Stoichiometry of the Hydroboration of Some Representative Hindered Olefins

BY HERBERT C. BROWN AND A. W. MOERIKOFER[1]

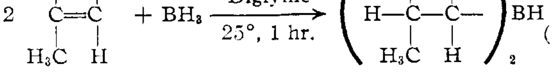
RECEIVED SEPTEMBER 5, 1961

A quantitative study was made of the rates and stoichiometry of the hydroboration of a number of representative hindered olefins in order to establish convenient procedures for the synthesis of mono- and dialkylboranes. Among the trisubstituted aliphatic olefins, 2-methyl-2-butene reacts readily at 0° to form bis-3-methyl-2-butylborane (disiamylborane), whereas the reaction of 2,4,4-trimethyl-2-pentene may be controlled to produce a monoalkylderivative, 2,4,4-trimethyl-3-pentylborane. Similarly, the reaction of the tetrasubstituted olefin, 2,3-dimethyl-2-butene may be controlled to yield the related derivative, 2,3-dimethyl-2-butylborane (thexylborane). In the case of the simple cyclic olefins, the reaction of cyclopentene is not readily controlled short of the tricyclopentyl stage. However, cyclohexene is readily converted into dicyclohexylborane. 1-Methylcyclopentene, 1-methylcyclohexene and α-pinene, all trisubstituted olefins, are readily converted into the corresponding dialkylboranes, although diisopinocampheylborane (from α-pinene) exhibits some tendency toward a reversible dissociation. Finally, the possible synthesis of the corresponding dialkylboranes from 2-methyl-1-propene, 2-methyl-1-butene, 2,4,4-trimethyl-1-pentene and β-pinene was explored. Addition of the olefins to a solution of the theoretical quantity of diborane in tetrahydrofuran at 0° give yields of 60–70% of the desired dialkylboranes, 10% of free borane and 20% of the corresponding trialkylborane. Consequently, this investigation has opened up convenient synthetic procedures for the synthesis of a number of mono- and dialkylboranes of interest as selective hydroborating and reducing agents.

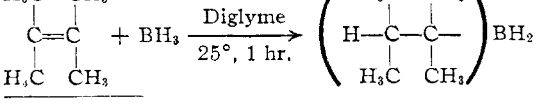
In our initial exploration of the scope of the hydroboration reaction, we observed that the great majority of olefins reacted readily under the standard conditions, 1 hr. at 25°, to yield the corresponding trialkylborane (1).[2] However, in the

$$6RCH{=}CH_2 + B_2H_6 \xrightarrow[25°,\ 1\ \text{hr.}]{\text{Diglyme}} 2(RCH_2CH_2)_3B \quad (1)$$

case of certain highly substituted olefins, such as 2-methyl-2-butene and 2,3-dimethyl-2-butene, the reaction appeared to stop short of this stage, yielding the corresponding dialkylborane (2) and monoalkylborane (3).



$$2\,(CH_3)_2C{=}CHCH_3 + BH_3 \xrightarrow[25°,\ 1\ \text{hr.}]{\text{Diglyme}} \left(H{-}\overset{H_3C}{\underset{H_3C}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}\right)_2 BH \quad (2)$$



$$(CH_3)_2C{=}C(CH_3)_2 + BH_3 \xrightarrow[25°,\ 1\ \text{hr.}]{\text{Diglyme}} \left(H{-}\overset{H_3C}{\underset{H_3C}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\right) BH_2 \quad (3)$$

Since that time the product from 2-methyl-2-butene, bis-3-methyl-2-butylborane or disiamylborane,[3,4] has proven of major value as a selective hydroborating[5–7] and reducing agent.[8] Similarly, the trimethylamine addition compound of *t*-butylborane has been utilized as a hydroborating agent.[9] Consequently, it appeared desirable to explore in more detail the reaction of a number of representative hindered olefins with diborane in the hope of defining conditions which would permit the convenient synthesis of monoalkyl- and dialkylboranes.

Results and Discussion

The olefins included in this study, grouped according to structural type, are listed below.

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[1] Post-doctorate research associate, 1960–1961, on a Research Award (585-C) provided by the Petroleum Research Fund of the American Chemical Society.

[2] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

[3] It is convenient to discuss these compounds as derivatives of borane, BH_3, even though both borane and these alkyl derivatives normally exist as dimers.[4] Similarly, it is convenient to discuss the reactions in terms of the molecules of olefin reacting under the indicated conditions with each borane (BH_3) or borane equivalent ($^3/_4NaBH_4 + BF_3$).

[4] H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, in press (1962).

[5] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

[6] H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961); G. Zweifel, K. Nagase and H. C. Brown, *ibid.*, **84**, 190 (1962).

[7] H. C. Brown and A. Moerikofer, *ibid.*, **83**, 3417 (1961).

[8] H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).

[9] M. F. Hawthorne, *ibid.*, **83**, 2541 (1961).

I. Trisubstituted acyclic, $R'HC{=}CR_2$
  - 2-Methyl-2-butene
  - 2,4,4-Trimethyl-2-pentene

II. Tetrasubstituted acyclic, $R_2C{=}CR_2$
  - 2,3-Dimethyl-2-butene

III. Simple cyclic, $\underline{CH{=}CH(CH_2)n}$
  - Cyclopentene
  - Cyclohexene

IV. Substituted cyclic, $R\underline{C{=}CH(CH_2)}n$
  - 1-Methylcyclopentene
  - 1-Methylcyclohexene
  - α-Pinene

V. Disubstituted terminal, $RR'C{=}CH_2$
  - 2-Methyl-1-propene
  - 2-Methyl-1-butene
  - 2,4,4-Trimethyl-1-pentene
  - β-Pinene

The procedure consisted of mixing the olefin in diglyme with the calculated quantity of sodium borohydride (generally 3 olefins per borane equivalent). Hydroboration was achieved by adding boron trifluoride in diglyme to the solution, maintaining the temperature constant at either 0 or 25°. At appropriate intervals of time, samples were removed and analyzed for residual olefin by gas chromatographic analysis.

In a number of cases an alternate procedure was utilized. The olefin was added to a standard solution of diborane in tetrahydrofuran at 0° or 25°, and the decrease of the olefin with time followed as above.

Finally, in the case of the disubstituted terminal olefins, Group V, it proved necessary to have recourse to an alternative procedure to follow the reaction course, since the reactions were exceedingly fast and the olefin was completely utilized immediately following addition. In these cases only two olefins per borane were reacted. Methanol was then added to convert the reaction products to methyl borate, borinic and boronic methyl esters. Then distillation was utilized to achieve an analysis of the reaction products.[10]

2-Methyl-2-butene.—At 25° in diglyme, 2-methyl-2-butene (1.5 *M*) reacts rapidly with sodium borohydride–boron trifluoride (0.5 *M* in borane equivalent) to form disiamylborane, and the reaction then proceeds at a modest rate toward the formation of trisiamylborane (Fig. 1). At 0°, the initial product, disiamylborane, precipitates from solution as a white solid. Reaction proceeds beyond this stage, but at a relatively slow pace—even after 24 hr., the formation of trisiamylborane is only 40% complete (Fig. 1).

In the same way, 2-methyl-2-butene in tetrahydrofuran was added to a solution of diborane in the same solvent at 0°, giving a solution which was 1.5 *M* in the olefin and 0.5 *M* in borane. In this solvent no precipitation of disiamylborane was observed. Here also a rapid reaction to form disiamylborane was observed, with the subsequent reaction to the trisiamylborane stage proceeding at a much slower pace (Fig. 2).

The reaction in diglyme appears to proceed at a somewhat faster pace than that in tetrahydrofuran, in spite of the precipitation of the intermediate in the diglyme system. Thus, after 24 hr. at 0°, the olefin utilization in diglyme was 2.40 per borane equivalent, whereas in tetrahydrofuran it was 2.33.

These experiments involved the use of a large excess of olefin over that required to form disiamylborane. However, the large difference in rates of the first two hydroboration steps (to form $SiaBH_2$ and Sia_2BH) with that of the third, clearly indicates the practicality of proceeding cleanly to the disiamylborane stage.

Accordingly, experiments were run in which the olefin (1.5 *M*) was treated at 0° with the theoretical quantity of diborane (0.75 *M* BH_3) to form disiamylborane. The results are shown in Fig. 2. A careful study of the initial phases of the reaction with a somewhat less concentrated solution (1.2 *M* 2-methyl-2-butene, 0.6 *M* borane) revealed that the olefin reaction is 94% complete in 1 hr., 96.5% in 2 and 98% in 4 (Fig. 3). In 6–9 hours, the utilization of the olefin is essentially complete. These conditions were adopted for the synthesis of disiamylborane in a study of the rate of reaction of this derivative with *cis–trans* and cyclic olefins.[7]

2,4,4-Trimethyl-2-pentene.—Hydroboration of 2,4,4-trimethyl-2-pentene in diglyme at 25° under the standard conditions (1.5 *M* in olefin, 0.5 *M* in borane equivalent) proceeds rapidly to the monoalkylborane stage but relatively slowly beyond. After 24 hr. the uptake of olefin was only 1.8 per borane equivalent (Fig. 4). A separation of the reaction mixture into two liquid phases was observed during the course of the reaction.

At 0° the reaction also proceeded rapidly to the monoalkylborane stage (40 min.) but only very slowly beyond. After 24 hr., the olefin reacted per borane equivalent was only 1.3 (Fig. 4). Here also a separation into two phases was observed (the lower phase constituted about one-fifth of the total volume).

In order to avoid possible complications arising from the separation into two phases, the concentrations of the reactants were reduced. At 25° a reaction mixture 1.0 *M* in 2,4,4-trimethyl-2-pentene and 0.33 *M* in borane equivalent, remained homogeneous. The uptake of olefin approached the value 2 asymptotically, corresponding to the complete formation of the dialkylborane in 4 days (Fig. 5).

In view of the marked difference in rates of the first and second hydroboration stages, it appeared that it might be possible to direct the reaction at 0° to the formation of the monoalkylborane, 2,4,4-trimethyl-3-pentylborane. Accordingly, the concentration of the hydroborating reagent was maintained constant (0.5 *M* in borane equivalent) while the concentrations of the olefin were varied to give initial ratios of 2,4,4-trimethyl-2-pentene/BH_3 of 3.0, 1.5, 1.2 and 1.0. The results are shown in Fig. 6.

In the experiments involving an excess of 2,4,4-trimethyl-2-pentene, the reactions proceed quite rapidly to the monoalkylborane stage, but further reaction with the excess olefin occurs, even if quite slowly. Thus in 24 hr., the observed ratios

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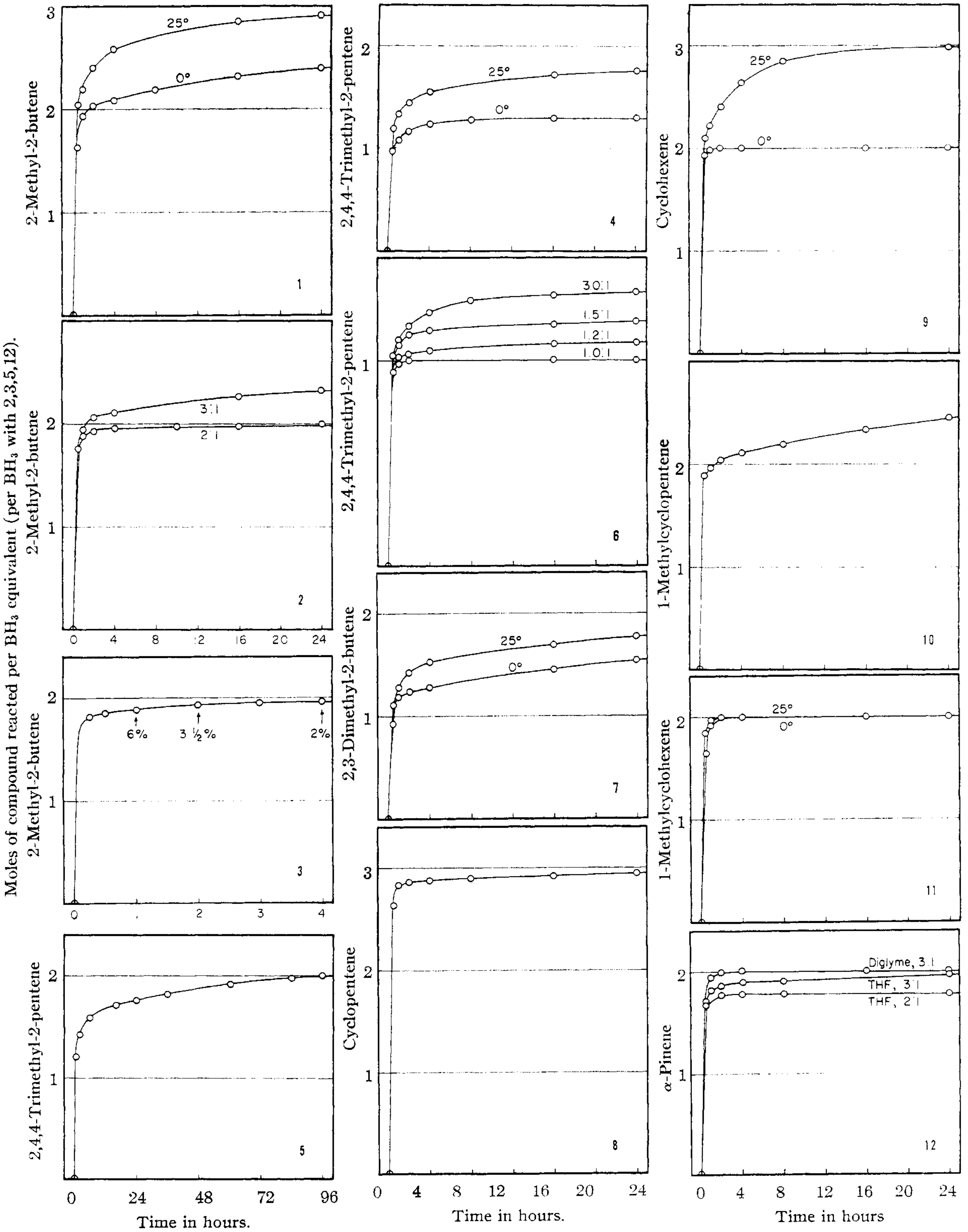
(10) The procedure was similar to that utilized in a study of the equilibration of diborane with tri-*n*-pentylborane and tricyclopentylborane. H. C. Brown, A. Tsukamoto and D. B. Bigley, *J. Am. Chem. Soc.*, **82**, 4703 (1960).



of olefin reacted per BH_3 were 1.35, 1.20 and 1.08 for reaction mixtures with an initial ratio of olefin BH_3 of 3.0, 1.5 and 1.2, respectively.

However, in the experiment involving the theoretical quantity of 2,4,4-trimethyl-2-pentene, the reaction appears to proceed cleanly to the desired monoalkylborane.[11,12]

Similar reactions were carried out in tetrahydrofuran solutions at 0° with initial olefin/BH_3 ratios

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[11] To establish rigorously that the reaction proceeds cleanly in a 1:1 ratio would require the demonstration of the absence of any residual diborane or the isolation of the reaction product. These experiments are described in the following paper dealing with the isolation and characterization of these mono- and dialkylboranes.[1]

[12] The hydroboration of *trans*-di-*t*-butylethylene has been

Fig. 1.—Reaction of 2-methyl-2-butene (1.5 M) with sodium borohydride-boron trifluoride (0.5 M in borane equivalent) in diglyme at 0 and 25°.

Fig. 2.—Reaction of 2-methyl-2-butene (1.5 M) with diborane (0.5 M in BH_3) in tetrahydrofuran at 0°. Reaction of 2-methyl-2-butene (1.5 M) with diborane (0.75 M in BH_3) in tetrahydrofuran at 0°.

Fig. 3.—Preparation of disiamylborane: reaction of 2-methyl-2-butene (1.2 M) with diborane (0.6 M BH_3) in tetrahydrofuran at 0°.

Fig. 4.—Reaction of 2,4,4-trimethyl-2-pentene (1.5 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 0 and 25°.

Fig. 5.—Reaction of 2,4,4-trimethyl-2-pentene (1.0 M) with sodium borohydride-boron trifluoride (0.33 M in borane equivalent) in diglyme at 25°.

Fig. 6.—Reaction of 2,4,4-trimethyl-2-pentene in various initial concentrations (1.5 M, 0.75 M, 0.60 M, 0.50 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 0°.

Fig. 7.—Reaction of 2,3-dimethyl-2-butene with sodium borohydride-boron trifluoride (0.5 M in borane equivalent) in diglyme at 0 and 25°.

Fig. 8.—Reaction of cyclopentene (1.5 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 0.

Fig. 9.—Reaction of cyclohexene (1.5 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 0 and 25°.

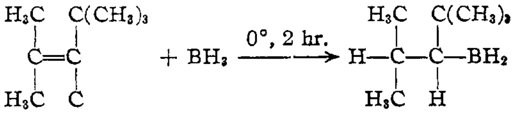
Fig. 10.—Reaction of 1-methylcyclopentene (1.5 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 0°.

Fig. 11.—Reaction of 1-methylcyclohexene (1.5 M) with sodium borohydride-boron trifluoride (0.5 M in borane equivalent) in diglyme at 0 and 25°.

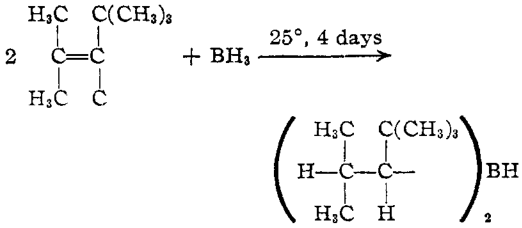
Fig. 12.—Reaction of α-pinene (1.5 M) with sodium borohydride–boron trifluoride (0.5 M in borane equivalent) in diglyme at 25°. Reaction of α-pinene (1.5 M) with diborane (0.5 M in BH_3) in tetrahydrofuran at 25°. Reaction of α-pinene (1.5 M) with diborane (0.75 M in BH_3) in tetrahydrofuran at 25°.

of 3:1 and 1:1. The results were almost identical with those realized in diglyme and need not be described in detail. In this case also the reaction in tetrahydrofuran appears to be slightly slower than the corresponding reaction in diglyme. Thus in the 3:1 experiment, a total of 1.2 olefins per borane had reacted in 24 hr. in tetrahydrofuran at 0°, as compared to the value of 1.3 observed for the corresponding experiment in diglyme.

In summary, it appears that at 0°, with the theoretical quantity of 2,4,4-trimethyl-2-pentene, the reaction can be directed to the synthesis of 2,4,4-trimethyl-3-pentylborane (eq. 4), whereas at 25°, with excess olefin and a long reaction time, it is possible to drive the reaction to the formation of bis-(2,4,4-trimethyl-3-pentyl)-borane (eq. 5).



$$\underset{H_3C\quad C}{\overset{H_3C\quad C(CH_3)_3}{C{=}C}} + BH_3 \xrightarrow{0^\circ,\ 2\text{ hr.}} H{-}\underset{H_3C\quad H}{\overset{H_3C\quad C(CH_3)_3}{C{-}C}}{-}BH_2 \qquad (4)$$

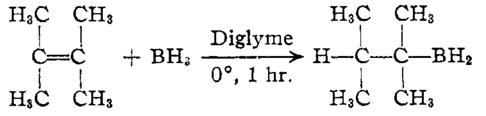


$$2\ \underset{H_3C\quad C}{\overset{H_3C\quad C(CH_3)_3}{C{=}C}} + BH_3 \xrightarrow{25^\circ,\ 4\text{ days}} \left(H{-}\underset{H_3C\quad H}{\overset{H_3C\quad C(CH_3)_3}{C{-}C}}{-}\right)_2 BH \qquad (5)$$

2,3-Dimethyl-2-butene.—The hydroboration of 2,3-dimethyl-2-butene resembles that of 2,4,4-trimethyl-2-pentene quite closely. Thus at 25° the hydroboration in diglyme proceeds rapidly to the monoalkylborane stage, with further reaction to the dialkylborane stage proceeding at a moderate pace. In 24 hr. the olefin/BH_3 ratio rises to 1.78. At 0°, the second stage is significantly slower, with the olefin/BH_3 ratio rising to 1.52 in 24 hr. The results are summarized in Fig. 7. During the greater portion of the reaction, the solution remains clear. Only in the latter stages of the reaction at 25° is a white precipitate observed. This is believed to be the dialkylborane derivative.

It therefore appears that the steric influence of the four methyl groups of 2,3-dimethyl-2-butene are quite similar to that of the three alkyl groups of 2,4,4-trimethyl-2-pentene (two methyl and one t-butyl).

As in the case of 2,4,4-trimethyl-2-pentene, it proved possible to proceed to the formation of the monoalkylborane[13] by treating the theoretical quantity of the olefin with hydroborating agent, in diglyme, tetrahydrofuran or ethyl ether[4] (eq. 6).



$$\underset{H_3C\quad CH_3}{\overset{H_3C\quad CH_3}{C{=}C}} + BH_3 \xrightarrow[0^\circ,\ 1\text{ hr.}]{\text{Diglyme}} H{-}\underset{H_3C\quad CH_3}{\overset{H_3C\quad CH_3}{C{-}C}}{-}BH_2 \qquad (6)$$

Cyclopentene.—The hydroboration of cyclopentene in diglyme at 0° proceeded rapidly to the formation of the tricyclopentylborane. Within 1 hr. the observed ratio of cyclopentene utilized per borane equivalent was essentially quantitative, 2.9, and did not change significantly with time (Fig. 8). A white precipitate, presumably tricyclopentylborane, was observed.

The results indicated that it would not be possible to achieve by these methods a simple synthesis of dicyclopentylborane. It should be pointed out that an earlier experiment in which cyclopentene was added to excess diborane in tetrahydrofuran had produced a 64% yield of dicyclopentylborane.[10] However, while the presence of excess diborane and cyclopentylborane offered no important disadvantage for the synthesis and isolation of dicyclopentylborinic acid,[10] the presence of these by-products introduces major difficulties for the present objective—the convenient synthesis of pure mono- and dialkylboranes for application as selective hydroborating and reducing agents.

Cyclohexene.—In the case of cyclohexene the reaction at 25° proceeded rapidly to the dicyclo-

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observed to cease at the monoalkylborane stage. T. J. Logan and T. J. Flaut, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

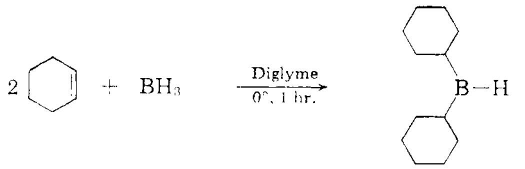
[13] The product, 2,3-dimethyl-2-butylborane, promises to be a valuable reagent for selective hydroborations and reductions, as in the case of the related product, disiamylborane. In view of the advantages of having a common name for a substance in general use, we have adopted the term thexylborane (contracted from t-hexyl) to refer to this derivative.

hexylborane stage, with further reaction to the formation of tricyclohexylborane being definitely slower. Indeed, at 0° the reaction proceeds cleanly to the formation of dicyclohexylborane, with no significant further reaction indicated (Fig. 9).

Both di- and tricyclohexylborane possess very limited solubilities in diglyme, so the reactions at both 0 and 25° are accompanied by the precipitation of product.

In large part, the ready formation of dicyclohexylborane at 0° must be the result of the low solubility of the compound in diglyme at that temperature. However, cyclohexene is also much less reactive toward hydroboration than cyclopentene.[6,7] This lower reactivity of cyclohexene probably also contributes to the ready synthesis of dicyclohexylborane.

In any event, the controlled hydroboration of cyclohexene provides a simple synthetic route to dicyclohexylborane (eq. 7).

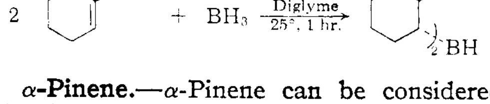


(7)

1-Methylcyclopentene.—The hydroboration of 1-methylcyclopentene resembles closely the corresponding reactions of 2-methyl-2-butene. At 0°, the reaction proceeds rapidly to the dialkylborane stage and slowly beyond to the trialkylborane. Thus, the formation of the dialkylborane appeared to be essentially complete in 1 hr. and had proceeded to an olefin/BH_3 ratio of 2.10 after 4 hr. and 2.46 after 24 hr. (Fig. 10). The reaction proceeded with the formation of a heavy precipitate, presumably bis-(*trans*-2-methylcyclopentyl)-borane.

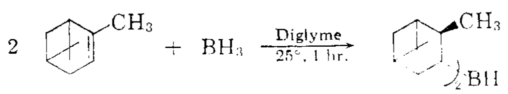
1-Methylcyclohexene.—In the parent olefins, cyclopentene and cyclohexene, the change from the 5- to the 6-ring greatly facilitated the formation of the dialkylborane. The same effect of ring size is observed in the 1-methyl derivatives. Thus, both at 0° and 25°, the hydroboration of 1-methylcyclohexene proceeds rapidly and cleanly to the formation of the dialkylborane, bis-(*trans*-2-methylcyclohexyl)-borane, with no tendency evident for the reaction to proceed to the trialkylborane stage (Fig. 11).

Here also the product is essentially insoluble in the reaction mixture and precipitates during the course of the reaction. Presumably the clean formation of the dialkylborane is facilitated by both the low solubility of the product and the low reactivity of the 1-methylcyclohexene (eq. 8).



(8)

α-Pinene.—α-Pinene can be considered a derivative of 1-methylcyclohexene. Under the usual conditions (1.5 *M* α-pinene, 0.5 *M* borane equivalent, 25°, diglyme) α-pinene is readily converted into diisopinocampheylborane, which precipitates from solution (eq. 9).



(9)

A similar experiment, carried out with diborane in tetrahydrofuran, gave similar results. The product, although it precipitated from the solution, was evidently more soluble in tetrahydrofuran than in diglyme. Indeed, at 40° all of the material dissolved.

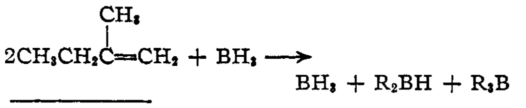
In tetrahydrofuran the reaction did not proceed as completely toward the formation of diisopinocampheylborane as in the related experiment in diglyme (Fig. 12). It appeared that we might be dealing with an equilibrium situation, in which the much lower solubility of the product in diglyme forced the reaction essentially to completion. This conclusion is confirmed by the results of treating α-pinene with diborane in tetrahydrofuran in a ratio of olefin/BH_3 of 2:1. In this case, a maximum of 1.8 moles of α-pinene react per mole of borane present (Fig. 12). Consequently, it appears that in this case diglyme offers advantages for the formation of a pure product.[14,15]

Disubstituted Terminal Olefins.—The study of the hydroboration of 2-methylpropene (isobutylene), 2-methyl-1-butene, 2,4,4-trimethyl-1-pentene and β-pinene was undertaken in the hope that this would lead to a practical synthesis of one or more dialkylboranes in which the alkyl groups would have smaller steric requirements than in the syntheses previously developed.

The methods utilized in the earlier experiments proved not to be applicable. Thus treatment of β-pinene (1.5 *M*) in tetrahydrofuran with diborane in the same solvent (0.5 *M* in borane) at 0° led to a rapid reaction. The first point, taken within a few minutes after the reagents had been mixed, showed essentially complete utilization of the β-pinene.

Accordingly, the procedure was modified. The olefin was added slowly to the theoretical quantity of diborane in tetrahydrofuran (2 olefin per borane) at 0°. After 2 hr., methanol was added to convert diborane and the alkylboranes into the corresponding methyl esters. Distillation readily yielded a mixture of methyl borate and tetrahydrofuran, which could be analyzed for boron by titration with mannitol.

In the case of 2-methylpropene and 2-methyl-1-butene,[16] distillation at low pressure revealed the essential absence of the monoalkylboronic ester. Consequently, in these cases the reaction must proceed to form only the dialkylborane and trialkylborane (eq. 10).


$$2CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2 + BH_3 \longrightarrow BH_3 + R_2BH + R_3B \quad (10)$$

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[14] A more detailed study of the equilibrium was made with the aid of infrared spectroscopy. The results will be reported in another paper.[4]

[15] Diisopinocampheylborane has proven to be very useful as an asymmetric hydroborating agent. It has made possible the synthesis of alcohols with optical purities in the range of 80–90%. H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961).

[16] We wish to express our appreciation to Dr. D. B. Bigley who carried out this particular experiment.

This reaction was assumed for the hydroboration of 2,4,4-trimethyl-1-pentene and β-pinene. On this basis, each mole of free diborane found in the reaction product means the formation of 2 moles of trialkylborane and an equivalent decrease in yield of the desired dialkylborane.

The results are summarized in Table I.

TABLE I

PRODUCTS OF THE REACTION OF OLEFIN WITH DIBORANE (2 OLEFIN/1 BH_3) IN TETRAHYDROFURAN

	Reactants					
Olefin	Olefin, mmoles	BH_3, mmoles	BH_3[a]	Products, % RBH_2	R_2BH	R_3B
2-Methylpropene	300	150	12	0[b]	64[d]	24
2-Methyl-1-butene	300	150	11	0[b]	53[d]	24
2,4,4-Trimethyl-1-pentene	100	50	10	0[c]	70	20
β-Pinene	100	50	13	0[c]	61	26

[a] Determined as methyl borate after methanolysis. [b] No methyl ester of the alkylborinic acid obtained on distillation of the reaction products. [c] Assumed on basis of results for 2-methylpropene and 2-methyl-1-butene. [d] Isolated as methyl esters.

The results are quite similar in the four cases. The reaction proceeds with the formation of 10–13% of residual borane, indicating the formation of 20–26% of trialkylborane. Although the formation of 60–70% of the dialkylborane is far from the essentially quantitative syntheses described for other cases in this paper, there are instances where these derivatives could be useful. We shall explore this question in a subsequent study.

Conclusions.—The present study has indicated the conditions whereby the convenient synthesis of a number of mono- and dialkylboranes may be achieved *via* hydroboration. These include disiamylborane, 2,4,4-trimethyl-3-pentylborane, thexylborane, dicyclohexylborane, bis-(*trans*-2-methylcyclopentyl)-borane, bis-(*trans*-2-methylcyclohexyl)-borane and diisopinocampheylborane.

A study of the physical and chemical properties of several of these derivatives is reported in the following paper.[4] Several of these derivatives exhibit very useful characteristics as selective hydroborating and reducing agents. A detailed report of these observations will be published shortly.[17]

Experimental Part

Materials and Techniques.—The olefins utilized, the purification of the solvents and the general techniques have been described in previous papers of this series.

Procedure.—The general procedure may be described in detail for the reaction of 2-methyl-2-butene with diborane.

The apparatus consisted of a 200-ml. three-neck flask, equipped with a condenser, a thermometer and a pressure-equalized dropping funnel. A magnetic stirrer with a teflon-covered stirrer bar was used to provide good mixing. The flask was equipped with a short side-arm, fitted with a rubber serum cap to permit samples to be withdrawn with a hypodermic syringe without disturbing the system. All equipment was vigorously dried and a static nitrogen atmosphere with a pressure several mm. above atmospheric was maintained throughout each experiment.

In the flask was placed 1.44 g. (0.039 mole, 4% excess) of sodium borohydride, 10.5 g. (0.150 mole) of 2-methyl-2-butene and 3.5 g. (0.050 mole) of cyclohexane (utilized as an internal standard for the gas chromatographic analyses) in sufficient diglyme to provide 86.5 ml. of solution. The dropping funnel contained 13.5 ml. of a 3.7 M solution of boron trifluoride (0.050 mole) in diglyme. Hydroboration was achieved by adding the boron trifluoride over a period of 25–30 min., maintaining the temperature constant (±1%) by an external bath. Initially, the sodium borohydride precipitates from the olefin–diglyme solution, but it redissolves during the course of the addition of the boron trifluoride.

Thirty minutes after the beginning of the experiment (*i.e.*, almost immediately following completion of the addition of the boron trifluoride), a 0.5 ml. sample was withdrawn for the analysis. Further samples were removed after 1,2,4, 16 and 24 hr. Each sample, removed with a hypodermic syringe, was injected directly into a small vial containing 0.03 ml. of 1-hexene to react with residual boron–hydrogen bonds in order to quench the reaction. The vials were maintained at −78° prior to the analysis. To proceed with the analysis, 0.5 ml. of a saturated solution of sodium chloride in water was added to each vial at 0° to provide a clear organic layer. An aliquot of this layer was removed and analyzed for the cyclohexane/2-methyl-2-butene ratio on an adiponitrile column.

The results are shown in Fig. 1.

To illustrate the material balances realized, 2.8 mmoles of hydrogen were evolved during the hydroboration at 0°. After 24 hr., 120 mmoles of 2-methyl-2-butene had been utilized, corresponding to 120 mmoles of hydride. Residual hydride was determined as hydrogen gas by injecting 10 ml. of 50% aqueous ethylene glycol into the reaction flask. There was evolved 28 mmoles of hydrogen. Thus the total hydride accounted for is 150.8 mmole.

The procedure in tetrahydrofuran was quite similar. Standard solutions of diborane in tetrahydrofuran (2.0–2.4 M in BH_3) were prepared and stored at 0° in the cold room.[5-7] The solutions were analyzed for hydride by treating an aliquot with water and for boron by titrating the hydrolyzed aliquot with base in the presence of mannitol. The same equipment was utilized for the hydroboration. In the flask was placed 10.5 g. (0.150 mole) of 2-methyl-2-butene, 25 ml. of a 6.0 M solution, 3.5 g. (0.050 mole) cyclohexane, 8.3 ml. of a 6.0 M solution and 42.9 ml. of tetrahydrofuran. The mixture was cooled to 0° and 23.8 ml. of a 2.10 M solution of borane in tetrahydrofuran (0.050 moles) was added dropwise from the funnel over 25–30 min. This procedure provided a total volume of solution of 100 ml., 0.5 M in BH_3, 1.5 M in olefin. The solution remained homogeneous. Aliquots were removed as before, quenched with 1-hexene and analyzed on adiponitrile columns. (In these experiments, the treatment with saturated sodium chloride solution was omitted, since the solutions were already clear.)

During the hydroboration, 5.4 mmoles of hydrogen were evolved. After 24 hr., 116.8 mmoles of olefin had reacted. Hydrolysis with 50% aqueous ethylene glycol indicated the presence of 23.8 mmoles of hydrogen. Thus, the material balance accounts for 145 of the 150 mmoles of hydride introduced.

Similar material balances on hydride were realized in all of the experiments.

Hydroboration of 2-Methyl-1-butene.—Over a period of 1 hr., 21.0 g. (0.300 mole) of 2-methyl-1-butene was added at 0° to 150 ml. of a standardized solution of diborane in tetrahydrofuran (1.00 M in BH_3). After a second hour at 0°, 100 ml. of methanol was added slowly. Hydrogen was evolved, being completed under gentle reflux. A total of 130 mmoles was collected. The solvent, excess methanol and methyl borate were removed by distillation. Analysis by sodium hydroxide titration in presence of mannitol indicated the presence of 17 mmoles of methyl borate, corresponding to 11% of the original borane.

The residue was distilled under reduced pressure: 14.5 g. (79 mmoles) of bis-(2-methyl-1-butyl)-borinic methyl ester, b.p. 90–95° at 20 mm., a yield of 54%, and 7.9 g. (36 mmoles) of tris-(2-methyl-1-butyl)-borane, b.p. 125–130° at 20 mm., a yield of 24%. No fraction corresponding to the methyl ester of 2-methyl-1-butylboronic acid was observed.

The methyl ester of bis-(2-methyl-1-butyl)-borinic acid was redistilled: b.p. 91° at 20 mm., $n^{20}D$ 1.4225.

Anal. Calcd. for $C_{11}H_{25}BO$: C, 71.75; H, 13.69. Found: C, 71.90; H, 13.58.

The tris-(2-methyl-1-butyl)-borane was analyzed, $n^{20}D$ 1.4353.

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[17] With Dr. George Zweifel.

Anal. Calcd. for $C_{15}H_{33}B$: C, 80.4; H, 14.8. Found: C, 79.5; H, 14.5.

Hydroboration of β-Pinene.—β-Pinene, 100 mmoles, in 100 ml. of tetrahydrofuran was added slowly over 90 min. at 0° to 50 mmoles of borane in 50 ml. of the solvent. The clear solution was allowed to warm up to room temperature, then treated with methanol. There was obtained 49.8 mmoles of hydrogen. Distillation under reduced pressure yielded 6.37 mmoles of methyl borate, a yield of 12.8%.

Acknowledgment.—We are deeply indebted to Dr. Gerald J. Klender for his generous assistance with several of the experiments.

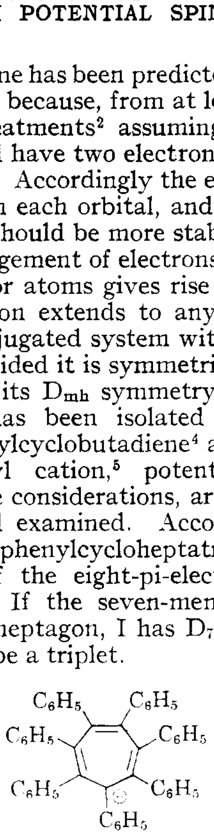
COMMUNICATIONS TO THE EDITOR

HEPTAPHENYLCYCLOHEPTATRIENYL ANION, A SINGLET WITH POTENTIAL SPIN DEGENERACY[1]

Sir:

Cyclobutadiene has been predicted to have a triplet ground state because, from at least some molecular orbital treatments[2] assuming four-fold symmetry, it should have two electrons in a degenerate pair of orbitals. Accordingly the electrons could be unpaired, one in each orbital, and the resulting diradical species should be more stable than one with any other arrangement of electrons. An equivalent consideration for atoms gives rise to Hund's rules.

This prediction extends to any derivative of a monocyclic conjugated system with 4n pi electrons in the ring provided it is symmetrically substituted so as to retain its D_{mh} symmetry, but to date no such system has been isolated and examined.[3] Both tetraphenylcyclobutadiene[4] and pentaphenylcyclopentadienyl cation,[5] potential triplets according to these considerations, are too unstable to be isolated and examined. Accordingly we have prepared heptaphenylcycloheptatrienyl anion (I), a derivative of the eight-pi-electron cycloheptatrienyl anion. If the seven-membered ring is a planar regular heptagon, I has D_{7h} symmetry[6] and is predicted to be a triplet.



I

Heptaphenylcycloheptatrienyl bromide (II), prepared by the elegant procedure of Battiste,[7] was suspended in dimethoxyethane and treated with an excess of potassium metal in a modified Schlenk tube *in vacuo*. The resulting deep purple solution (0.04 m.) of the potassium salt of I was filtered into another compartment and a portion was sealed into a tube and examined in the n.m.r. A complex multiplet for the phenyls was found at 3.25 τ, and there was no measurable broadening of the solvent line. No e.s.r. signal was detectable. The remainder of the solution was quenched with D_2O, and the organic residue isolated was found to be pure heptaphenylcycloheptatriene,[8] containing a deuteron on the seven-membered ring (the aliphatic proton of heptaphenylcycloheptatriene is found at 4.73 τ in the n.m.r.; this band is missing in our product and in authentic deuterated material prepared by $LiAlD_4$ reduction of II). The aqueous solution, by titration, contained an equivalent amount of KOD. If diethyl ether was used as solvent the potassium salt of I could be collected as a purple precipitate; this salt with D_2O also yielded the deuteriocycloheptatriene as the only organic product. The 0.04 *m* solution of I in dimethoxyethane was examined on the Gouy balance, and no net paramagnetism was detectable.

By contrast, solvent line broadening[9] was observed with a 0.004 *m* solution of di-*t*-butylnitroxide[10] in dimethoxyethane and was quite pronounced with a 0.04 *m* solution. The latter solution also gave easily detectable paramagnetism in measurements on the Gouy balance. Accordingly, it is apparent that I is not a diradical. This conclusion is confirmed by the observation that when the solution of I was added to an excess of II, the resulting russet solution now gave a strong e.s.r. signal, and paramagnetism was detected by Gouy balance measurements and from considerable solvent line broadening in the n.m.r. Spins have thus been unpaired in this reaction, most obviously by formation of heptaphenylcycloheptatrienyl radical.

Several special explanations are available for our finding that I is a singlet. It may be that there is unsymmetrical coördination of I with a potassium ion, although the crowding predicted from models because of the extreme non-planarity of the phenyls should make specific interaction difficult.[11] Alternatively, the central ring may be non-planar, although models show that any distortion tends im-

(1) This work was supported by grants from the Sloan Foundation and the Petroleum Research Fund.

(2) For a review, *cf.* A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 261-262.

(3) Cycloöctatetraene would be such a system if it were planar.

(4) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

(5) R. Breslow and H. W. Chang, *ibid.*, **83**, 3727 (1961).

(6) This refers only to symmetry with respect to chemical interactions. The seven phenyls are undoubtedly out of the plane, and unless they are 90° out of plane the geometric space-group is no longer D_{7h}, but this could only affect the calculations if direct electronic interactions between phenyl groups were taken into account.

(7) M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961); we wish to thank Dr. Battiste for making his results available to us before publication.

(8) M. A. Battiste, *Chem. & Ind.*, 550 (1961).

(9) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 207 ff.

(10) A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4672 (1961).

(11) The absence of vinyl hydrogens in the n.m.r. spectrum of I excludes the possibility of ring-chain tautomerism involving the phenyls.[8]