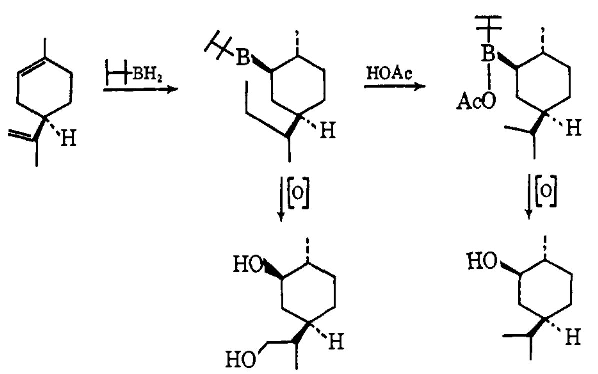


IV

Twenty milliliters each of 1.5 *M* D-(+)-limonene (bp 171–173° (743 mm), n^{20}D 1.4724, αD +99°) and thexylborane[5] were simultaneously added to 50 ml of tetrahydrofuran at 0° over 1 hr. After oxidation with alkaline hydrogen peroxide, the aqueous phase was saturated with potassium carbonate. Distillation yielded the diol, bp 152–155° (4.8 mm),[6] converted to the diacetate, bp 143–145° (5 mm). Examination of the diacetate by glpc (polyphenyl ether column) revealed a minimum 92% yield of the "*m-cis*" diol, with only trace amounts of the "*m-trans*" present.

Following preparation of the cyclic intermediate as above, 90 ml of anhydrous acetic acid was added,[7] tetrahydrofuran was distilled off until the temperature in the flask reached 110°, and the temperature was maintained there for 12 hr. Oxidation produced 3.59 g, 75% yield, of D-(−)-carvomenthol,[8] bp 85–88° (0.4 mm), n^{20}D 1.4609, $[\alpha]$D −23.0° (*c* 16, CCl$_4$). Glpc examination revealed the absence of D-(+)-isocarvomenthol.

It is evident that this approach provides a new, simple procedure to achieve stereochemical control of the direction of hydroboration and of the many derivatives into which organoboranes can be converted. We are also exploring the possibility of achieving similar control by the introduction of a suitable temporary "anchor" for the hydroborating agent.

[7] The selective protonolysis of primary carbon–boron bonds was previously observed by K. J. Murray, Ph.D. Thesis, Purdue University.

[8] D. K. Shumway and J. D. Barnhurst, *J. Org. Chem.*, **29**, 2320 (1964).

[9] Research assistant on funds provided by the Southern Utilization Research and Development Division of the U. S. Department of Agriculture (Contract No. 12-14-100-7152(72)) and the National Institutes of Health (5 ROI-GM-10937).

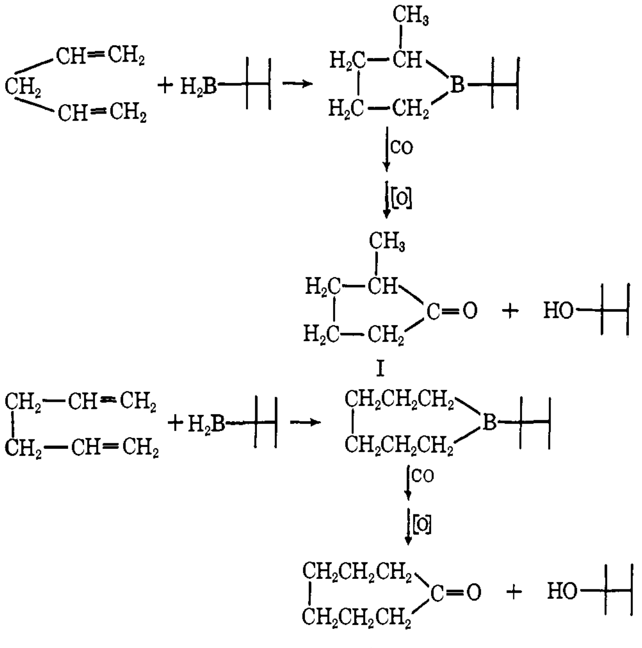
Herbert C. Brown, Carl D. Pfaffenberger[9]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

Received August 3, 1967

Carbonylation of the Organoboranes from the Cyclic Hydroboration of Dienes with Thexylborane. A Simple Procedure for the Conversion of Dienes into Cyclic Ketones

Sir:

Our recent studies on the carbonylation of trialkylboranes indicate that the alkyl groups are transferred intramolecularly from boron to carbon[1] and that the migratory aptitude of a tertiary alkyl group, such as the thexyl (2,3-dimethyl-2-butyl) group, is much lower than that of primary or secondary groups.[2] This suggested that the 1-thexylboracyclanes and related derivatives produced in the cyclic hydroboration of dienes with thexylboranes[3] should be transformed by carbonylation–oxidation into the corresponding ketones (I, II).



I

II

In fact the procedure works very satisfactorily. In two cases we isolated the cyclic organoborane by distillation prior to carbonylation. However, there appears to be no advantage to such prior isolation. Direct carbonylation of the crude solution resulting from the cyclic hydroboration procedure[3] proved to be entirely satisfactory.

In this way isoprene was converted into 3-methylcyclopentanone and 1,4-pentadiene into 2-methylcyclopentanone. 2,3-Dimethylbutadiene yielded a 69:31 mixture of *cis*- and *trans*-3,4-dimethylcyclopentanones. 1,5-Hexadiene yielded cycloheptanone predominantly, with a minor amount of 2,5-dimethylcyclopentanone.

The results are summarized in Table I.

Table I. Cyclic Ketones from Dienes *via* Hydroboration–Carbonylation–Oxidation

Reactant	Ketone yield %,[a]	Ketone products (%)
1-Thexyl-3-methylboracyclopentane	86	3-Methylcyclopentanone (100)
Isoprene	46	3-Methylcyclopentanone (100)
2,3-Dimethyl-diene	69	*cis*-3,4-Dimethylcyclopentanone (69) *trans*-3,4-Dimethylcyclopentanone (31)
1,4-Pentadiene	75	2-Methylcyclopentanone (81) Cyclohexanone (19)
1,5-Hexadiene	80	Cycloheptanone (78) 2-Methylcyclohexanone (1) 2,5-Dimethylcyclopentanone (21)
1-Vinylcyclohexene	66[b]	*trans*-1-Hydrindanone (100)

[a] By glpc. [b] Isolated: 60%.

---

[1] H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 4528 (1967).

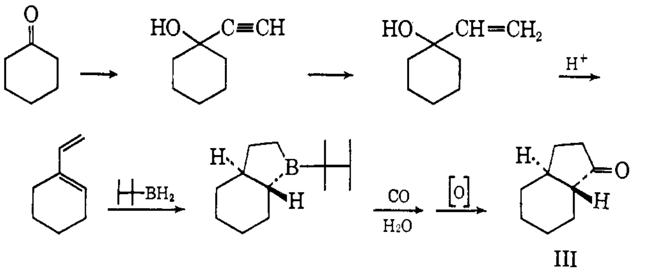
[2] H. C. Brown and E. Negishi, *ibid.*, **89**, 5285 (1967).

[3] H. C. Brown and C. D. Pfaffenberger, *ibid.*, **89**, 5475 (1967).

As far as we can ascertain, the yields are very high based on the amount of cyclic organoborane produced in the cyclic hydroboration. For example, we realized only a 46% yield of 3-methylcyclopentanone from isoprene. However, we have previously observed that conjugated dienes such as 1,3-butadiene and isoprene undergo considerable initial attack at an internal position.[4] This would lead to the formation of polymer rather than to the desired cyclic species. Indeed, distillation of the crude hydroboration mixture gave a yield of only 54% of distillate, identified as 1-thexyl-3-methylboracyclopentane (bp 55° (4 mm), $n^{20}\text{D}$ 1.4429) from its analysis and infrared and pmr spectra. Carbonylation of the distilled cyclic species gave an 86% yield of 3-methylcyclopentanone based on the cyclic borane.

The results suggest that the ketones realized correspond to the structures of the cyclic organoboranes actually present in the reaction mixtures. However, one minor anomaly should be pointed out. The yield of 21% 2,5-dimethylcyclopentanone from the organoborane produced in the cyclic hydroboration of 1,5-hexadiene is considerably greater than the yield of 2,5-hexanediol obtained in the oxidation of the intermediate. Possibly this indicates some isomerization of the organoborane intermediate during the carbonylation stage. This discrepancy is under investigation.

Finally, to test the utility of this procedure for complex synthetic problems, we undertook to use it for the stereospecific synthesis of the thermodynamically unfavorable *trans*-1-hydrindanone[5] (III) by the following procedure.[6]



No difficulty was encountered in obtaining a 60% isolated yield of *trans*-1-hydrindanone, as follows. A 300-ml flask equipped with a septum inlet, a condenser, a stirring bar, and a mercury-sealed outlet was flushed with nitrogen. Into the flask was introduced 50 ml of dry THF, followed by the simultaneous slow addition at 20 to 25°,[7] over a period of 3 hr, of 28.2 ml of 1.77 *M* thexylborane[2] (50 mmoles) and 5.95 g (55 mmoles) of 1-vinylcyclohexene[6] in 25 ml of THF. After stirring at room temperature for 5 hr to complete the cyclization,[7] 1.8 ml (100 mmoles) of water was added, and the mixture was transferred into a 250-ml autoclave under nitrogen and carbonylated at 1000 psi[8] and 50°. Although absorption was complete in 1 hr, the reaction was allowed to proceed for 3 hr. The reaction mixture was transferred to a glass flask and oxidized in the usual manner with 20 ml of 3 *M* sodium acetate and 20 ml of 30% hydrogen peroxide; the temperature was maintained between 30 and 50°. The reaction mixture was maintained at 50° for 1 hr to complete the oxidation, cooled, and saturated with potassium carbonate, and the product was isolated. Distillation of a 45-mmole aliquot yielded 3.7 g (60%) of *trans*-1-hydrindanone, bp 40–43° (0.5 mm), $n^{20}\text{D}$ 1.4782, oxime mp 145–146° (lit.[9] mp 146°).

It is evident that this procedure should be capable of wide ramification in synthesizing ring compounds, including the presence of functional substituents,[2] and in making possible the stereospecific construction of additional rings onto a basic framework. We continue to explore the potentialities of this new synthesis.

---

[4] G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

[5] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963).

[6] In applying this procedure our work was facilitated by a generous gift of 1-vinylcyclohexene, prepared as indicated, from C. A. Brown.

[7] For the other experiments in Table I a temperature of 0–5° was used, together with a much shorter reaction time after mixture of the reagents. In the present case the cyclization stage, resulting in the formation of the rigid bicyclic, is evidently slow, making the higher temperature and longer reaction time desirable.

[8] As was pointed out earlier[2] these thexyl derivatives react only sluggishly with carbon monoxide at atmospheric pressure.

[9] W. Hückel, M. Sachs, J. Yantschulewitsch, and F. Nerdel, *Ann.* 518, 155 (1935).

[10] Postdoctorate research associate on a grant supported by the National Institutes of Health (ROI-GM 10937).

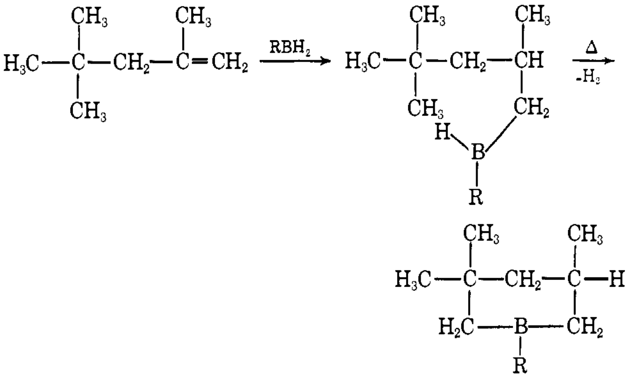
Herbert C. Brown, Eiichi Negishi[10]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

Received August 3, 1967

Carbonylation of Perhydro-9b-boraphenalene to Form Perhydro-9b-phenalenol. A New General Synthesis of Polycyclic Derivatives

Sir:

The remarkably easy addition of the boron–hydrogen bond to carbon–carbon double and triple bonds,[1] the less easy but still facile substitution of carbon–hydrogen bonds by boron–hydrogen bonds,[2] and the ready isomerization of organoboranes[3] all combine to give the organic chemist an unparalleled opportunity to utilize the unique characteristics of boron to bring together widely separated portions of a carbon structure into a more compact cyclic or polycyclic entity. Some representative examples follow.



I[4]

II[5]

---

[1] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[2] R. Köster, *Angew. Chem. Intern. Ed. Engl.*, **3**, 174 (1964).

[3] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966); **89**, 561 (1967).