boranes[9] and a more detailed knowledge of the influence of structure on the migratory aptitude of various groups. However, even in the present state of our knowledge, it is evident that we have a new, highly convenient synthetic route to a wide variety of mixed tertiary alcohols, secondary alcohols, and ketones.

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(9) For example, the commercial availability of dimethylborane and diethylborane in a conveniently handled form would make the methyl and ethyl ketones readily available from any derivative which can be hydroborated to form the mixed organoborane.

(10) National Science Foundation Fellow, 1964–1966.

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The Carbonylation of Mixed Trialkylboranes Containing Substituents as a Synthetic Route to Unsymmetrical Ketones with Such Functional Substituents. A New Simple Route for the Conversion of Olefins, $RCH{=}CH_2$, into the Corresponding Carboxylic Acids, $RCH_2CH_2CO_2H$

Sir:

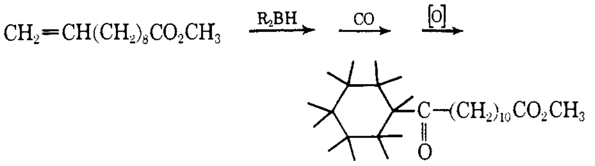
The hydroboration reaction can tolerate the great majority of functional groups. We wish to report that the carbonylation of organoboranes[2,3] is likewise tolerant of functional groups. Hydroboration–carbonylation–oxidation provides a synthetic route to tertiary alcohols, secondary alcohols, ketones, and methylol derivatives, compounds characteristic of many types of syntheses involving the reactive Grignard reagent. However, whereas the use of the Grignard reagent is necessarily restricted to the use of building blocks which do not contain reactive substituents, the present synthetic approach is evidently capable of utilizing building blocks containing a wide variety of reactive functional groups.

To explore the synthetic possibilities of this new development we decided to utilize dicyclohexylborane as a reagent to react with a number of olefins containing a variety of representative functional groups. Carbonylation of the resulting organoborane in the presence of water should yield a functionally substituted cyclohexyl monoalkyl ketone,[4] provided that the substituent does not interfere with the desired reaction.

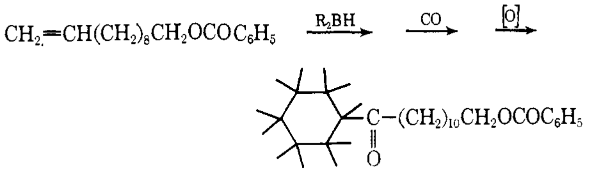
Previously, we had carried out the carbonylation at 100°.[4] The high temperature made it necessary to utilize a solvent of relatively low volatility, such as diglyme. However, the remarkable reactivity of the dicyclohexylmonoalkylboranes encouraged us to explore the use of lower temperatures (45°), permitting the use of the more convenient solvent, tetrahydrofuran. As an additional bonus, we discovered that the lower reaction temperature results in a considerably more selective migration of the alkyl group. Thus, carbonylation of dicyclohexyl-*n*-octylborane at 100°, followed by oxidation, produces a 90% yield of ketones, composed of 79% cyclohexyl *n*-octyl ketone and 21% dicyclohexyl ketone. When the same reaction is carried out in tetrahydrofuran at 45°, the total yield of ketone was 86%, composed of 92% cyclohexyl *n*-octyl ketone and only 8% dicyclohexyl ketone.

We applied this reaction to methyl 10-undecenoate, 10-undecenyl benzoate, allyl benzoate, ethyl vinylacetate, and allyl cyanide. We encountered difficulties in attempting to put some of these polyfunctional derivatives through the gas chromatograph. Consequently, we finally decided to rely on the isolation of either crystallized or distilled products.

The functional groups tested offered no evident difficulty. Thus methyl 10-undecenoate was converted into methyl 12-cyclohexyl-12-oxododecanoate, mp 37.5–38.0°, in 53% isolated yield (1). Similarly, 10-undecenyl benzoate was converted into the corresponding cyclohexyl ketone, mp 43.5–44°, in 61% yield (2).

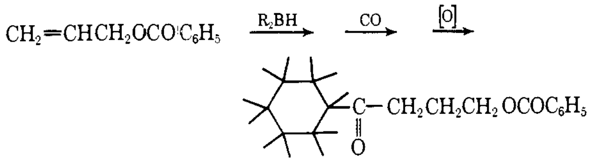


(1)

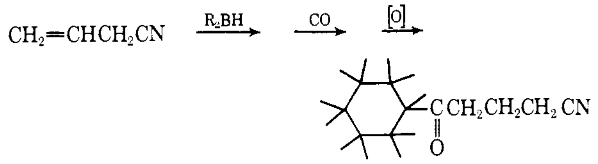


(2)

It is extremely promising that even in cases where the functional group is quite close to the double bond, as in allyl benzoate (3) and allyl cyanide (4), the reaction apparently proceeds without significant complications.



(3)



(4)

The experimental results are summarized in Table I.

The following procedure for the conversion of 10-undecenyl benzoate into 12-cyclohexyl-12-oxododecyl benzoate is representative. A dry 300-ml flask equipped with a thermometer well and magnetic stirring bar was attached to the carbonylation apparatus,[4] and the system was flushed with nitrogen. A solution of 8.2 g (100 mmoles) of cyclohexene in 22 ml of tetrahydrofuran was introduced and the flask was immersed in an ice-water bath. Hydroboration was achieved by the dropwise addition of 28 ml of a solution of diborane (50 mmoles of BH_3) in tetrahydrofuran. The solution was stirred at room temperature and 13.4 g of 10-un-

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

(2) M. E. D. Hillman, *J. Am. Chem. Soc.*, 84, 4719 (1962); 85, 982, 1636 (1963).

(3) H. C. Brown and M. W. Rathke, *ibid.*, 89, 2737 (1967); 89, 2738 (1967); M. W. Rathke and H. C. Brown, *ibid.*, 89, 2740 (1967).

(4) H. C. Brown and M. W. Rathke, *ibid.*, 89, 2738 (1967).

Table I. Products from the Carbonylation–Oxidation of Representative Dicyclohexylmonoalkylboranes Containing Functional Groups

Unsaturated compound	Product[a]	Physical properties	Yield,[b] %
1-Octene	Cyclohexyl *n*-octyl ketone		(79)[c]
1-Dodecene	Cyclohexyl *n*-dodecyl ketone		(84)[c]
Methyl 10-undecenoate	Methyl 12-cyclohexyl-12-oxododecanoate	Mp 37.5–38.0°	53
10-Undecenyl benzoate	12-Cyclohexyl-12-oxododecyl benzoate	Mp 43.5–44.0°	61
Allyl benzoate	4-Cyclohexyl-4-oxobutyl benzoate	Mp 60–61°	43
Ethyl vinylacetate	Ethyl 5-cyclohexyl-5-oxopentanoate	Bp 96° (0.35 mm), $n^{20}{}_D$ 1.4643	44
Allyl cyanide	4-Cyclohexyl-4-oxobutyl cyanide	Bp 102° (0.5 mm), $n^{20}{}_D$ 1.4731	45

[a] Analytical data within accepted limits were obtained for all new compounds. [b] Isolated, except where otherwise indicated. [c] Analysis by glpc.

decenylbenzoate (50 mmoles) was added. The solution was heated to 45° for 1 hr to complete the hydroboration. Then water, 1.4 ml, was added, and the carbonylation initiated, maintaining the temperature at 45°. A total of 44 mmoles of carbon monoxide was taken up in 20 hr.[5] The mixture was then oxidized by the addition of 17 ml of 3 *M* sodium acetate,[6] followed by the dropwise addition of 17 ml of 30% hydrogen peroxide, maintaining the temperature at 50–60°. After an additional 0.5 hr at this temperature, the reaction mixture was cooled and extracted with pentane. Crystallization from the pentane solution afforded 12 g (61%) of 12-cyclohexyl-12-oxododecyl benzoate.

It has been established that the Baeyer–Villiger oxidation of a wide variety of cyclohexyl alkyl ketones proceeds with the preferred migration of the cyclohexyl grouping to form the corresponding cyclohexylcarboxylates.[7] This suggested the possibility of using this new ketone synthesis as a means of introducing the carboxylate linkage into olefins. This is illustrated by the following conversion of 1-octene into nonanoic acid.

A solution of 2.24 g (10 mmoles) of cyclohexyl *n*-octyl ketone (from 1-octene, Table I) in 50 ml of methylene chloride was introduced into a 100-ml flask. *m*-Chloroperbenzoic acid, 4.42 g, was added, and the mixture was heated to reflux. Trifluoroacetic acid (60 mmoles) was added, and the mixture was heated under reflux for 24 hr. The methylene chloride was stripped off, and the mixture hydrolyzed with 2 *M* potassium hydroxide and extracted with ether to remove cyclohexanol and other neutral materials. Ether extraction of the acidified solution revealed a 79% yield of nonanoic acid (glpc).

Similarly, 1-dodecene has been converted into tridecanoic acid, methyl 10-undecenoate into dodecanedioic acid (5), and 10-undecenyl alcohol into 12-hydroxydodecanoic acid.[8] (6)

$$CH_2{=}CH(CH_2)_8CO_2CH_3 \longrightarrow HO_2C(CH_2)_{10}CO_2H \qquad (5)$$

$$CH_2{=}CH(CH_2)_8CH_2OH \longrightarrow HO_2C(CH_2)_{10}CH_2OH \qquad (6)$$

It is apparent that this simple synthesis of ketones containing functional substituents is capable of wide variations which should be of considerable value synthetically. We continue to explore the scope of this synthesis.

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(5) Actually, the reaction can be completed in less time. However, the carbonylation proceeds automatically, and it was convenient to allow it to run overnight.

(6) In the usual procedure[4] sodium hydroxide is used. However, the presence of groups which are sensitive to alkali made a shift to sodium acetate desirable.

(7) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958); M. F. Hawthorne and W. D. Emmons, *ibid.*, **80**, 6398 (1958).

(8) Clathration with urea provides a convenient means to separate such straight-chain derivatives from *m*-chlorobenzoic acid and other by-products in the reaction mixture: H. Schlenck and R. Holman, *J. Am. Chem. Soc.*, **72**, 5001 (1950).

(9) This study was assisted by financial support provided by Grant No. 5 ROI-GM-10937 from the National Institutes of Health.

(10) National Science Foundation Fellow, 1964–1966.

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A Novel Method for the Synthesis of Both *cis*- and *trans*-Vinyl Bromides from 1-Alkynes *via* Hydroboration

Sir:

It was recently reported that the halogenation of the vinylalane from the reaction of 1-hexyne with diisobutylaluminum hydride produces the isomerically pure *trans*-1-hexenyl halide.[1] We wish to report that addition of bromine to *trans*-1-hexenyldisiamylborane,[2] derived from the reaction of 1-hexyne with bis(3-methyl-2-butyl)borane, gives either *cis*- or *trans*-1-bromo-1-hexene, depending upon the procedure used to eliminate the elements of disiamylboron bromide from the dibromide intermediate.

Hydrolysis yields the *cis* derivative, thermal decomposition (in refluxing carbon tetrachloride) yields the *trans*. Since the reaction of bromine presumably proceeds through the usual bromonium ion mechanism to give *trans* addition to the double bond, solvolysis must involve a *trans* elimination[3] and thermal decomposition a *cis*[4] (1).

This procedure was applied to a number of 1-alkynes, with essentially identical results. However, when it was extended to phenylacetylene, we were surprised to note that in this case solvolysis of the intermediate yielded *trans*-bromostyrene, with thermal decomposition yielding the *cis*—the precise opposite of the

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(1) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967).

(2) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(3) D. S. Matteson and J. D. Liedtke, *ibid.*, **87**, 1526 (1965), have suggested that bromine adds *trans* to vinylboronic acids and that deboronobromination involves a stereospecific *trans* elimination.

(4) In the case of the alanes[1] it was assumed that the reaction involves a direct attack of the halogen on the carbon–aluminum bond, with retention. This is reasonable. However, the possibility cannot now be excluded that the reaction involves both a fast addition of the halogen to the double bond and a fast thermal *cis* elimination, in analogy to the present observation.