Table I. Conversion of Olefins into Trialkylcarbinols by the Hydroboration–Carbonylation Reaction

Olefin	Product	$T_{50\%}$,[a] min	$T_{100\%}$,[a] min	Isolated yield, %	n^{20}D (mp, °C)[b] Obsd	Lit.
1-Butene	Tri-n-butylcarbinol	50	500	90	1.4446	1.4434
2-Butene	Tri-sec-butylcarbinol	12	60	87	1.4558	
Isobutene	Triisobutylcarbinol[c]	28 hr[c]	95 hr[c]	90	1.4392	1.4390
1-Octene	Tri-n-octylcarbinol	45	300	90	1.4550	1.4565
Cyclopentene	Tricyclopentylcarbinol	15	50	90	1.5128	
Cyclohexene	Tricyclohexylcarbinol[d]	9	30	80	(94.5–95°)	(93°)
Norbornene	Tri-2-norbornylcarbinol	10	45	80	(137–137.5°)	

[a] Time for half and complete uptake of CO at 100°. [b] Analytical data within the usual accepted limits were obtained for all compounds. [c] Carbonylation at 125°. [d] Bromide derivative: mp 136° dec; lit. 136°.

solution was stirred at room temperature for 1 hr. Ethylene glycol, 10 ml, was added and the solution was heated and maintained at 100°. The system was flushed with carbon monoxide and the reaction initiated by vigorously stirring the contents of the flask magnetically. After 1 hr, absorption was complete. The system was flushed with nitrogen and then heated to 150° for 1 hr to ensure the migration of the alkyl groups. The flask

Figure 1. Reaction of carbon monoxide at atmospheric pressure with tri-n-octylborane in diglyme (0.5 M) at various temperatures.

was then immersed in an ice–water bath and 33 ml of 6 N sodium hydroxide was added, followed by dropwise addition of 33 ml of 30% hydrogen peroxide, maintaining a temperature just under 50°. The solution was then heated to 50° for 3 hr to complete the oxidation. Addition of water, 300 ml, to the cooled solution caused the precipitation of tri-2-norbornylcarbinol. The material was crystallized from pentane. There was obtained 25 g (80% yield) of pure tri-2-norbornylcarbinol, mp 137–137.5°.

Liquid trialkylcarbinols were isolated by extracting the diluted oxidized mixtures with pentane. The al-
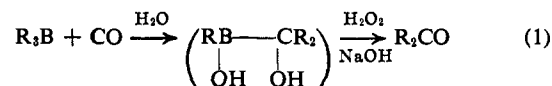
cohols were obtained analytically pure merely by stripping off the solvent.

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Reaction of Carbon Monoxide at Atmospheric Pressure with Trialkylboranes in the Presence of Water. A Convenient Synthesis of Dialkylketones via Hydroboration

Sir:

In the preceding communication we reported that trialkylboranes in diglyme solution react readily at 100° with carbon monoxide at atmospheric pressure. Oxidation of the organoboron intermediate with alkaline hydrogen peroxide provides the trialkylcarbinols in excellent yields.[1]

We now wish to report that the addition of small quantities of water to the reaction mixture inhibits the migration of the third alkyl group from boron to carbon.[2] Consequently, oxidation of the organoborane intermediate obtained in the presence of water produces the corresponding dialkyl ketone, instead of the trialkylcarbinol realized in the reaction in the absence of water (1).

$$R_3B + CO \xrightarrow{H_2O} \begin{pmatrix} RB{-}{-}CR_2 \\ | \quad\quad | \\ OH \quad OH \end{pmatrix} \xrightarrow[NaOH]{H_2O_2} R_2CO \qquad (1)$$

The following results illustrate the marked effect of the presence of relatively small quantities of water. Carbonylation of 100 mmoles of tri-n-butylborane in diglyme solution at 100° in the absence of any additive produces 60 mmoles of tri-n-butylcarbinol and 40 mmoles of di-n-butylketone. In the presence of 2.7 g of water (150 mmoles) under otherwise identical conditions oxidation of the reaction mixture with alkaline hydrogen peroxide produces 90 mmoles of di-n-butyl ketone, 100 mmoles of n-butyl alcohol, and only 6 mmoles of tri-n-butylcarbinol (2).

(1) H. C. Brown and M. W. Rathke, J. Am. Chem. Soc., 89, 2737 (1967).
(2) M. E. D. Hillman, ibid., 84, 4715 (1962), utilized excess water as a reaction medium for the carbonylation of primary trialkylboranes and was able to control the migration of alkyl groups during carbonylation at high pressures by operating between 75 (transfer of two groups) and 150° (transfer of three groups).
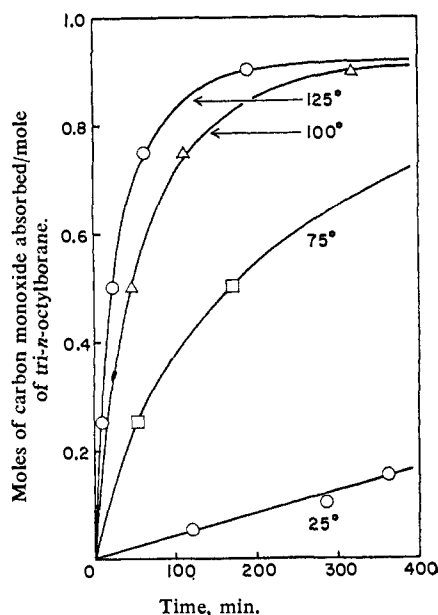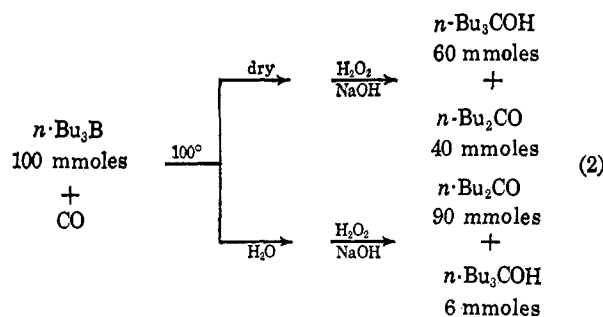
Table I. Conversion of Olefins into Dialkyl Ketones by the Hydroboration–Carbonylation Reaction

Olefin	Product[a]	$T_{50\%}$,[b] min	$T_{100\%}$,[b] min	Isolated yield, %[c]	n^{20}D (mp, °C) Obsd	Lit.
1-Butene	Di-n-butyl ketone	98	500	85	1.4201	1.4191
2-Butene	Di-sec-butyl ketone	40	150	81	1.4214	1.4193
1-Octene	Di-n-octyl ketone	101	500	80	(49.5–50.5°)	(50°)
Cyclopentene	Dicyclopentyl ketone[d]	47	161	90	1.4796	...
Cyclohexene	Dicyclohexyl ketone	25	78	80	1.4847	...
Norbornene	Di-2-norbornyl ketone[e]	52	150	82	(53–54°)	...

[a] Satisfactory derivatives were prepared of all ketones. Satisfactory analyses were obtained for all new ketones. [b] Time for half and complete uptake of carbon monoxide. [c] The yield is based on the formation of 1 mole of ketone and 1 mole of alcohol from each mole of trialkylborane. [d] 2,4-Dinitrophenylhydrazone, mp 93–94°. [e] 2,4-Dinitrophenylhydrazone, mp 142–145°.

$$n\text{-Bu}_3\text{B} \; 100 \text{ mmoles} + \text{CO} \xrightarrow{100°} \begin{cases} \xrightarrow[\text{dry}]{} \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}_2} & \begin{matrix} n\text{-Bu}_3\text{COH} \\ 60 \text{ mmoles} \\ + \\ n\text{-Bu}_2\text{CO} \\ 40 \text{ mmoles} \end{matrix} \\ \xrightarrow[\text{H}_2\text{O}]{} \xrightarrow[\text{NaOH}]{\text{H}_2\text{O}_2} & \begin{matrix} n\text{-Bu}_2\text{CO} \\ 90 \text{ mmoles} \\ + \\ n\text{-Bu}_3\text{COH} \\ 6 \text{ mmoles} \end{matrix} \end{cases} \quad (2)$$

Consequently, the carbonylation in the presence of added water of organoboranes, now readily synthesized via hydroboration,[3] provides a highly convenient synthetic route to ketones.[4]

The scope of the reaction was explored with representative aliphatic, alicyclic, and bicyclic olefins. In this way 2-butene was readily converted into di-sec-butyl ketone, cyclopentene into dicyclopentyl ketone (3), cyclohexene into dicyclohexyl ketone, and norbornene into di-2-norbornyl ketone[5] (4), in yields of 80–90%. The results are summarized in Table I.
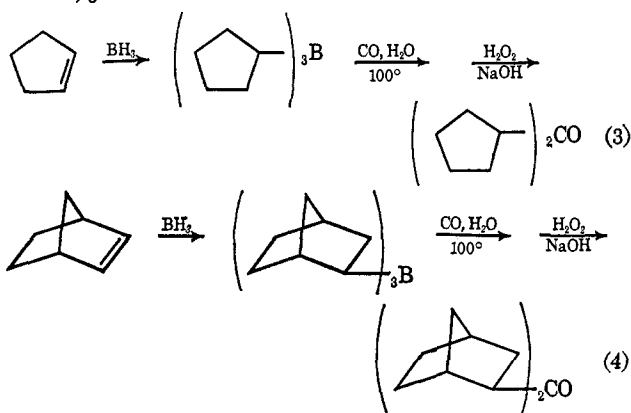
The following procedure for the conversion of cyclopentene into dicyclopentyl ketone is representative. The apparatus was set up as described previously.[1] A solution of 20.4 g (300 mmoles) of cyclopentene in 150 ml of diglyme was introduced into the flask and the latter was cooled with an ice–water bath as hydroboration was achieved by the dropwise addition of 50 ml of a 2.00 M solution of borane in tetrahydrofuran.[6] The

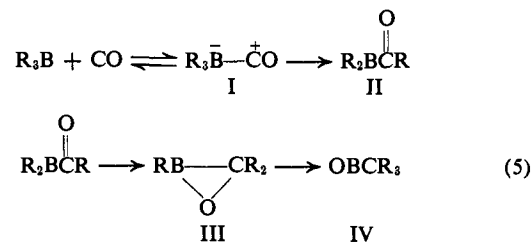(3) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) We are currently exploring the synthesis of cyclic, bicyclic, and polycyclic derivatives utilizing this reaction. These results will be reported shortly.

(5) The product is probably di-exo-norbornyl ketone. However, we did not attempt to establish the stereochemistry at this time. See earlier discussion[1] for the synthesis of tri-2-norbornylcarbinol.

(6) We avoided the usual procedure of hydroborating with sodium

solution was stirred at room temperature for 1 hr. The tetrahydrofuran was removed by distillation under reduced pressure. Water (2.7 ml, 150 mmoles) was then added, and the solution was brought to 100°. The system was flushed with carbon monoxide, and reaction was initiated by magnetically stirring the contents of the flask. Absorption of the carbon monoxide proceeded automatically and ceased after 2.5 hr. The flask was then cooled in an ice–water bath and oxidation accomplished by the addition of 3 N sodium hydroxide followed by dropwise addition of 23 ml of 30% hydrogen peroxide, keeping the temperature under 35°. After the addition had been completed, the reaction mixture was stirred for an additional hour at 30 to 35°. The solution was poured into 300 ml of water and extracted once with 100 ml of pentane. The pentane solution was back-extracted twice with 300-ml portions of water to remove diglyme. The pentane solution was dried over calcium hydride and vacuum distilled. There was obtained 15.0 g (90%) of dicyclopentyl ketone, bp 86° (5 mm).
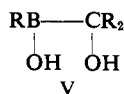
Although we have been too preoccupied with exploring the scope of this synthetic approach to investigate the mechanism, we can rationalize the results in terms of the following mechanism adapted from that previously suggested by Hillman[2] (5). In the absence

$$\text{R}_3\text{B} + \text{CO} \rightleftharpoons \text{R}_3\bar{\text{B}}\text{—}\overset{+}{\text{C}}\text{O} \longrightarrow \underset{\text{II}}{\text{R}_2\text{B}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}}$$
$$\underset{}{\text{R}_2\text{B}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}} \longrightarrow \underset{\text{III}}{\text{RB}\overset{}{\underset{\text{O}}{\diagdown\diagup}}\text{CR}_2} \longrightarrow \underset{\text{IV}}{\text{OBCR}_3} \quad (5)$$

of hydroxylic solvents III can readily dimerize into the 2,5-diboradioxanes, isolated by Hillman, or undergo migration of the third alkyl group to give the intermediate IV, isolated by Hillman as the trimeric boroxine. The intermediate IV, or the ester produced by reaction of IV with ethylene glycol, or the trimeric boroxine are all oxidized to the trialkylcarbinol and boric acid by alkaline hydrogen peroxide. Under our conditions all three alkyl groups migrate unless something is done to inhibit the migration of the third group.

The presence of water is presumed to convert the hypothetical boraepoxide III into the hydrate V. Oxidation produces the ketone.[7]

borohydride and boron trifluoride diglymate since we had some indication that the presence of sodium fluoroborate facilitated the migration of the third alkyl group.

Communications to the Editor

$$\begin{array}{c} \text{RB}\!-\!-\!-\!\text{CR}_2 \\ | \qquad | \\ \text{OH} \quad \text{OH} \\ \text{V} \end{array}$$

According to this mechanism, the successful trapping of intermediate II would provide a valuable means of converting olefins into their methylol derivatives. This is described in the following communication.[8]

(7) Hillman realized only dialkylcarbinols in his oxidations, with only traces of dialkyl ketones. We are unable to account for the difference between his results and our own, unless the presence of the diglyme protects the intermediate V from the hydrolysis by the base prior to the addition of the hydrogen peroxide. We have been able to obtain dialkylcarbinols by subjecting the reaction product to hydrolysis with aqueous alkali at elevated temperatures prior to oxidation with alkaline hydrogen peroxide.

(8) M. W. Rathke and H. C. Brown, J. Am. Chem. Soc., 89, 2740 (1967).

(9) National Science Foundation Fellow, 1964–1966.
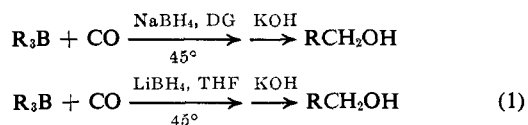
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Reaction of Carbon Monoxide at Atmospheric Pressure with Trialkylboranes in the Presence of Sodium or Lithium Borohydride. A Convenient Procedure for the Oxymethylation of Olefins via Hydroboration

Sir:

We wish to report that both sodium and lithium borohydrides markedly catalyze the rate of absorption of carbon monoxide at atmospheric pressure by trialkylboranes in ether solvents. The reaction can be controlled to achieve the transfer of but one alkyl group from boron to carbon. Consequently, hydrolysis of the reaction intermediate with ethanolic potassium hydroxide produces the homologated alcohol (1).

$$R_3B + CO \xrightarrow[45°]{\text{NaBH}_4,\ DG} \xrightarrow{\text{KOH}} RCH_2OH$$

$$R_3B + CO \xrightarrow[45°]{\text{LiBH}_4,\ THF} \xrightarrow{\text{KOH}} RCH_2OH \quad (1)$$

Consequently, carbonylation of organoboranes can now be controlled to achieve migration of all three groups from boron to carbon, providing the trialkylcarbinol;[1] two groups, providing the ketone or dialkylcarbinol;[2] or one group, providing the corresponding methylol derivative of the olefin.

By means of this latter reaction, described in this communication, we have been able to achieve the conversion of 1-octene into 1-nonanol, cyclopentene into cyclopentylmethanol, cyclohexene into cyclohexylmethanol, and norbornene into 2-exo-norbornylmethanol, in yields of 70–85%.

In previous experiments[1,2] we found it necessary to operate at 100–125° in order to achieve absorption of carbon monoxide by trialkylboranes at a convenient rate. However, the rate of absorption is markedly enhanced by the presence of alkali metal borohydrides. Thus, the presence of 200 mmoles of sodium borohydride in a solution of 100 mmoles of triethylborane in 100 ml of diglyme caused the uptake of carbon monoxide to be complete in 1 hr at 45°. Hydrolysis with

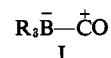(1) H. C. Brown and M. W. Rathke, J. Am. Chem. Soc., 89, 2737 (1967).

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

Table I. The Reaction of Carbon Monoxide at Atmospheric Pressure with Solutions of Triethylborane (1.00 M) at 45° in the Presence of Varying Amounts of Sodium Borohydride

Sodium borohydride, mmoles	Triethylborane, mmoles	Carbon monoxide absorbed, mmoles	Products, mmoles	
			Ethanol	1-Propanol
200	100	142	180	80
100	100	142	195	85
50	100	140	202	82
25	100	81	240	42

ethanolic potassium hydroxide, followed by oxidation with hydrogen peroxide, produced 180 mmoles of ethanol, 80 mmoles of 1-propanol, and 12 mmoles of diethylcarbinol. No trace of 1-butanol, corresponding to the doubly homologated alcohol, was found by glpc analysis.[3]

It is possible that the borohydride functions by reducing the initially formed carbonyl (I) of the proposed mechanism.[2] This would be followed by trans-

$$R_3\bar{B}\!-\!\overset{+}{C}O$$
I

fer of one alkyl group from boron to carbon. However, at this stage we were more concerned with exploring the scope of this new synthesis than in investigating the mechanism.

The data summarized in Table I indicate the stoichiometry for sodium borohydride to be $0.5\text{NaBH}_4/\text{Et}_3\text{B}$.

Analysis of the solutions for residual hydride indicated the following over-all stoichiometry (2).

$$2R_3B + 3CO + 4H^-(\text{NaBH}_4) \longrightarrow \longrightarrow$$
$$4ROH + 2RCH_2OH \quad (2)$$
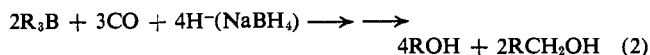
The amount of carbon monoxide consumed in these reactions is not yet understood. We observed approximately 1.5 moles of carbon monoxide to be absorbed per mole of trialkylborane in all cases investigated, although the homologated alcohols isolated, the major product, plus the much smaller by-product of dialkylcarbinol, accounted for only 1 mole of the gas. Possibly the excess consumption of carbon monoxide is the result of a direct reduction by an intermediate.

The observation that the reaction proceeds rapidly at 45° suggested the desirability of utilizing the more convenient solvent, tetrahydrofuran, for both the hydroboration and carbonylation stages. Lithium borohydride was therefore selected for its solubility in this solvent. Results obtained with this system are summarized in Table II

The following procedure for the synthesis of exo-2-norbornylmethanol is representative. A dry 300-ml flask, equipped with thermometer well, septum inlet, and magnetic stirrer, was attached to the carbonylation apparatus, set up as previously described.[1] The system was flushed with nitrogen. Then, a solution of 14.2 g (150 mmoles) of norbornene in tetrahydrofuran (26.6 ml) was introduced into the flask and the latter was immersed in an ice–water bath. Hydroboration was achieved by adding dropwise 23.4 ml of a solution of

(3) The convenient synthesis of homologated alcohols by the reaction of dimethyloxosulfonium methylide with trialkylboranes has recently been reported: J. J. Tufariello and T. L. C. Lee, ibid., 88, 4757 (1966). However, this procedure produces appreciable amounts of the higher homologated alcohols.