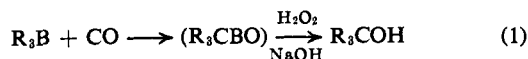


Communications to the Editor

Reaction of Carbon Monoxide at Atmospheric Pressure with Trialkylboranes. A Convenient Synthesis of Trialkylcarbinols *via* Hydroboration

Sir:

Carbon monoxide at atmospheric pressure readily reacts at 100–125° with trialkylboranes, synthesized *in situ* in diglyme solution, to provide a convenient, high-yield synthetic route to the corresponding trialkylcarbinols (1). In this way olefins, such as 2-butene,



cyclohexene, and norbornene, may be readily converted into the highly hindered tertiary alcohols, tri-*sec*-butylcarbinol, tricyclohexylcarbinol, and tri-2-norbornylcarbinol, products available only in very low yield by the usual Grignard synthesis.

It was recently reported by Hillman that trialkylboranes react with carbon monoxide at high pressures in excess of 500 atm to give products oxidizable to trialkylcarbinols.¹ When the reaction was attempted at atmospheric pressure, only low yields of alcohols were obtained, less than 40% after 24-hr reaction.

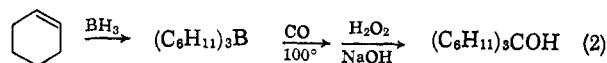
Trialkylboranes are now readily available *via* the hydroboration of olefins.² It was therefore apparent that the carbonylation of trialkylboranes thus prepared should offer a versatile route to the corresponding trialkylcarbinols. However, the apparent necessity of carrying out the carbonylation at high pressures represents a severe inconvenience for laboratory synthesis. Accordingly, we undertook to explore the possibility of accomplishing the carbonylation stage at atmospheric pressure in the same flask utilized for the hydroboration, utilizing the automatic hydrogenator previously described³ as adapted for carbonylations.⁴

With tri-*n*-octylborane in diglyme solution (0.5 *M*) as a standard substrate, we observed that at 25° approximately 1 mole of carbon monoxide was absorbed per mole of trialkylborane. The reaction was indeed slow, complete absorption of the gas requiring some 5 days. However, the rate of absorption increased with increasing temperature, so that at 125° complete carbonylation could be achieved in 3 hr. These results are summarized in Figure 1. The reaction mixture obtained in the carbonylation at 125° was oxidized with alkaline hydrogen peroxide, producing tri-*n*-octylcarbinol in 90% yield.

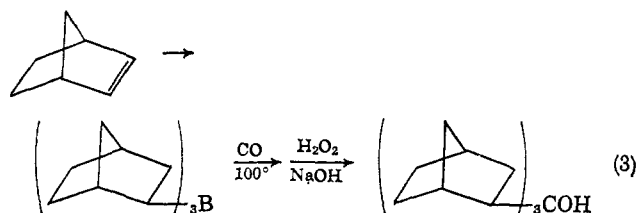
To explore the scope of this convenient synthesis, a number of representative olefins were hydroborated and the resulting organoboranes were carbonylated *in situ* at 100° in the presence of ethylene glycol.⁵ The reac-

tion mixtures were then oxidized with alkaline hydrogen peroxide and the trialkylcarbinols isolated.

It is noteworthy that this procedure yields trialkylcarbinols with highly branched alkyl groups, products which cannot be obtained in satisfactory yield by the methods presently available. Thus, 2-butene and isobutene were converted into tri-*sec*-butylcarbinol and triisobutylcarbinol in yields of 87 and 90%, respectively. Similarly, cyclopentene was converted into tricyclopentylcarbinol in 90% yield, and cyclohexene was converted into tricyclohexylcarbinol in 80% yield (2).



For comparison, tricyclohexylcarbinol is obtained in 7% yield from cyclohexyl chloride *via* the Grignard synthesis,⁶ and the yield is increased to 19% by the use of a special procedure involving sodium.⁷ Finally, 2-norbornylmagnesium halides rapidly equilibrate to a mixture of *exo* and *endo* derivatives.⁸ The hydroboration product of norbornene is known to provide the essentially pure tri-*exo*-norbornylborane.² This was rapidly converted into a crystalline tri-2-norbornylcarbinol, melting sharply at 137–137.5°. Although we did not establish the stereochemistry, it is highly probable from previous experience with organoboranes² that the reaction proceeds with retention to yield tri-



exo-norbornylcarbinol (3). The experimental results are summarized in Table I.

The following procedure describing the conversion of norbornene into tri-2-norbornylcarbinol is representative. A dry 500-ml flask equipped with a septum inlet, thermometer well, and magnetic stirrer was attached to the carbonylation apparatus,⁹ set up as previously described.⁴ The system was flushed with nitrogen. A solution of 2.84 g (75 mmoles) of sodium borohydride in 150 ml of diglyme was introduced, followed by 28.3 g (300 mmoles) of norbornene. The flask was immersed in an ice-water bath and the hydroboration achieved by the dropwise addition of 27.4 ml (100 mmoles) of boron trifluoride diglymate.¹⁰ The

(5) In most cases the reaction proceeded satisfactorily in the absence of added ethylene glycol. In some cases, however, we noted the formation of a less reactive, possibly polymeric, intermediate. The presence of the ethylene glycol circumvented this difficulty.

(6) O. Nuenhoeffer, *Ann.*, **509**, 115 (1934).

(7) P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **67**, 141 (1945).

(8) F. R. Jensen and K. L. Nakamaya, *ibid.*, **88**, 3437 (1966).

(9) We used a commercial model of the hydrogenator from Delmar Scientific Laboratories, Maywood, Ill. 60154.

(10) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **88**, 1433 (1966).

(1) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 982, 1636 (1963).

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

(3) C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966).

(4) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 2606 (1966).

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- <i>n</i> -butylcarbinol	50	500	90	1.4446	1.4434
2-Butene	Tri- <i>sec</i> -butylcarbinol	12	60	87	1.4558	
Isobutene	Trisobutylcarbinol ^c	28 hr ^c	95 hr ^c	90	1.4392	1.4390
1-Octene	Tri- <i>n</i> -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

cohols were obtained analytically pure merely by stripping off the solvent.

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

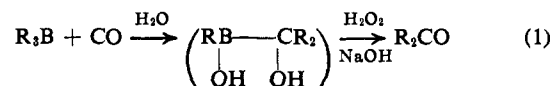
Herbert C. Brown, Michael W. Rathke¹¹
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907
Received March 28, 1967

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).



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).

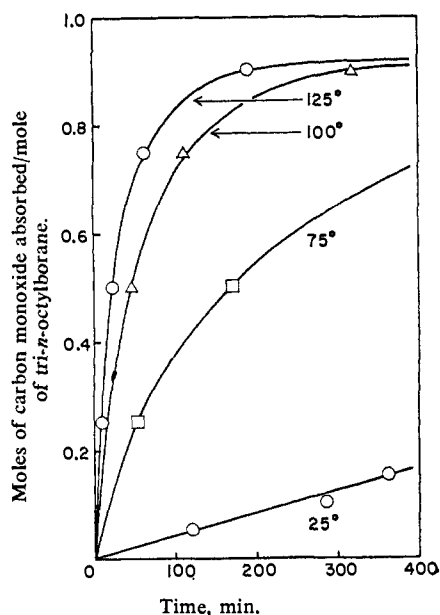


Figure 1. Reaction of carbon monoxide at atmospheric pressure with tri-*n*-octylborane in diglyme (0.5 *M*) at various temperatures.

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-