geneous rhodium compounds (intermediates) have been identified which are thought to contain two carbon–metal bonds at the 1 and 3 positions of propanes from the reactions of cyclopropyl compounds.[17]

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(17) H. C. Volger, H. Hogeveen, and M. M. P. Gasbeek, *J. Amer. Chem. Soc.*, 91, 218, 2137 (1969); H. Hogeveen and H. C. Volger, *ibid.*, 89, 2486 (1967); *Chem. Commun.*, 1133 (1967); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968); L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 92, 3515 (1970); T. J. Katz and S. A. Cerefice, *ibid.*, 91, 2405, 6519 (1969).

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The Base-Induced Reaction of Organoboranes with Bromine. A Convenient Procedure for the Anti-Markovnikov Hydrobromination of Terminal Olefins *via* Hydroboration–Bromination

Sir:

Organoboranes from terminal olefins react rapidly with bromine at 0° in the presence of sodium methoxide in methanol to give the corresponding primary alkyl bromides with utilization of all three alkyl groups of the organoborane. Consequently, this reaction provides a convenient procedure for the anti-Markovnikov hydrobromination of terminal olefins *via* hydroboration–bromination.

The dark reaction of trialkylboranes with bromine in various inert solvents at 25° gives a maximum conversion of only one alkyl group into the corresponding bromide.[1] Consequently, the reaction is of limited synthetic value for the preparation of alkyl bromides.

Previous work had revealed that organoboranes obtained by the hydroboration of terminal olefins undergo a very rapid reaction with iodine under the influence of sodium hydroxide.[2] The conversion of two of the three alkyl groups of a trialkylborane into the alkyl iodide occurred in less than 5 min at 25°. Consequently, the hydroboration–iodination procedure has made possible a simple synthetic route from terminal olefins to primary iodides.

Since the reaction of organoboranes with iodine was greatly facilitated by the addition of sodium hydroxide, the present study was undertaken to determine what effect sodium hydroxide or other bases would have on the reaction of organoboranes with bromine in THF. Direct adaptation of the iodination procedure resulted in the conversion of less than two of the three alkyl groups into the corresponding alkyl bromide. Bromination in the presence of sodium hydroxide was further complicated by concurrent oxidation of the organoborane to give the alcohols as a major by-product.

Trialkylboranes have been shown to undergo oxidation by sodium hypochlorite to give the corresponding alcohols.[3] Therefore, in the present study the alcohol is presumably formed *via* an oxidation of the organoborane with sodium hypobromite. Only 1-hexanol and a trace of 2-hexanol were formed when a THF solution of tri-*n*-hexylborane was added to a colorless solution of bromine in methanolic sodium hydroxide at 0°.[4] The oxidation is probably occurring *via* a reaction sequence analogous to the mechanism proposed by Kuivila and coworkers for the hypohalite oxidation of areneboronic acids.[5]

The procedure reported[2] for the iodination reaction was to add the iodine to the organoborane in THF, followed by the dropwise addition of methanolic sodium hydroxide. By changing to a simultaneous dropwise addition of bromine and base to the organoborane in THF, the yield of primary bromide derived from a terminal olefin could be increased to around 67%. If enough sodium hydroxide was added to completely decolorize all of the bromine, then a quantitative recovery of all three alkyl groups was obtained (eq 1).

$$R_3B + 3Br_2 + 4NaOH \longrightarrow 2RBr + ROH + B(OH)_3 + 4NaBr \quad (1)$$

We now wish to report that this undesirable oxidation side reaction proved to be easily circumvented by using sodium methoxide in methanol as the base, presumably because the reaction of bromine with sodium methoxide does not result in the formation of sodium hypobromite.[6] Table I gives a summary of the results that were obtained when sodium methoxide was used to induce the bromination of various representative trialkylboranes.

Study of the reaction resulted in the development of two different procedures. Procedure A involves the addition of bromine (33% excess) to the organoborane in THF, followed by a solution of sodium methoxide (67% excess) in methanol, all at 0°. Procedure B involves the simultaneous addition of bromine and base (10% excess) at 25°. Procedure A provided essentially quantitative conversions of monosubstituted olefins into primary bromides. Unfortunately, the yield dropped with the secondary and the more hindered primary alkyl groups. Procedure B provides more satisfactory yields for these derivatives.

The hydroboration–bromination of methyl 10-undecenoate is representative of procedure A. A dry 300-ml flask equipped with septum inlet, thermometer well, pressure-equalizing dropping funnel, and magnetic stirrer was flushed with nitrogen and then maintained under a positive nitrogen pressure. The flask was charged with 75 ml of dry THF and 33.5 ml (150 mmol) of dry methyl 10-undecenoate and cooled to ~0° with an ice–water bath. Hydroboration was achieved by the dropwise addition of 19.5 ml of a 2.58 *M* solution of borane (151 mmol of hydride) in THF. The solution was stirred for 30 min at 0° and 30 min at 20°. Then 1 ml of methanol was added to destroy excess

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(1) C. F. Lane and H. C. Brown, manuscript in preparation.

(2) H. C. Brown, M. W. Rathke, and M. M. Rogić, *J. Amer. Chem. Soc.*, 90, 5038 (1968).

(3) H. C. Brown and W. R. Heydkamp, unpublished results.

(4) The reactive oxidizing agent is assumed to be the hypobromite ion, $Br_2 + 2OH^- \rightarrow Br^- + BrO^- + H_2O$.

(5) H. G. Kuivila, L. E. Benjamin, C. J. Murphy, A. D. Price, and J. H. Polevy, *J. Org. Chem.*, 27, 825 (1962).

(6) The reaction of bromine with sodium methoxide presumably gives extremely unstable methyl hypobromite which does not react under these conditions with trialkylboranes. For example, when bromine (30 mmol) was added to sodium methoxide (60 mmol) in methanol at 0°, a clear solution and a white precipitate resulted. This slurry was then passed into a THF solution of tri-*n*-hexylborane (30 mmol) *via* a stream of dry nitrogen. Glpc analysis of the resulting mixture indicated that neither 1-hexanol nor 1-bromohexane was formed in any detectable amount.

Table I. Conversion of Terminal Olefins into Primary Bromides *via* Hydroboration–Bromination

Organoborane from olefin[a]	Bromine, mmol	Sodium methoxide, mmol	Procedure	Product	Yield, %[b]
1-Butene	40	50	A	*n*-Butyl bromide	91
1-Hexene	10	10	A	*n*-Hexyl bromide	32
	20	20	A		61
	30	30	A		72
	40	40	A		82
	40	50	A		93[c,d]
	30	33	B		85[d]
1-Octene	40	50	A	*n*-Octyl bromide	94[d]
Methyl 10-undecenoate	40	50	A	Methyl 11-bromoundecanoate	92 (85)[d]
11-Chloro-1-undecene	40	50	A	1-Bromo-11-chloroundecane	(75)[d]
10-Undecenyl acetate	40	50	A	11-Bromoundecyl acetate	(77)[d]
2-Methyl-1-pentene	40	50	A	1-Bromo-2-methylpentane	99
2,4,4-Trimethyl-1-pentene	40	50	A	1-Bromo-2,4,4-trimethylpentane	80
	30	33	B		80 (70)
α-Methylstyrene	40	50	A	1-Bromo-2-phenylpropane	68
	30	33	B		74 (63)
β-Pinene	40	50	A	*cis*-Myrtanyl bromide	55
	30	33	B		65 (59)
Cyclopentene	40	50	A	Cyclopentyl bromide	31
	30	33	B		69
Cyclohexene	30	33	B	Cyclohexyl bromide	64
2-Butene	30	33	B	*sec*-Butyl bromide	74

[a] All reactions involve 10 mmol of R$_3$B. [b] Glpc yields (isolated yields in parentheses). The yields are based on the amount of starting olefin. [c] This is essentially a quantitative yield, since hydroboration of 1-hexene proceeds to place 94% of the boron on the terminal carbon: H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962. [d] Small amounts of 2-bromoalkane (1–2%) are also present.

hydride. The solution was cooled to below 0° with an ice–salt bath and 10 ml (200 mmol) of bromine was added at such a rate that the temperature of the reaction mixture never rose above 0°. Then 60 ml of a 4.16 *M* solution of sodium methoxide (250 mmol) in methanol was added dropwise over a period of 45 min. The temperature was not permitted to rise above 5° during the addition of the base. The reaction was then placed in a water bath at 20–25° and treated with pentane (50 ml), water (20 ml), and saturated aqueous potassium carbonate (20 ml). The organic layer was separated from the aqueous layer, and the aqueous layer was extracted with pentane (3 × 50 ml). The pentane extracts were combined with the organic layer and washed with water (2 × 50 ml) and once with 50 ml of saturated aqueous sodium chloride. After drying the solution with anhydrous potassium carbonate, the pentane was removed on a rotary evaporator under reduced pressure, leaving 41.2 g of a colorless oil, purity $\sim$99% by glpc.[7] Vacuum distillation of this oil gave 35.4 g (85%) of methyl 11-bromoundecanoate, bp 126–128° (0.65 mm), $n^{20}\text{D}$ 1.4638 (lit.[8] $n^{16}\text{D}$ 1.4665).

The hydroboration–bromination of β-pinene is representative of procedure B. The hydroboration was carried out in a manner similar to that described in procedure A, using 100 ml of dry THF, 47.2 ml (300 mmol) of dry β-pinene, and 39.0 ml of a 2.68 *M* solution of borane (315 mmol of hydride) in THF. Excess hydride was destroyed by the addition of 2 ml of methanol. Bromine (16 ml, 300 mmol) was placed in an addition funnel and a solution of sodium methoxide in methanol (86 ml of a 3.84 *M* solution, 330 mmol) was placed in a second addition funnel. The bromine and base were added simultaneously at a rate such that the reaction mixture was always slightly yellow. The flask was cooled intermittently during the 30-min addition period in order to maintain a reaction temperature of 20–25°. Isolation of the product as described for procedure A gave 38.5 g (59%) of *cis*-myrtanyl bromide, bp 94° (14 mm), $n^{20}\text{D}$ 1.5109.

The convenient and in many cases quantitative anti-Markovnikov addition of the elements of hydrogen bromide to a terminal olefin *via* hydroboration–bromination provides yet another promising synthetic reaction to be added to the rapidly expanding list of synthetic applications for the versatile organoboranes.

(7) The product contained approximately 1% of an isomer, assumed to be methyl 10-bromoundecanoate.

(8) S. Geiger-Berschandy, *Bull. Soc. Chim. Fr.*, 994 (1955).

(9) Graduate research assistant on Grant No. GM 10937 from the National Institutes of Health.

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A Route to 3-Deoxy Glycals *via* an Abnormal Lithium Aluminum Hydride Reductive Rearrangement of Some Unsaturated Acetals

Sir:

The evidence indicating that acetals are stable toward LAH in the absence of acid catalysis is overwhelming.[1–3] We therefore report "a very odd reaction"[4] in which certain allylic acetals are reductively rearranged to vinyl ethers by LAH. Thus *chloride-free* LAH converts hex-2-enopyranosides (such as **1**) to 1,2,3-trideoxy-D-*erythro*-hex-1-enopyranoses (such as **9**). The latter

(1) (a) E. L. Eliel and M. N. Rerick, *J. Org. Chem.*, **23**, 1088 (1958); (b) E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961); (c) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, **84**, 2371 (1962); (d) E. L. Eliel and F. W. Nader, *ibid.*, **92**, 3045 (1970).

(2) B. E. Leggeter, U. E. Diner, and R. K. Brown, *Can. J. Chem.*, **42**, 2113 (1964); U. E. Diner, H. A. Davis, and R. K. Brown, *ibid.*, **45**, 207 (1967); U. E. Diner and R. K. Brown, *ibid.*, **45**, 1297 (1967).

(3) H. M. Doukas and T. D. Fontaine, *J. Amer. Chem. Soc.*, **75**, 5355 (1953).

(4) We are indebted to a referee for this epithet.