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.

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(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).

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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

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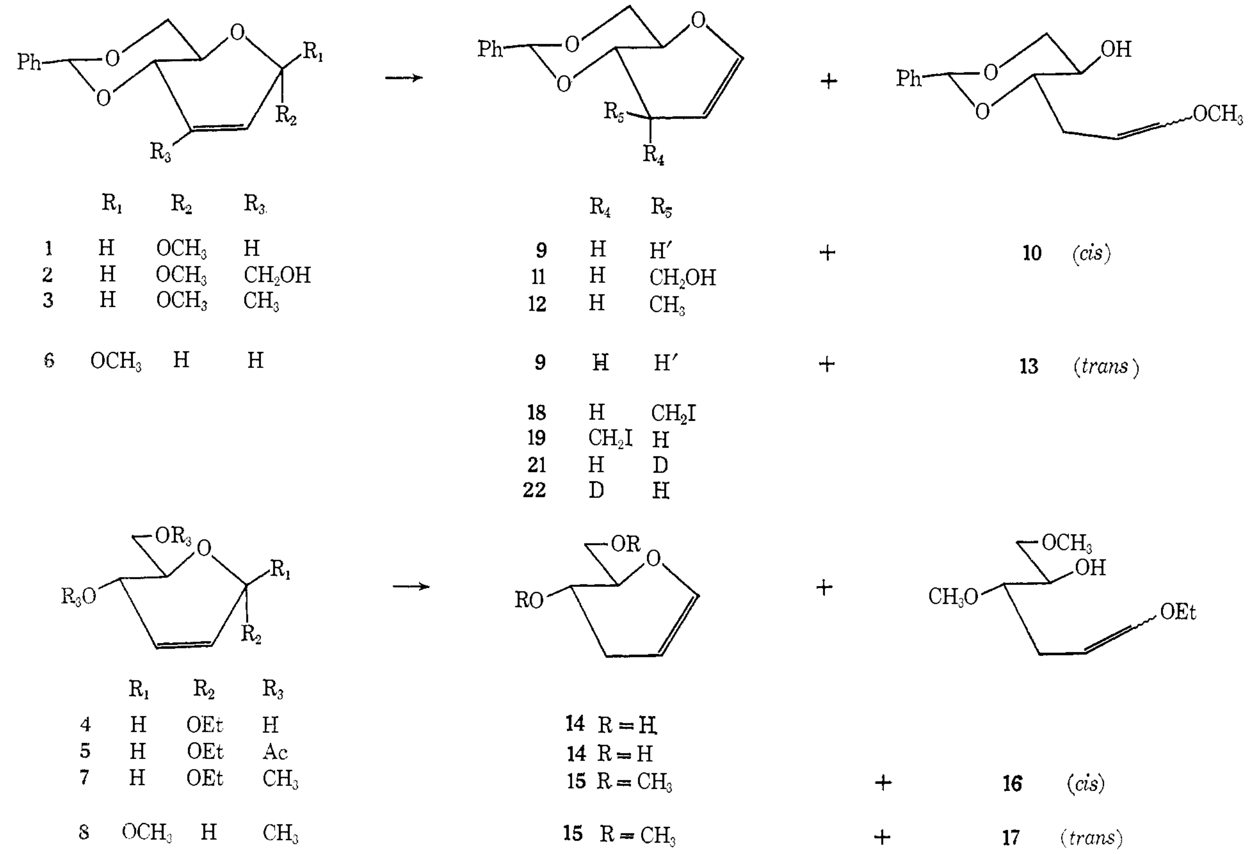
(1) (a) E. L. Eliel and M. N. Rerick, *J. Org. Chem.*, **23**, 1088 (1958); (b) E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961); (c) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, **84**, 2371 (1962); (d) E. L. Eliel and F. W. Nader, *ibid.*, **92**, 3045 (1970).

(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.

Chart I



	R_1	R_2	R_3		R_4	R_5		
1	H	OCH_3	H	9	H	H′	+	10 (*cis*)
2	H	OCH_3	CH_2OH	11	H	CH_2OH		
3	H	OCH_3	CH_3	12	H	CH_3		
6	OCH_3	H	H	9	H	H′	+	13 (*trans*)
				18	H	CH_2I		
				19	CH_2I	H		
				21	H	D		
				22	D	H		

	R_1	R_2	R_3			
4	H	OEt	H	14 R = H		
5	H	OEt	Ac	14 R = H		
7	H	OEt	CH_3	15 R = CH_3	+	16 (*cis*)
8	OCH_3	H	CH_3	15 R = CH_3	+	17 (*trans*)

vinyl ethers are 3-deoxy glycals, and are new members of a family of unsaturated carbohydrates[5] with a distinguished history in synthesis of amino[6] and branched-chain[7] sugars, and for mechanistic studies in carbohydrate chemistry.[8]

The reaction of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, **1** (2.48 g, 0.01 mol), with LAH (0.40 g, 0.01 mol) in refluxing ethyl ether (75 ml) was complete after 10 hr. There were two products. The major one (2.08 g, 95%) was apparently **9** because of infrared absorptions for a vinyl ether (μ_{max} 6.08, 8.10, 9.25) and its elemental composition (*Anal.* Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.74; H, 6.43). The nmr spectrum in $CDCl_3$ (TMS) provided independent evidence for the structure **9**: H-1, τ 3.65; H-2, τ 5.27, $J_{12} = 7.0$ Hz; H-3 and H-3′ were accidentally equivalent at τ 7.72; as a result $J_{13} = J_{13'} = 2.0$ Hz, and $J_{23} = J_{23'} = 3.5$ Hz.[9] The other product (0.098 g, 3.5%) was the acyclic vinyl ether **10**[13] ($J_{12} = 6.0$ Hz).

In a similar manner to the foregoing, hex-2-enopyranosides **2**–**8** were converted to vinyl ethers **11**–**17**.[13] In general, products arising from cleavage at the exocyclic alkoxy group predominated over those arising from cleavage at the lactol oxygen.[14] Indeed in the cases of **2**, **3**, **4**, and **5** only exo cleavage occurred, while at the other extreme in **7**, there were equal amounts of products from both modes of cleavage.

In each case, the reaction, conveniently monitored by tlc, contained only the starting olefin and/or the product(s) indicated (Chart I), and where necessary the cyclic ether (Chart I) could be separated easily from the acyclic product by silica-column chromatography. Complete conversion with ether as solvent required only patience ranging from 1 hr to 2 weeks. However, in order to deemphasize the latter requirement as well as improve the versatility of the solvent, tetrahydrofuran and dioxane were examined. As is apparent from Table I, both had a salutary effect on the reaction, dioxane being clearly the favorite for an ether-insoluble substance such as **4** or for a sluggish reactant such as **6**. Changing the solvent did not appear to profoundly alter the ratio of the products.

The stereospecific reduction of **2** and **3** to **11** and **12**, respectively,[13,15] suggested a highly ordered transition state such as that envisaged for the pentacoordinate complex **20**. If so, the product from LAD reduction ought to incorporate deuterium on the face of the molecule from which the alkoxy group is departing. Ac-

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(5) R. J. Ferrier, *Advan. Carbohydr. Chem.*, **20**, 67 (1965); *ibid.*, **24**, 199 (1969).

(6) R. U. Lemieux and S. W. Gunner, *Can. J. Chem.*, **46**, 397 (1968); R. U. Lemieux and T. L. Nagabhushan, *ibid.*, **46**, 401 (1968); T. L. Nagabhushan, *ibid.*, **48**, 257 (1970).

(7) A. Rosenthal, *Advan. Carbohydr. Chem.*, **23**, 59 (1968).

(8) R. U. Lemieux and S. Levine, *Can. J. Chem.*, **40**, 1926 (1962); **42**, 1473 (1964); R. U. Lemieux and B. Fraser-Reid, *ibid.*, **42**, 532 (1965); **43**, 1460 (1965); R. U. Lemieux and A. R. Morgan, *ibid.*, **43**, 2191, 2199, 2205 (1965); R. J. Ferrier, *J. Chem. Soc.*, 5443 (1964); R. J. Ferrier and N. Prasad, *ibid.*, *C*, 570, 581 (1969).

(9) The values for the various couplings between H-1, H-2, H-3, and H-3′ of **9** may be estimated from the 220-MHz nmr spectra ($CDCl_3$, TMS) of the epimeric substances **18**[10] and **19**[11] in which $|J_{13}| = 2.7$ and 1.3 Hz, respectively, and $|J_{23}| = 2.0$ and 5.2 Hz, respectively. The observed couplings of **9** should be, and indeed are found to be, the average[12] of these relevant values.

(10) B. Fraser-Reid and B. Radatus, *Chem. Commun.* 779 (1970).

(11) B. Fraser-Reid and B. Radatus, *Can. J. Chem.*, **47**, 4095 (1969).

(12) R. J. Abraham and H. J. Bernstein, *ibid.*, **39**, 216 (1961).

(13) All new compounds gave satisfactory mass spectral and/or elemental as well as spectroscopic analyses.

(14) For a pertinent example, see E. L. Eliel, B. E. Nowak, R. A. Daignault, and V. G. Badding, *J. Org. Chem.*, **30**, 2441, 2448 (1965).

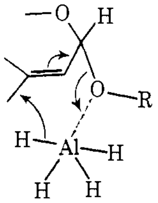
(15) The stereochemistry at carbon-3 in **11** and **12** is as indicated in Chart I, since in both compounds $J_{23} = 2.0$ Hz.[16]

Table I. Preparation of 3-Deoxy Glycals from Some Hex-2-enopyranosides Using Different Solvents[a]

Re-act-ant	Reagent[b]	Solvent: Ether	Solvent: Tetrahydro-furan	Solvent: Dioxane
1	LAH	10 hr,	4 hr	0.5 hr
	LAD	3 days		5 hr
6	LAH	14 days, incomplete	8 days	20 hr
	LAD			2 days
4	LAH	3 days	17 hr	2.5 hr

[a] The solutions were 0.135 *M* in both reactant and reagent except in the case of **4**, where the reagent was in threefold excess. The solutions were refluxed. [b] The more sluggish reaction of LAD is a phenomenon which has also been observed by Eliel.[1d]

cordingly, the β-D olefin **6** gave **21**, while the α-D anomer **1** gave **22**, as the only deuterated cyclic ether in each case.[16, 17]



20

Brown has rationalized the course of LAH–AlCl$_3$ hydrogenolysis of acetals on the basis of a stable oxocarbonium intermediate.[2] It is conceivable that in complex **20** there exists considerable carbonium-ion character in the -O—C$_1$—C$_2$=C$_3$- array. In this connection it should be noted that the carbon-4 methoxy of compound **7** is available for formation of a complex (akin to **20**) which would deliver the hydride ion at carbon-2 and give the olefin at carbon-3. The complete absence of such a product in spite of the formation of **15** and **16** is in complete accord with a carbonium-ion-like intermediate.

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[16] The stereochemistry at carbon-3 can be determined by comparing the spacing for J_{23} with the corresponding value in the iodide **18**[9, 10] (2.0 Hz) or its 3-epimer **19**[9, 11] (5.2 Hz).

[17] The observed values for J_{12} and J_{23} are:[16] in **21**, 7.0 and 1.7 Hz; in **22**, 7.0 and 6.0 Hz, respectively.

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Reaction of (3)-1,2-B$_9$C$_2$H$_{13}$ with Aluminum Trialkyls. Synthesis of 1,2-B$_9$C$_2$H$_{12}$AlR$_2$ and 1,2-B$_9$C$_2$H$_{11}$AlR Complexes, with Crystallographic Characterization of 1,2-B$_9$C$_2$H$_{11}$Al(C$_2$H$_5$)

Sir:

The (3)-1,2-dicarbollide ion, B$_9$C$_2$H$_{11}^{2-}$, has previously been shown capable of accepting a variety of transition metal ions[1] and main group species through insertion reactions.[2] The acidic carborane (3)-1,2-B$_9$C$_2$H$_{13}$ has been employed in an analogous insertion reaction in only one reported case, the synthesis of 1-trimethylamino-1-beryl-2,3-dicarba-*closo*-dodecaborane(12), B$_9$C$_2$H$_{11}$BeN(CH$_3$)$_3$.[3]

We wish to report the results of extending this latter synthetic route to trialkylaluminum derivatives and the structural characterization of one of the products.

The slow addition of an equimolar benzene solution of triethylaluminum to a benzene solution of (3)-1,2-B$_9$C$_2$H$_{13}$[4] under dry nitrogen, followed by heating to 50° for 1 hr, led to the release of 1 mol equiv of ethane and the initial formation of 1,2-B$_9$C$_2$H$_{12}$Al(C$_2$H$_5$)$_2$ (I). Removal of solvent gave a quantitative yield of crude microcrystalline product which was purified by recrystallization from cold, dry *n*-hexane: yield 79% of clear large crystals, mp 34.5–35.5° (uncor) in a sealed capillary.

Upon heating I in benzene at 77° for 25 hr, a second mole equivalent of ethane was released. Removal of solvent left a quantitative yield of crude microcrystalline 1,2-B$_9$C$_2$H$_{11}$Al(C$_2$H$_5$) (II). Recrystallization from benzene-*n*-hexane solution gave medium-sized clear crystals of pure product: yield 72%, mp 97–99° (uncor) in a sealed capillary.

Trimethylaluminum was found to give completely analogous derivatives, 1,2-B$_9$C$_2$H$_{12}$Al(CH$_3$)$_2$ (III) and 1,2-B$_9$C$_2$H$_{11}$Al(CH$_3$) (IV). In this case, however, higher temperatures and longer reaction times were necessary.

During the course of these investigations the synthesis of an ethyl-substituted aluminocarborane–tetrahydrofuran (THF) adduct, 1,2-B$_9$C$_2$H$_{11}$Al(C$_2$H$_5$)·2THF, prepared from (3)-1,2-B$_9$C$_2$H$_{11}^{2-}$ and Al(C$_2$H$_5$)Cl$_2$ in THF, was reported.[5] It was alleged by these authors from microanalysis and melting-point data that the complex contained the aluminum atom incorporated in such a manner as to form an icosahedral carborane skeleton solvated with 2 molecules of THF.

We have repeated and confirm this synthesis. Moreover, when II was dissolved in THF and excess solvent pumped off, the identical product, 1,2-B$_9$C$_2$H$_{11}$Al(C$_2$H$_5$)·2THF, was obtained. That II forms a THF adduct is not surprising, since trialkylaluminum–THF adducts have been reported previously[6,7] and the possibility of opening the icosahedral structure by THF complexation exists.

Both I and II appear to be monomeric in solution, their proton nmr spectra remaining unchanged, except for viscosity broadening, in toluene solution to −95°. Under these conditions the bridging and terminal alkyl resonances of trialkylaluminum dimers have been resolved.[8]

Both I and II were slowly hydroyzed by diffusion exposure to air and subsequently dissolved in water (they both violently enflame on contact with water). The product recovered from the aqueous solution,

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[1] M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

[2] R. W. Rudolph, R. L. Voorhees, and R. E. Cochoy, *J. Amer. Chem. Soc.*, **92**, 3351 (1970).

[3] 3-Trimethylamino-3-beryl-1,2-dicarba-*closo*-dodecaborane(12), using the nomenclature system of the present communication: G. Popp and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968).

[4] R. A. Wiesboeck and M. F. Hawthorne, *ibid.*, **86**, 1642 (1964).

[5] B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **5**, 1153 (1968).

[6] W. R. Kroll, *Chem. Commun.*, 1969, 844.

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[8] K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *J. Phys. Chem.*, **69**, 3418 (1965).