The nmr spectrum of **5** requires that the molecule possess C_s symmetry and, further, that it exist in the sterically favorable conformation shown in **5** (EEE), where both dihedral angles, H_a–H_b and H_c–H_b, are estimated at ~90°.[12]

Prolonged exposure of **4** at 198°, in benzene, leads cleanly and irreversibly ($k = 1.36 \pm 0.15 \times 10^{-5}$ sec^{-1}; $\Delta G^{\ddagger} = 38.5$ kcal/mol)[13] to **6** [mp 97–97.5°; nmr (60 MHz, C_6D_6) τ 3.8–4.5 (4 H, $H_d + H_c$), 5.82 (2, H dd, H_b, $J_{bc} = 4.5$ Hz, $J_{ba} = 2$ Hz), 6.52 (2 H, d, H_a, $J_{ab} = 2$ Hz); uv $\lambda_{max}^{C_6H_{14}}$ 237 nm (sh, ϵ 680), 245 (sh, 950), 253 (1200), 262 (1240), 272 (720); *m/e* 136 (P^+, 59%)] by what appears to be an unprecedented $[1,5]_s$ thermal shift of an oxa bridge. The assignment of an anti dioxa structure to **6** follows from the magnitude of J_{ab} (2 Hz)[14] and confirms the trans disposition of the oxirane groups in **4**.

In sharp contrast to the **4** → **6** conversion thermolysis of **3** at 202°, in benzene, produces an equilibrium mixture consisting (nmr) of ~60% **3** and 40% **7** [mp 33–34°; nmr (60 MHz, $CDCl_3$) τ 3.72 (2 H, d, H_d, $J_{dc} = 8$ Hz), 5.50 (2 H, dd, H_c, $J_{cd} = 8$ Hz, $J_{cb} = 2.5$ Hz), 6.60 (2 H, s, H_a), 7.25 (2 H, br s, H_b); uv $\lambda_{max}^{C_6H_{14}}$ 206 nm (ϵ ~3700), 218 (3400); *m/e* 136 (P^+, 33%)] and materializing with $k_1 = 5.0 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger} = 37.6$ kcal/mol, and $k_{-1} = 7.87 \pm 0.23 \times 10^{-5}$ sec^{-1}, $\Delta G^{\ddagger} = 37.2$ kcal/mol. With regard to mechanism, we note that the obvious requirement of coiled forms **3** (FF) and **7** (FF) for bond relocation (Scheme II) coupled with the undoubted natural tendency of these substances to favor sterically less demanding conformations, *e.g.*, **3** (EE), introduces at this stage some uncertainty as to whether the measured activation reflects the EE to FF ring inversion,[10] the productive **3** (FF) $\rightleftharpoons$ **7** (FF) "Cope" process, or possibly a combination of both.

Compared to dioxides **3** and **4**, trioxirane **5** displays striking thermal stability, remaining unchanged (nmr) on heating at 255° for ~20 hr.

Despite their requirement for high thermal activation, the bond relocations of **3** and **4** proceed entirely along symmetry-allowed pathways, the failure of either substrate to rearrange to the symmetry-disallowed isomer **9** being especially notable in this connection. Orbital symmetry control must also be responsible for the resistance of these substances to thermolyze into monocyclic structures, which sharply contrasts the tendency of their $C_6H_6O_2$ and $C_6H_6O_3$ counterparts to do so readily.[15] Specifically, cross-link disrotation of **2**, **3**, **4**, and **5** to all-cis monocyclic frames is predicted to be possible in the electronically excited state but not in the ground state. Preliminary experimentation designed to test this prediction has, to date, been frustrated by the lack of effective chromophores in these substances.

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[12] The conformational rigidity of **5** is perhaps best understood in light of the fact that ring inversion would necessarily convert the arrangement shown in **5** (EEE) into the sterically less accessible FFF form.

[13] The rate of rearrangement in C_6D_6 was monitored by nmr spectroscopy.

[14] Examination of Dreiding molecular models reveals the H_a–H_b dihedral angle to be ~20° for **6** and ~80° for the alternate (exo) stereochemical arrangement. The association of $J = 2$ Hz with the 20° dihedral angle of the endo stereochemical variant (**6**) follows from a well-documented correlation of *J vs.* dihedral angle among cyclic epoxides: K. Tori, T. Komeno and T. Nakagawa, *J. Org. Chem.*, **29**, 1136 (1964); see also ref 15a.

[15] (a) H. J. Alterbach and E. Vogel, *Angew. Chem.*, **84**, 985 (1972); (b) E. Vogel, H.-J. Altenbach, and D. Cremer, *ibid.*, **84**, 983 (1972); (c) E. Vogel, H.-J. Altenbach, and C.-D. Sommerfeld, *ibid.*, **84**, 986 (1972); (d) R. Schwesinger and H. Prinzbach, *ibid.*, **84**, 990 (1972).

The Fast Base-Induced Reaction of α,α-Dichloromethyl Methyl Ether with Organoboranes. A New General Route from Organoboranes to the Corresponding Carbon Structures

Summary: The base-induced reaction of α,α-dichloromethyl ether with a representative series of organoboranes provides a new convenient low temperature route to tertiary carbinols in high yield.

Sir: The reaction of organoboranes with α,α-dichloromethyl methyl ether (DCME) induced by lithium triethylcarboxide provides a convenient route to the corresponding tertiary carbinols in excellent yield (eq 1). The initial transfer reaction is very rapid, being

$$R_3B + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[25^\circ]{THF} \xrightarrow{NaOH,\ H_2O_2} R_3COH \quad (1)$$

complete within 15 min at 25 or 0°, and the boron intermediates are oxidized readily to the corresponding carbinols. Consequently, this reaction provides a valuable means of converting organoboranes into the corresponding carbon structures under relatively mild conditions of time and temperature.

This procedure (eq 2) provides a simple alternative

$$(n\text{-}Bu)_3B + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[15\ min]{THF,\ 25^\circ} [\ ] \xrightarrow{[O]} \underset{94\%}{(n\text{-}Bu)_3COH} \quad (2)$$

to the reaction of organoboranes with carbon monoxide[1-3] (eq 3) or with sodium cyanide and trifluoroacetic

$$(n\text{-}Bu)_3B + CO \xrightarrow[8\ hr]{diglyme,\ 125^\circ} [\ ] \xrightarrow{[O]} \underset{90\%}{(n\text{-}Bu)_3COH} \quad (3)$$

anhydride[4] (eq 4) as synthetic routes for the replace-

$$[(n\text{-}Bu)_3BCN]^-Na^+ \xrightarrow[-78^\circ,\ then\ 45^\circ\ for\ 12\ hr]{(CF_3CO)_2O} [\ ] \xrightarrow{[O]} \underset{73\%}{(n\text{-}Bu)_3COH} \quad (4)$$

ment of boron in organoboranes by carbon. Treatment of a representative series of organoboranes, many of which are readily prepared by the hydroboration of

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[1] M. E. Hillman, *J. Amer. Chem. Soc.*, **84**, 4715 (1962).

[2] H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 2737 (1967).

[3] For a review of the carbonylation reaction of organoboranes with pertinent literature references, see H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

[4] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, 1048 (1971).

olefins,[5,6] with DCME and lithium triethylcarboxide provides yields of tertiary carbinols comparable to or greater than those obtained by the previous two procedures. The results are presented in Table I.

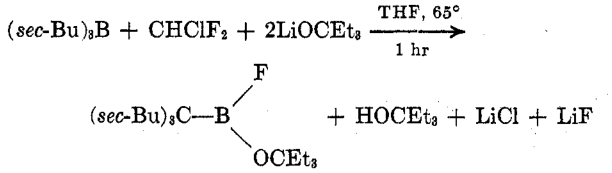
TABLE I

SYNTHESIS OF TERTIARY CARBINOLS *via* THE REACTION OF REPRESENTATIVE ORGANOBORANES WITH DCME AND LITHIUM TRIETHYLCARBOXIDE

Organoborane	Tertiary carbinol obtained on oxidation	Yield of carbinol, %[a]
Tri-*n*-butylborane	Tri-*n*-butylcarbinol	94[b]
Tri-*sec*-butylborane	Tri-*sec*-butylcarbinol	95 (85)[c]
Triisobutylborane	Triisobutylcarbinol	99
Tricyclopentylborane	Tricyclopentylcarbinol	97 (91)[c]
Tricyclohexylborane	Tricyclohexylcarbinol	92
Tri-*exo*-norbornylborane	Tri-2-norbornylcarbinol	84[d]
B-Cyclohexylborinane[e]	1-Cyclohexylcyclohexanol	71[f]
Triphenylborane	Triphenylcarbinol	95[g]

[a] Glpc analysis. [b] 30% excess base and DCME are required. Stoichiometric amounts result in only an 85% yield of tri-*n*-butylcarbinol. [c] Isolated yields by distillation of the product under reduced pressure. Products were compared with authentic samples obtained from carbonylation of the trialkylboranes.[2] [d] 50% excess base and DCME are required. Stoichiometric amounts result in only a 69% yield of tri-2-norbornylcarbinol. [e] H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971). [f] Use of 100% excess base increased the yield of 1-cyclohexylcyclohexanol to 79%. [g] Use of 100% excess base is required. Stoichiometric amount results in only a 54% yield of triphenyl transfer products. Oxidation using sodium acetate-hydrogen peroxide is necessary to avoid protonolysis of the benzylic organoboron intermediate. Oxidation with sodium hydroxide-hydrogen peroxide gives triphenylmethane (59%) and triphenylcarbinol (33%).

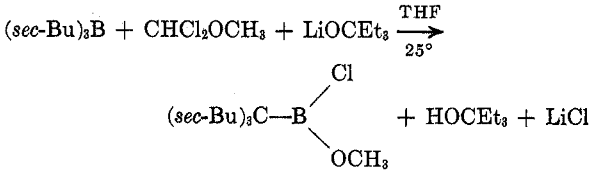
We previously reported that chlorodifluoromethane reacts with tri-*n*-butylborane and lithium triethylcarboxide to produce tri-*n*-butylcarbinol on oxidation in essentially quantitative yields.[7] This reaction appeared very promising. However, extension to tri-*sec*-butylborane and other secondary and hindered organoboranes gave poor results which were traced to the intermediate formation of highly hindered triethylcarbinol esters of *tert*-alkylfluoroboronic acids[8] (eq 5)



(5)

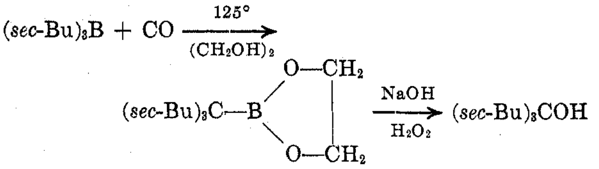
in essentially quantitative yield, but remarkably resistant to oxidation to the trialkylcarbinols.

This difficulty led us to seek a more favorable route for the conversion of organoboranes to the corresponding carbinols. We had noted that the reaction of organoboranes with chlorodifluoromethane and other trisubstituted methanes required 2 equiv of lithium triethylcarboxide, whereas DCME required only 1.[7] This suggested that the reaction with DCME might not involve the formation of such a hindered boronic ester of triethylcarbinol. This proved to be the case. Treatment of tri-*sec*-butylborane with 1 equiv each of lithium triethylcarboxide and DCME revealed the presence in the reaction mixture of 1 equiv of free triethylcarbinol. Nmr revealed the intermediate to be the methyl *tert*-alkylchloroboronic ester[9] (eq 6). This intermediate is



(6)

readily oxidized with alkaline hydrogen peroxide in a manner similar to that previously noted for the ethylene glycol esters of the *tert*-alkylboronic acids formed in the carbonylation of organoboranes in diglyme[2] (eq 7).



(7)

Thus, treatment of the reaction product from DCME and lithium triethylcarboxide with alkaline hydrogen peroxide provided a 95% yield of tri-*sec*-butylcarbinol. Equally satisfactory results were realized with other organoboranes (Table I). Consequently, the DCME–lithium triethylcarboxide treatment of organoboranes provides the desired general route for replacement of the boron atom by carbon. As was pointed out, this transformation has major possibilities for the synthesis of carbon structures.

As indicated previously, the reaction of organoboranes with DCME and lithium triethylcarboxide is very rapid at room temperature or even 0°. In fact, the reaction is complete shortly after the addition of the alkoxide. Addition of 1 molar equiv of lithium triethylcarboxide to a solution of tri-*sec*-butylborane and DCME at 0° followed by warming to room temperature for merely 10 min results in a 95% yield of tri-*sec*-butylcarbinol on oxidation. Stirring at 0° for 15 min gives a 90% yield of the tertiary carbinol. The simplicity of the reaction, the moderate temperature, and the speed with which it occurs offer major advantages over the procedures previously availabe for converting organoboranes to the corresponding carbon structures (eq 3 and 4). It clearly possesses very wide generality, as indicated by its use to synthesize 1-cyclohexylcyclohexanol and triphenylcarbinol (Table I).

Because of the marked facility of the reaction, we thought that less hindered alkoxides than lithium triethylcarboxide might be effective. However, the less hindered trialkylboranes proved to be highly sensitive to the steric requirements of the alkoxide, whereas the more hindered trialkylboranes can tolerate less hindered alkoxides than lithium triethylcarboxide. The results realized with three lithium alkoxides of increasing steric bulk with a series of trialkylboranes of varying steric requirements and DCME are presented in Table II. Lithium alkoxides are superior to sodium or potas-

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

(6) H. C. Brown, "Boranes in Organic Synthesis," Cornell University Press, Ithaca, N. Y., 1972.

(7) H. C. Brown, B. A. Carlson, and R. H. Prager, *J. Amer. Chem. Soc.*, **93**, 2070 (1971).

(8) H. C. Brown and B. A. Carlson, *J. Organometal. Chem.*, in press.

(9) Nmr shifts of the methoxy protons were correlated with those of the corresponding dimethyl-*tert*-alkylboronic ester and other methylalkylchloroboronic esters and dimethylalkylboronic esters reported by H. Vahrenkamp and V. Noth, *J. Organometal. Chem.*, **12**, 23 (1968).

TABLE II

REACTION[a] OF TRIALKYLBORANES WITH DCME UNDER THE INFLUENCE OF A SERIES OF LITHIUM ALKOXIDES OF INCREASING STERIC BULK

Lithium alkoxide	Yield of trialkylcarbinol oxidation product, %[b] $(n\text{-Bu})_3B$	$(sec\text{-Bu})_3B$	$(c\text{-Hex})_3B$
Lithium *tert*-butoxide	33	86	77
Lithium *tert*-amyloxide	55	88	79
Lithium triethylcarboxide	84	95	92

[a] Carried out under standard conditions of addition of 1 molar equiv of lithium alkoxide to a stirred solution of 1 molar equiv of trialkylborane plus 1.1 molar equiv of DCME in THF at 0° followed by warming to room temperature for 30 min and oxidation with alkaline hydrogen peroxide. [b] Analysis by glpc.

sium alkoxides, as previously observed for the reaction of tri-*n*-butylborane with chlorodifluoromethane.[7]

The following procedure describing the preparation of tricyclopentylcarbinol from tricyclopentylborane is representative. In an oven-dried 300-ml flask, maintained under a nitrogen atmosphere and fitted with a septum inlet, magnetic stirrer, and reflux condenser, are placed 50 ml of a 1 *M* solution of tricyclopentylborane in THF prepared by the hydroboration of cyclopentene.[5,6] The solution is cooled to 0° and 55 mmol (5.33 g) DCME are added followed by the addition of 50 mmol of lithium triethylcarboxide (27 ml of a 1.84 *M* solution in hexane) over 5 min. The reaction is then allowed to warm to room temperature for 30 min during which time a heavy white precipitate of lithium salt forms. Then, 50 ml of 95% ethanol is added followed by 12 g of sodium hydroxide. Oxidation is accomplished by the slow, careful addition of 40 ml of 30% hydrogen peroxide at 0° followed by warming to 50–60° for 1 hr. The aqueous phase is salted out with anhydrous potassium carbonate and the organic phase is separated. The solvents are removed on a rotary evaporator and the residue is fractionally distilled under reduced pressure giving 10.8 g (91%) of tricyclopentylcarbinol, bp 152–153° (2 mm). Nmr, ir, and glpc were checked against those of an authentic sample of tricyclopentylcarbinol obtained from the carbonylation of tricyclopentylborane.[2]

It is of great interest why the reaction of DCME ($HCCl_2OCH_3$) is so much faster than the corresponding reaction of chloroform ($HCCl_3$).[7] Hine has suggested that DCME, in contrast to chloroform, may react with bases by a concerted mechanism to go directly to methoxychlorocarbene.[10,11] However, discussion of this possibility will be deferred until we can complete an investigation now underway.

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(10) J. Hine, R. J. Rosscup, and D. C. Duffey, *J. Amer. Chem. Soc.*, **82**, 6120 (1960).

(11) Methoxycarbene, presumably formed from lithium alkyls and DCME, does not give the clean reaction with organoboranes observed here: A. Suzuki, S. Nozawa, N. Miyaura, M. Itoh, and H. C. Brown, *Tetrahedron Lett.*, 2955 (1969).

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