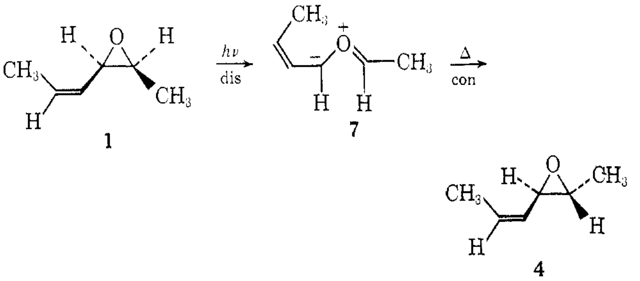
tained photochemically. However, we failed to observe any geometrical isomerization of the epoxides under either conditions. The thermal rearrangements could be occuring by a radical path or by an ionic catalyzed wall reaction. In the photolysis these ketones are generated by a 1,2-hydrogen atom shift. Radical 1,2 shifts occur rarely, if at all, and they are symmetry forbidden.[4] However, 1,2-radical migrations might indeed be quite favorable starting from a 1,3 diradical since the energy gained from concurrent formation of the carbonyl group may overcome the orbital symmetry considerations.

In view of the failure of C–O bond opening by both ionic or thermal (Table II) conditions to produce any epoxide isomerization and the demonstrated formation of carbonyl ylides in the photochemistry of aryl-substituted epoxides,[5] it is tempting to assign the intermediate in pathway "b" (Scheme II) to a carbonyl ylide. Similar carbonyl ylides have also been generated thermally.[6] In the present case isomerization could be explained by a photochemically allowed disrotatory ring opening followed by a thermally allowed conrotatory ring closure as shown below for the conversion of **1** to **4**. However, a carbonyl ylide intermediate (*i.e.*, **7**) seems unlikely for several reasons. Photolysis of **1** in acetone solutions containing various amounts of dimethyl acetylenedicarboxylate (an efficient carbonyl ylide trapping agent[6]) at 25 or at −78° failed to produce any adduct of a carbonyl ylide. The only effect of the trapping agent was to slightly decrease the rate of product formation. Secondly, if **7** were generated in the photolysis of **1**, it seems highly likely that ring closure to a 4,5-dihydrofuran would occur. We could find no evidence for any dihydrofuran formation at 25 or at −78°. The only effect of low temperature was to slow the rate of reaction. For example, the formation of **5** and **6** was ~1.5 times as slow at −78° as at 25°. However, the overall results were identical. Thermolysis of epoxide **1** in the presence of dimethyl acetylenedicarboxylate also failed to trap any carbonyl ylide intermediate.



The photochemical reactions described here are most likely triplet sensitized processes resulting from energy transfer from triplet state acetone. Supporting evidence for this is found in that the reactions are efficiently quenched by piperylene. The cis–trans isomerization of the olefinic functionality of the epoxides and the β,γ-unsaturated ketones are most likely analogous to the well-studied triplet sensitized isomerizations of alkenes. A very inefficient photoisomerization of **5** and **6** by direct irradiation has been observed.[7] More recently Engel has reported an example of acetone sensitized cis–trans isomerization of a β,γ-unsaturated ketone.[8] Thus the formation of **5** in the photolysis of **1** and **4** and the formation of **6** in the photolysis of **2** and **3** are due in part to photoisomerization of the enones.

From the results presented here it is clear that, whether the epoxide isomerization occurs *via* a carbonyl ylide which is too short lived to be trapped or *via* an initial C–O bond cleavage, the intermediate is able to undergo reversible ring closure. We currently favor pathway "a" in Scheme II with homolytic bond cleavage, but any of several ionic pathways can not be ruled out at this time. The mode of formation of the β,γ-unsaturated ketones was discussed in a previous paper.[1]

We are currently investigating the nature of the intermediate responsible for the epoxide isomerization as well as extending our studies to nonconjugated epoxy olefins.

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[4] M. J. Perkins in "Organic Reaction Mechanisms, 1968," B. Capon and C. W. Rees, Ed, Interscience Publishers, London, 1969, p 293.

[5] D. R. Arnold and L. A. Karnischky, *J. Amer. Chem. Soc.*, 1404 (1970); see also ref 2.

[6] H. Hamberger and R. Huisgen, *Chem Commun.*, 1190 (1971); A. Dakmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

[7] H. Morrison, *Tetrahedron Lett.*, 3653 (1964).

[8] P. S. Engel and M. A. Schnexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).

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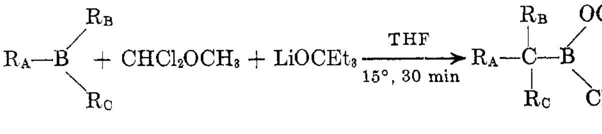
The Facile Transfer of Tertiary Alkyl Groups from Boron to Carbon in the Base-Induced Reaction of α,α-Dichloromethyl Methyl Ether with Organoboranes Containing Tertiary Alkyl Groups. A Novel Route to Highly Hindered Trialkylcarbinols Involving Exceptionally Mild Conditions

Summary: Trialkylboranes containing tertiary alkyl groups, such as *tert*-butyl and thexyl (2,3-dimethyl-2-butyl), undergo rapid reaction with α,α-dichloromethyl methyl ether and lithium triethylcarboxide at 25° to give the corresponding highly branched trialkylcarbinols after oxidation. B–C migration of the tertiary group occurs under exceedingly mild conditions without isomerization.

Sir: Treatment of relatively hindered trialkylboranes containing a tertiary alkyl group with α,α-dichloromethyl methyl ether (DCME) and lithium triethylcarboxide under mild conditions (25°) results in the transfer of all three groups from boron to carbon without rearrangement (eq 1). The product can then be

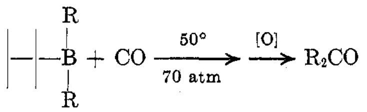


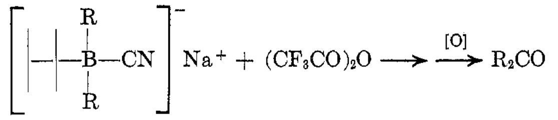
$$R_A{-}B(R_B)(R_C) + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[15°,\ 30\ min]{THF} R_A{-}C(R_B)(R_C){-}B(OCH_3)(Cl) \quad (1)$$

R_A = *tert*-butyl, thexyl (2,3-dimethyl-2-butyl) oxidized to the corresponding highly branched tertiary alcohol. This facile transfer of a tertiary alkyl group from boron to carbon in the present reaction is in marked contrast to the behavior of such groups in the related reactions with carbon monoxide[1] and sodium cyanide with trifluoroacetic anhydride.[2]

The reaction of carbon monoxide with trialkylboranes and the corresponding reaction of sodium cyanide with trialkylboranes induced by trifluoroacetic anhydride provides important procedures for replacing boron by carbon. This makes possible the "stitching" of relatively open structures with boron and the "riveting" of these structures by replacing the boron with carbon.[1]

One serious limitation has been the difficulty of extending these reactions to organoboranes containing tertiary alkyl groups. Such groups fail to migrate from boron to carbon under conditions suitable for primary and secondary. Advantage has been taken of this feature by using the thexyldialkylboranes for the synthesis of ketones[3,4] (eq 2 and 3).

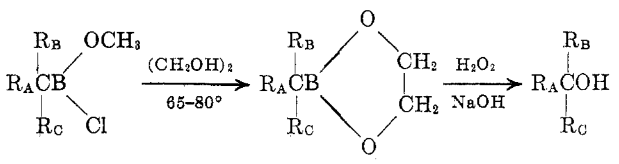

$$\overset{R}{\underset{R}{\vert\!-\!\vert\!-\!B}} + CO \xrightarrow[70\text{ atm}]{50^\circ} \xrightarrow{[O]} R_2CO \qquad (2)$$


$$\left[\overset{R}{\underset{R}{\vert\!-\!\vert\!-\!B}}\!-\!CN\right]^- Na^+ + (CF_3CO)_2O \longrightarrow \xrightarrow{[O]} R_2CO \qquad (3)$$

It proved possible to extend the carbonylation reaction to organoboranes containing a tertiary alkyl group by using higher temperatures, 3 hr at 150° under 70-atm pressure.[5] However, many highly hindered organoboranes are relatively labile. They are best prepared at relatively low temperatures[6] and it appeared undesirable to subject them to such comparatively high temperatures. Accordingly, we examined the applicability of the new reaction of organoboranes with DCME induced by lithium triethylcarboxide.[7]

We discovered that a wide variety of trialkylboranes containing a tertiary alkyl group (*tert*-butyl or thexyl) readily reacts with the reagent at 25° with transfer of all three alkyl groups from boron to carbon (eq 1). In the case of some of the more hindered derivatives use of an excess of the reagent improves the yield.

We did encounter a difficulty in the oxidation of the intermediate with alkaline hydrogen peroxide. With increasing steric bulk of the three alkyl substituents the rate of oxidation of the intermediate decreased[8] and required larger excesses of hydrogen peroxide. In the most hindered derivatives, such as thexyldiisobutylborane, thexyl-*sec*-butyl-*n*-pentylborane, and thexylcyclopentyl-*n*-pentylborane, it proved desirable to treat the initially formed intermediate with ethylene glycol to form the corresponding 2-(trialkylcarbinyl)-2-bora-1,3-dioxolane (eq 4). This cyclic ester proved to be more readily oxidized to the tertiary carbinol.



(4)

For example, when the intermediate from thexyldiisobutylborane was oxidized for 2 hr with a sixfold excess of sodium hydroxide and a tenfold excess of 30% hydrogen peroxide using ethanol as cosolvent at 50°, only 62% thexyldiisobutylcarbinol was obtained, with 20% residual boronic acid. Longer reaction times with double the amounts of sodium hydroxide raised the yield to 70%. However, prior conversion of the intermediate into the 2-bora-1,3-dioxolane by *in situ* treatment with ethylene glycol at 65-80° gave a faster oxidation, producing an 80% yield of the desired carbinol in 3 hr at 50°.

The results are summarized in Table I.

TABLE I
SYNTHESES OF TERTIARY CARBINOLS CONTAINING A TERTIARY ALKYL GROUP *via* REACTION OF TRIALKYLBORANES WITH DCME AND LITHIUM TRIETHYLCARBOXIDE

Trialkylborane	Procedure[a]	Trialkylcarbinol[b] obtained on oxidn	Yield,[c] % (by isoln)
Thexyldi-*n*-butyl	I	2,3,3-Trimethyl-4-(*n*-butyl)-4-octanol	84
Thexyldi-*n*-pentyl	I	2,3,3,-Trimethyl-4-(*n*-pentyl)-4-nonanol	85 (80)[d]
Thexyldiisobutyl	II	2,3,3,6-Tetramethyl-4-isobutyl-4-heptanol	80
Thexyl-*sec*-butyl-*n*-pentyl	II	2,3,3-Trimethyl-4-(*sec*-butyl)-4-nonanol	78.5
Thexylcyclopentyl-*n*-pentyl	II	2,3,3-Trimethyl-4-cyclopentyl-4-nonanol	75
tert-Butyldicyclohexyl	I	1,1-Dicyclohexyl-2,2-dimethyl-1-propanol	77
	I[e]	1,1-Dicyclohexyl-2,2-dimethyl-1-propanol	94 (90)[f]
B-(*tert*-butyl)-9-borabicyclo[3.3.1]nonane	I	9-(*tert*-Butyl)bicyclo[3.3.1]-nonan-9-ol	68
	I[e]	9-(*tert*-Butyl)bicyclo[3.3.1]-nonan-9-ol	83[g]

[a] I, stoichiometric quantities of DCME and lithium triethylcarboxide, oxidation with excess sodium hydroxide and hydrogen peroxide with ethanol as cosolvent as in the described procedure; II, 100% excess of DCME and lithium triethylcarboxide used, transformation of the intermediate borane into the ethylene trialkylcarbinylboronate and oxidation as in the described procedure. [b] Satisfactory nmr, ir, mass spectra, and elemental analyses data were obtained for all of the new compounds. [c] By glpc. [d] Bp 114° (0.2 mm), $n^{20}D$ 1.4621. [e] 100% excess of DCME and lithium triethylcarboxide used. [f] Bp 136-138° (0.7 mm), mp 46-49°. [g] Mp 67.8-69°.

The following procedure for the preparation of 2,3,3-trimethyl-4-(*n*-pentyl)-4-nonanol is representative. In an oven-dried 100-ml flask maintained under a nitrogen atmosphere and fitted with a septum inlet, magnetic stirrer, and reflux condenser was placed 50 mmol (25.2 ml of a 1.98 *M* solution) of thexylborane in

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[1] H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

[2] A. Pelter, *Chem. Ind. (London)*, 206 (1973).

[3] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5285, 5477 (1967).

[4] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, 1529 (1970).

[5] E. Negishi and H. C. Brown, *Synthesis*, 196 (1972).

[6] Research in progress with J.-J. Katz and E. Negishi.

[7] H. C. Brown and B. A. Carlson, *J. Org. Chem.*, **38**, 2422 (1973).

[8] The problem was encountered previously in the oxidation of derivatives, such as *sec*-$Bu_3BF(OCEt_3)$: H. C. Brown and B. A. Carlson, *J. Organometal. Chem.*, **54**, 61 (1973).

THF.[9] The solution was cooled to 0° and 100 mmol of 1-pentene (11 ml) was added dropwise. The mixture was stirred for an additional hour at 0° to ensure completion of the hydroboration. The reagent, DCME (5.0 ml, 55 mmol), was then added, followed by the addition of 50 mmol of lithium triethylcarboxide (27 ml of a 1.84 *M* solution in hexane) over 10 min. The reaction was allowed to come to room temperature over 30 min. The formation of a heavy white precipitate, presumably lithium chloride, was observed. Then 50 ml of 95% ethanol was added, followed by 12 g of sodium hydroxide. Oxidation was accomplished by the slow addition of 40 ml of 30% hydrogen peroxide at 0° followed by warming to 50–60° for 1 hr. The aqueous phase was salted out with sodium chloride and the organic phase separated. Solvents were removed with a rotary evaporator and the product, 2,3,3-trimethyl-4-(*n*-pentyl)-4-nonanol, was recovered by distillation under reduced pressure: 10.4 g, 80% yield, bp 114° (0.2 mm), $n^{20}\text{D}$ 1.4621.

For the more hindered derivatives, such as thexylcyclopentyl-*n*-pentylborane, a slightly modified procedure proved advantageous. To 5.0 mmol of thexylborane at −25° was added 5 mmol (0.44 ml) of cyclopentene. After 1 hr at this temperature, 5 mmol (0.55 ml) of 1-pentene was added and the solution was brought to 25° to complete the hydroboration. The addition of DCME and lithium triethylcarboxide in 100% excess was carried out as described in the procedure above. To the reaction mixture was added 10 mmol (0.60 ml) of ethylene glycol and the solvents (THF and hexane) were removed by distillation. The reaction mixture was cooled to 0°; 10 ml of ethanol was added, followed by 2.4 g of sodium hydroxide and 10 ml of 30% hydrogen peroxide. The reaction mixture was then brought to 50–55° and maintained there for 3 hr. The organic products were extracted into 10 ml of THF after salting out the aqueous phase. Glpc examination of the organic phase using tridecane as internal standard revealed 3.80 mmol, a yield of 75%, of 2,3,3-trimethyl-4-cyclopentyl-4-nonanol.

It is evident from the results presented in Table I that the present procedure is broadly applicable for the conversion of highly branched organoboranes into the corresponding carbinols. The cyanoborate reaction at present cannot handle such derivatives. Carbonylation can be used, but requires much more drastic conditions. In view of the lability of organoborane structures which contain tertiary alkyl groups, the mild conditions of the present procedure greatly extends the range of applicability of "stitching" and "riveting."

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JULY 5, 1973

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[9] H. C. Brown, Y. Yamamoto, and C. F. Lane, *Synthesis*, 304 (1972).

[10] Graduate research assistant on Grant No. GM 10937 supported by the National Institutes of Health.

[11] Graduate research assistant on Grant No. GP 6942X supported by the National Science Foundation.