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A CONVENIENT ROUTE TO SYMMETRIC 1,1-DIALKYLETHENES FROM 1,2-DIMETHOXYETHENYLLITHIUM AND TRIALKYLBORANES

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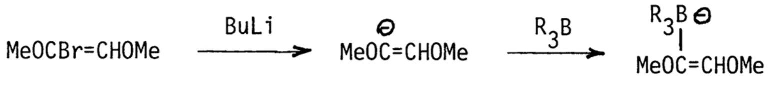
1,1-Dialkylethenes are prepared from 1,2-dimethoxyethenyllithium and organoboranes by treatment with trichloroacetic acid and then with sodium acetate-acetic anhydride and $TiCl_4/Ti(OPr^i)_4$.

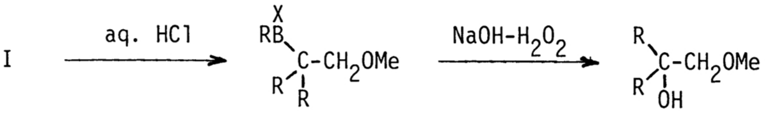
The synthetic versatility of unsaturated organoborates occupies an important position in the recent progress of organic synthesis.[1] In an attempt to develop a new synthetic utility of alkynyl- and alkenyltrialkylborates, we have previously reported several reactions for the syntheses of internal alkynes[2] and alkenes.[3] We wish to report here a new synthetic method for 1,1-dialkylethenes from 1,2-dimethoxyethenyllithium[4] and trialkylboranes.

Our first intention was to examine the reaction of alkenyltrialkylborates which have two leaving functions. Thus, lithium 1,2-dimethoxyethenyltrialkylborates (I) were selected as such borates, because they are readily prepared by the reaction of trialkylboranes with 1,2-dimethoxyethenyllithium[4] (eq. 1). Treatment of the borates (I) with diluted hydrochloric acid followed by the usual alkaline hydrogen peroxide oxidation was found to afford dialkyl(methoxymethyl)methanol as a main product. For example, dihexyl(methoxymethyl)methanol was obtained in an 88% yield with a trace of 2-hexyl-1-octene (<2%), when trihexylborane was used as a trialkylborane.



$$\mathrm{MeOCBr{=}CHOMe} \xrightarrow{\mathrm{BuLi}} \mathrm{Me}O\overset{\ominus}{\mathrm{C}}\mathrm{{=}CHOMe} \xrightarrow{R_3B} \mathrm{MeO}\overset{R_3B^{\ominus}}{\mathrm{C}}\mathrm{{=}CHOMe} \qquad (1)$$

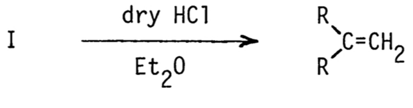
I



(2)

II

On the other hand, treatment of I with anhydrous hydrogen chloride in ether in place of diluted hydrochloric acid gave 2-hexyl-1-octene in a 65 % yield directly as shown in eq. 3.



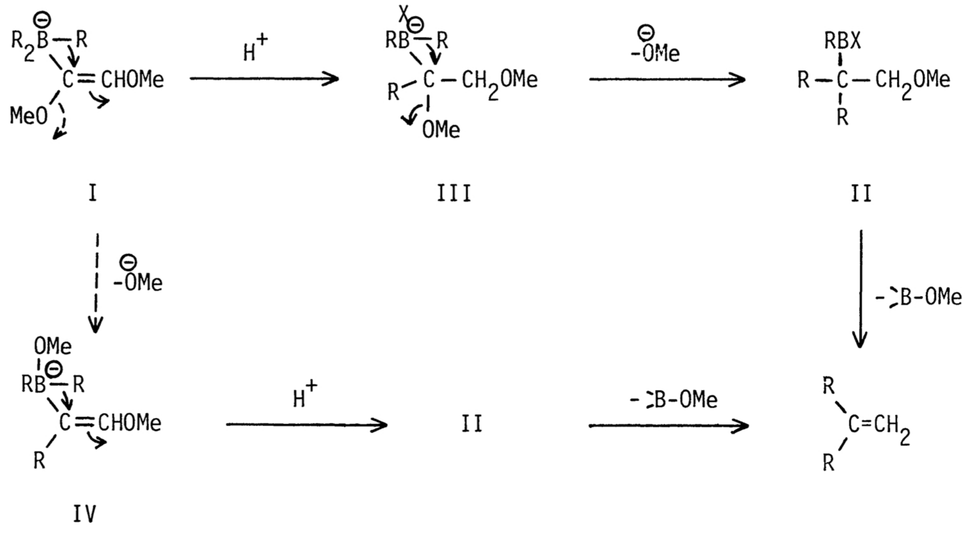
(3)

For such a synthesis of 1,1-di-*n*-alkylethenes, it was also found that acetic acid and sodium acetate-acetic anhydride are effective for the migration of alkyl groups from boron to carbon and for elimination of methoxyborane moiety, respectively. However, di-*sec*-alkyl and dicyclopentyl derivatives did not give corresponding products under such conditions.

In order to find a general procedure for the synthesis of 1,1-dialkylethenes, we tried many methods and found that β-elimination of >B-OMe moiety from the intermediate (II) proceeds under mild conditions in the presence of sodium acetate-acetic anhydride-Lewis acids. For example, the yields of 1,1-dicyclopentylethene increased in the order of $SnCl_4$, $ZnCl_2$, $AlCl_3$, $Ti(OPr^i)_4$, $BF_3:OEt_2$ and $TiCl_4$. Although $TiCl_4$ gave the highest yield, the products were a mixture of three isomers when tricylopentylborane was used. The best yield and selectivity were finally obtained by treatment with trichloroacetic acid followed by sodium acetate-acetic anhydride and $TiCl_4/Ti(OPr^i)_4$ (molar ratio, 3:1).

The following procedure for the preparation of 1,1-dicyclopentylethene is representative. To a solution of 1-bromo-1,2-dimethoxyethene (1.84 g, 11 mmol) in 30 ml of ether was added butyllithium in ether (6.9 ml of 1.6 M solution, 11 mmol) at -78°C under argon, and then the mixture was stirred at the same temperature for 1 h. Tricyclopentylborane (5.0 ml of 2.0 M solution in THF, 10 mmol) was added to the 1,2-dimethoxyvinyllithium suspension. The mixture was brought up to room temperature and then 3.5 g of trichloroacetic acid in 10 ml of THF was added at 0°C. After 1 h at room temperature, 2.0 g of sodium acetate and 10 ml of acetic anhydride were added, and then $TiCl_4$-$Ti(OPr^i)_4$ (1.65 ml + 1.50 ml) in 12 ml of CH_2Cl_2 was added dropwise at 0°C. The reaction mixture was stirred overnight at room temperature and was finally treated with 50 ml of 3N aqueous sodium hydroxide solution at 0°C. The organic layer separated was washed with a sodium hydroxide solution and then with a saturated sodium chloride solution. The solution was dried over magnesium sulfate and the solvent was evaporated. The residue was purified by chromatography (silica gel column, hexane) to give o.94 g (57 %) of 1,1-dicyclopentylethene. The representative results are summarized in Table 1.

The reaction mechanism is not yet clear. However, the formation of II is rationalized by an attack of a proton on I to give III followed by a second migration of alkyl with the displacing methoxy group as shown in eq. 4. Following elimination of >B-OMe moiety from the β-bora



(4)

Table 1. Synthesis of Symmetric 1,1-Dialkylethenes

Organoborane, R_3B, R=	Method [a)]	Yield of olefin, % [b)] $RRC{=}CH_2$	Isomeric purity of product, % [c)]
Isobutyl	A	65	100
sec-Butyl	A	60	100
Pentyl	A	73 [d)]	90
	B	60 [d)]	92
Cyclopentyl	A	68 (57) [e)]	100
Hexyl	A	78 [d)]	89
	B	65 [d)]	90
Cyclohexyl	A	45	100

a) Method A: By treatment with trichloroacetic acid at 0°C and then with sodium acetate-acetic anhydride and $TiCl_4/Ti(OPr^i)_4$ (molar ratio, 3/1).
Method B: By treatment with 4 equiv. of anhydrous hydrogen chloride in ether at -78°C and then at r.t. for 2 h.

b) Glpc yield based on the organoborane used.

c) When primary-alkylboranes were used, corresponding products were shown to be contaminated with isomeric olefins, $RR'C{=}CH_2$ (R = primary, R' = secondary).

d) Total yield of two isomers, $RRC{=}CH_2$ and $RR'C{=}CH_2$.

e) Isolated yield.

derivative (II) gives the expected 1,1-dialkylethene under acidic conditions. Another path, via the ate complex (IV), also explains the olefin formation. Recently, we have reported a novel synthesis of methoxycyclopropane derivatives from lithium methoxy allene and B-alkyl-9-BBN,[5] in which it was suggested that the methoxy group at the vinylic position of alkenylborates like I is a poor leaving group during alkyl migration. Consequently, although the formation of olefins would be considered via both ways, through III and IV as reported by Levy,[6] the former pathway through III seems to be more preferable in the present reaction.

Although cis-alkoxyboranes were reported to undergo elimination in some cases,[7] usually alkoxy groups are not quite adequate leaving partners from the β-bora derivative in the absence of acid catalysts.[8] The present procedure provides a new synthetic method for 1,1-dialkylethenes from organoboranes.[9] As the vinylborates (I) are considered to have potential synthetic utility for further applications, we are now actively investigating such reactions of I with other electrophiles, such as alkylating reagents.

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9. Most recently, we reported another synthetic procedure of 1,1-dialkylethenes by the reaction of iodine with vinyltrialkylborates derived from trialkylboranes and trisylhydrazones of methyl ketones. K. Avasthi, T. Baba, and A. Suzuki, Tetrahedron Lett., 945 (1980).

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