CHEMISTRY LETTERS, pp. 591-594, 1980.

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

Toshinobu YOGO and Akira SUZUKI*
Faculty of Engineering, Hokkaido University, Sapporo 060

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

$$\mathrm{MeOCBr{=}CHOMe} \xrightarrow{\mathrm{BuLi}} \mathrm{MeOC{=}CHOMe}^{\ominus} \xrightarrow{R_3B} \underset{\mathrm{I}}{\mathrm{MeOC{=}CHOMe}}\ (R_3B^{\ominus}) \qquad (1)$$

$$\mathrm{I} \xrightarrow{\text{aq. HCl}} \underset{\mathrm{II}}{\mathrm{RB(X)-C(R)(R)-CH_2OMe}} \xrightarrow{\mathrm{NaOH\text{-}H_2O_2}} \mathrm{R_2C(OH)-CH_2OMe} \qquad (2)$$

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.

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.

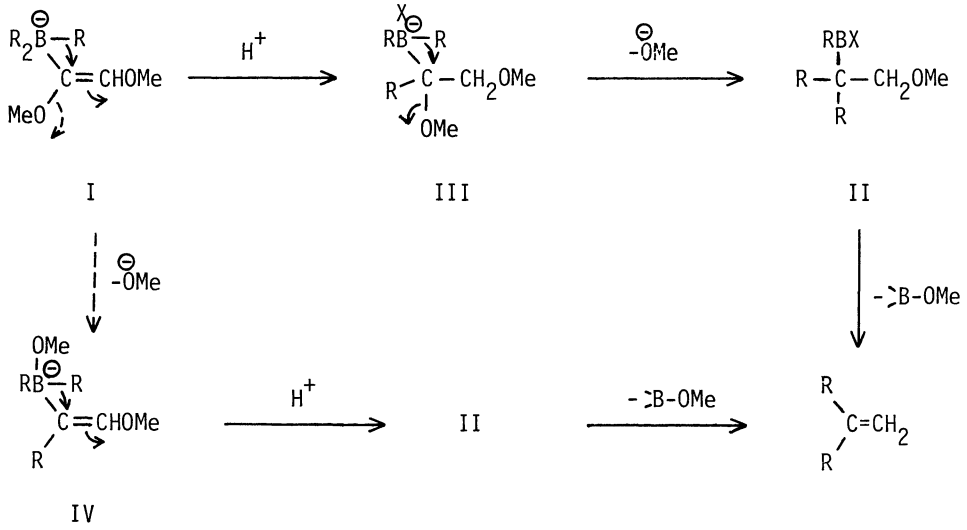
$$\mathrm{I} \xrightarrow[\mathrm{Et_2O}]{\text{dry HCl}} \mathrm{R_2C{=}CH_2} \qquad (3)$$

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.

References

1. For reviews, see (a) E. Negishi, in "New Applications of Organometallic Reagents in Organic Synthesis," Edited by D. Seyferth, Elsevier, Amsterdam, 1976, p. 93, and (b) G. M. L. Cragg and K. R. Koch, Chem. Soc. Rev., 6, 393 (1977).
2. (a) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, J. Amer. Chem. Soc., 95, 3080 (1973). (b) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, Tetrahedron Lett., 2961 (1974). (c) N. Miyaura, S. Abiko, M. Itoh, and A. Suzuki, Synthesis, 669 (1975). (d) K. Yamada, N. Miyaura, M. Itoh, and A. Suzuki, Tetrahedron Lett., 1961 (1975). (e) K. Yamada, N. Miyaura, M. Itoh, and A. Suzuki, Synthesis, 679 (1977).
3. N. Miyaura, H. Tagami, M. Itoh, and A. Suzuki, Chem. Lett., 1411 (1974).
4. C. N. Skold, Synth. Comm., 6, 119 (1976).
5. N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, Tetrahedron Lett., 537 (1980).
6. A. B. Levy, S. J. Schwartz, N. Wilson, and B. Christie, J. Organometal. Chem., 156, 123 (1978).
7. (a) H. C. Brown and E. F. Knight, J. Amer. Chem. Soc., 90, 4439 (1968). (b) D. J. Pasto and J. Hickman, J. Amer. Chem. Soc., 90, 4445 (1968).
8. (a) D. J. Pasto and Sr. R. Snyder, O. S. F., J. Org. Chem., 31, 2777 (1966). (b) H. C. Brown and R. L. Sharp, J. Amer. Chem. Soc., 90, 2915 (1968).
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).

(Received March 4, 1980)