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A Remarkable Rearrangement and Elimination **Reaction in the Solvolysis of Tertiary** α -Chloroboronates under Mild Conditions

Summary: Tertiary α -chloroboronic esters, readily available from the base-induced reaction of borinic esters with dichloromethyl methyl ether, undergo a remarkable rearrangement (with hydride or methide shifts) and elimination during solvolysis in aqueous solvents to produce the corresponding olefins in high yield.

Sir: Solvolysis of tertiary α -chloroboronates in 50% aqueous ethanol proceeds via hydride or methide shifts with the concurrent loss of the elements of chlorodimethoxyborane to form the corresponding olefin (eq 1). The reaction occurs

Table I Products Obtained in the Alkaline Hydrogen Peroxide Oxidation of α -Chloroboronic Esters, RR/CClB(OCH₃)₂

R	R '	Ketone, ⁴ %	Ole- fin, ^a sc %
Isobutyl	Isobutyl	86 ^b (56) ^c	~10
Cyclopentyl	Cyclopentyl	86 ^b (59) ^c	~10
exo-Norbornyl	exo-Norbornyl	62	29
Cyclohexyl	Cyclohexyl	95	0
3-Methyl-2-butyl	3-Methyl-2-butyl	54^{b}	30
2,3-Dimethyl-2-butyl	Cyclopentyl	43^d	35
2,3-Dimethyl-2-butyl	Cyclohexyl	31^d	29

^a By GLC on a 6 ft \times 0.25 in. 10% SE-30. ^b 1 equiv of DCME and 2 equiv of base were used. c 1 equiv of DCME and 1 equiv of base were used. d^{2} equiv of DCME and 2 equiv of base were used.

Table II Olefin Formation by the Reaction of α -Chloroboronic Esters, RR'CClB(OCH₃)₂, with Silver Nitrate in 50% Ethanol at 25°

			Yield,b
R	R	Olefin ^a	%
Cyclohexyl	Cyclohexyl	Cyclohexyl- idenecyclo- hexane	83
<i>exo-</i> Norbornyl	<i>exo-</i> Norbornyl	2-Norbornyl- idene- <i>exo</i> - norbornane	81
2,3-Dimethyl- 2-butyl	Cyclopentyl	2-Cyclopentyl- 3,4-dimethyl- 2-pentene°	82

^a By GLC on a 10% SE-30 column. ^b No other organic products were detected. ^c The stereochemistry of the methyl groups was not determined.



essentially instantaneously at room temperature in the presence of aqueous silver nitrate, providing an exceptionally mild route to internal olefins in high yield (eq 2).



In the course of the alkaline hydrogen peroxide oxidation of α -chloroboronic esters to ketones,¹ we observed formation of internal olefins in significant amounts accompanying the formation of the desired ketones. The amount of the olefin increased for the more hindered cases (Table I). In exploring the factors responsible for olefin formation, the reaction was carried out omitting hydrogen peroxide. However, the same olefins were produced. The possibility was next considered that the reaction might proceed through an E2 elimination of hydrogen chloride, followed by protonolysis of the resulting vinylboronate (eq 3). This

$$\begin{array}{c} H & R \\ | & | \\ -C - C - C - B(OCH_3)_2 & \xrightarrow{OH^-} \\ | & | \\ Cl & \\ -C = C - B(OH)_3 & \xrightarrow{\text{protonolysis}} -C = CHR \quad (3) \end{array}$$

possibility was excluded on the basis of the following observations. (1) The methyl migration obtained in the thexylcyclopentyl case would be difficult to rationalize in terms of a vinylboronate intermediate (eq 4). (2) Protonolysis of

vinylboronates is a very slow process under alkaline conditions.² (3) No deuterium is incorporated into the olefinic side products in the oxidation of the reaction products from both methyl bis(trans-2-methylcyclopentyl)borinate and methyl thexylcyclopentylborinate with DCME and base in deuterium oxide. Finally, (4) hydrolysis of 1 in 50% aqueous ethanol at 60° in the absence of base also yields the olefin (eq 1).

A possible explanation for these results is a mechanism involving the ionization of the chlorine substituent to produce the corresponding carbonium ion which then undergoes fast hydride (or methide) migration, followed by β elimination (eq 5).



This mechanism is also compatible with the facile vapor phase decomposition of these tertiary α -chloroboronates.³

If this carbonium ion mechanism is indeed the pathway, it appeared possible that the reaction could be facilitated by aqueous silver nitrate. Indeed, addition of a molar equivalent of silver nitrate to a solution of α -chloroboronate in ethanol leads to instantaneous precipitation of silver chloride. Analysis of the reaction mixture by NMR and gas chromatography reveals the presence of olefins in yields above 80%/ The results are summarized in Table II.

A representative procedure follows. To 5.0 mmol of the α -chloroboronate dissolved at room temperature in 5 ml of absolute ethanol under nitrogen is added 5.5 mmol of silver nitrate in 5 ml of distilled water. An immediate precipitate forms. The mixture is stirred an additional hour at 25°. The mixture (after addition of 5 ml of pentane) can be ana-

lyzed by GLC, using a hydrocarbon as internal standard. Alternatively, the olefin can be isolated by first filtering the silver chloride and then washing the precipitate with 2×10 ml of water and 2×10 ml of pentane. Distillation of the dried organic layer yields the olefin. The physical properties of the olefins, as well as their structures, are similar to those reported in the pyrolysis of α -chloroboronic esters.³

The elimination reaction could be avoided and substitution⁴ of the chloride atom successfully accomplished by treating a 1.0 M solution of α -chloroboronate in pentane with 1 equiv of sodium methoxide in anhydrous methanol (eq 6). The product, dimethyl (dicyclohexylmethoxycarbin-

$$C - B(OCH_3)_2 \xrightarrow[CH_3OH, pentane]{CH_3OH, pentane} CH_3OH, Pentane NaCl + CH_3OH_3 (6)$$

yl)boronate, mp 68-70°, is obtained in 87% yield. NMR confirmed the product to be the α -methoxy derivative. A singlet at δ 3.28 (3 H) was observed for the C-methoxy protons and another singlet at δ 3.63 (6 H) for the *B*-methoxy protons. Such replacement of the chlorine atom by a methoxy group, prior to the oxidation by alkaline hydrogen peroxide, avoids significant formation of olefins as side products and markedly improves the yields of ketone over those reported in Table I. Thus, it is possible by variation in the reaction conditions to achieve a facile conversion of α -chloroboronic esters to olefins or to the α -methoxy derivatives, readily oxidized to ketones.

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A General One-Carbon Homologation of Organoboranes via *a*-Thioorganoborate Anions

The reaction of trialkylboranes with Summary: thiomethoxymethyllithium or 2-lithiothiomethoxy-1,3thiazoline, followed by the treatment of the resultant α thioorganoborate complexes with methyl iodide, produces the one-carbon homologated organoboranes in high yields.

Sir: We wish to report a novel procedure for the one-carbon homologation of organoboranes via a-thiorganoborate anions.¹

The reaction of tri-*n*-butylborane with the α -lithio derivatives of methyl phenyl sulfone,² dimethyl sulfoxide,³ and dimethyl sulfide⁴ produces the corresponding organoborate complexes 1, 2, and 3, as judged by ${}^{1}\text{H}$ NMR⁵ [(THF-hex-