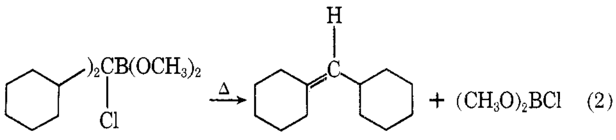
A Novel α Elimination in the Mild Thermal Treatment of α-Chloroboronic Esters. A New Route to Olefins

Summary: Mild thermal treatment of α-chloroboronic esters, readily available from the base-induced reaction of borinic esters with dichloromethyl methyl ether, converts them in high yield into the chloroborate ester and the corresponding internal olefin.

Sir: α-Chloroboronic esters are now readily available by the base-induced reaction of borinic esters with DCME[1] (eq 1).

$$R_2BOR' + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[30\ \text{min}]{\text{THF, }25^\circ} \underset{\textbf{1}}{R_2CClB(OCH_3)OR'} + Et_3COH + LiCl \quad (1)$$

At elevated temperatures, the products 1 were observed to undergo an essentially quantitative decomposition to the corresponding internal olefin (eq 2). This was of interest and we undertook to explore the thermal behavior of these α-chloroboronic esters.[2]



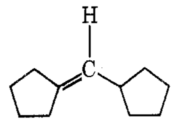
2 **3** (2)

Dimethyl dicyclohexylchlorocarbinylboronate (**2**, 1.98 g, 5.68 mmol), in a distilling flask, was heated for 2 hr in an oil bath which was maintained at 240–250°. There was obtained as distillate 0.48 g (89%) of dimethyl chloroborate, $(CH_3O)_2BCl$.[3] Remaining in the flask was 0.98 g (97%) of pure cyclohexylidenecyclohexane (**3**). Benzene was added as an internal standard. Examination of the product by nmr established that **3** had been formed in a yield of 94%.

Thermal treatment of the α-chloroboronic esters in a Kügelrohr oven[4] under aspirator vacuum provided an even simpler technique with the reaction being essentially complete in 10–20 min. In all cases, excellent yields of olefins were realized with no evidence for any isomerization of the double bond.

The following procedure is representative. In the Kügelrohr flask was placed 1.60 g (5.58 mmol) of dimethyl (dicyclohexylchlorocarbinyl)boronic ester **2**.[1] Aspirator vacuum was applied and the oven temperature raised to 240°; the decomposition was complete in 10 min. No residue was observed. The product was collected in an U-tube cooled at −78°. Nmr examination of the distillate prior to any work-up indicated the quantitative presence of vinyl protons. The distillate was washed out with 10 ml of pentane and stirred vigorously for 2–3 hr with a mixture of 5 ml of 3 *M* NaOH and 5 ml of brine, 10 ml pentane was then added, the organic layer was separated, and the mixture was dried over anhydrous magnesium sulfate. The solvent was removed. There was obtained 0.86 g, (86.5% yield) of cyclohexylidinecyclohexane **3**: $n^{20}D$ 1.4948; ≥95% pure by nmr (only a trace of the endocyclic isomer was present at δ 5.4 ppm) (CCl_4, TMS) δ 0.8–2.5 (m, 21 H), 4.83–4.96 (d, 1 H, J = 8 Hz) ppm; exact mass calcd for $C_{13}H_{22}$, 178.1722; found, 178.1690.

No difficulty was experienced in extending the reaction to the *n*-butyl, cyclopentyl, and *exo*-norbornyl derivatives. Thus, olefins **4** and **5** were readily obtained.



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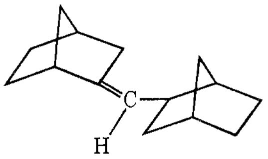

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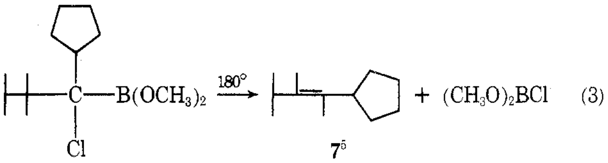
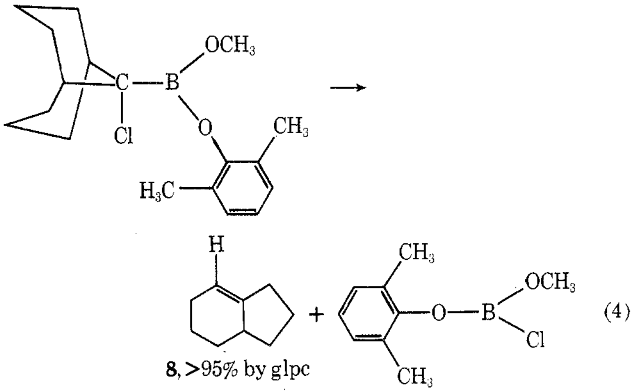
An unexpected development was the observation that the α elimination proceeds with exceptional ease in the case of dimethyl thexylcyclopentylchlorocarbinylboronate (**6**). Moreover, the olefin product (**7**) arises not from migration of the tertiary hydrogen, as in other cases, such as **3**, **4**, and **5**, but from migration of a methyl group (eq 3).



6 **7**[5] (3)

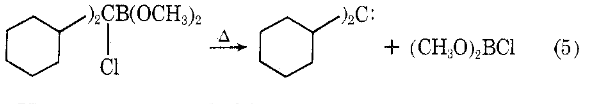
Finally, the promise of this new synthetic route to olefin is indicated by the result realized in the thermal treatment of the α-chloro derivative from 9-borabicyclo[3.3.1]-nonane. There was obtained a 70% yield of bicyclo[4.3.0]-non-1(2)-ene (**8**, eq 4). The earlier routes to this bicyclic olefin involved either the acid treatment of hydrindan alcohols[6] or solvolysis of hydrindan *p*-nitrobenzoate esters;[7] however, a mixture of all isomers were obtained.



8, >95% by glpc (4)

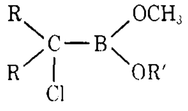
The results are summarized in Table I.

It is tempting to suggest that the reaction proceeds through a concerted α elimination to give the carbene (eq 5). A simple migration of the tertiary hydrogen atom would give **3**. However, a remarkable feature of these eliminations is the simplicity of the product and the nearly quantitative yields. We have failed to detect any cyclopropyl derivatives such as are accepted as characteristic of dialkylcarbenes.[8]



(5)

Table I
Preparation of Internal Olefins from Pyrolysis of α-Chloroboronic Esters

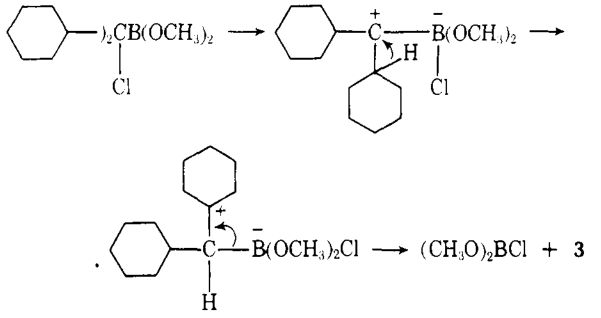


R	R	R'	Temp, °C	Olefin	Yield,[a] % (isolated)
n-Butyl	*n*-Butyl	2,6-Dimethylphenyl	240	4-Nonene[b]	80
Cyclopentyl	Cyclopentyl	2,6-Dimethylphenyl	220	Cyclopentylidenecyclopentane (**4**)[c]	80
Cyclohexyl	Cyclohexyl	Methyl	240–250	Cyclohexylidenecyclohexane (**3**)[c]	86.5
exo-Norbornyl	*exo*-Norbornyl	Methyl	220	2-Norbornylidene-*exo*-norbornane (**5**)[c,d]	88
2,3-Dimethyl-2-butyl	Cyclopentyl	Methyl	180	1-Cyclopentyl-1,2,3-trimethyl-1-butene (**7**)[e]	85
9-Bicyclo[3.3.1]nonanyl		2,6-Dimethylphenyl	190	Bicyclo[4.3.0]non-1(2)-ene[f]	70

[a] All olefins gave satisfactory ir, nmr, and mass spectral data. [b] 78% cis-22% trans determined by glpc. [c] All cyclic olefins were exocyclic, as evidenced by nmr analysis (doublets $J \sim 8$-9 Hz). [d] Exists as a pair of "in-out" isomers, as demonstrated by an overlapping pair of doublets ($J = 10$ Hz) at $\delta = 4.83$ and 5.03 ppm. [e] Almost no vinylic proton resonance was observed at δ 5.2 ppm. Microozonolysis of the olefinic product confirmed the structure **7**. Methyl isopropyl ketone was the predominant product and only a small amount (≤5%) of cyclopentanone was observed. No stereochemistry implied. [f] Spectroscopic data were in agreement with the reported values.[6]

Consequently, it is necessary to conclude either that the carbenes in this reaction undergo unusually clean conversion to olefin or that the elimination is not a concerted process.

In the latter case, the reaction could be a carbonium ion process involving transfer of the tertiary chloride from carbon to boron, followed by consecutive transformation as shown in eq 6.



(6)

Even though it is not possible at this time to give a definitive mechanism, the reaction provides a remarkably simple elimination leading to a wide variety of olefinic structures. Irrespective of whether the reaction proceeds through a dialkylcarbene (eq 5) or through an intermediate carbonium ion (eq 6), it is evident that this reaction offers promise of new, very simple mechanistic pathways.

References and Notes

(1) B. A. Carlson, J.-J. Katz, and H. C. Brown, *J. Organomet. Chem.*, **67**, C39–C42 (1974).
(2) The mass spectral examination of **2** revealed interesting features. The molecular ion was not observed. The highest mass was 250 (rel intensity 0.2), corresponding to loss of hydrogen chloride. The ion of highest intensity was 178 (rel intensity 100), corresponding to the ionized olefin. Similar spectra were realized with the other derivatives.
(3) E. Wiberg and W. Sütterlin, *Z. Anorg. Allgem. Chem.*, **202**, 1 (1931); **222**, 92 (1935).
(4) Available from Büchi. A pyrolysis tube was used and filled with glass beads.
(5) See Table I, note *e*.
(6) C. Arnal, J. M. Bessière, H. Cristol, and R. Vanel, *Bull. Soc. Chim. Fr.*, 2479 (1967).
(7) R. C. Fort, R. E. Hornish, and Gao A. Liang, *J. Amer. Chem. Soc.*, **92**, 7558 (1970).
(8) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.
(9) Graduate research assistant on Grant GM 10937 supported by the National Institutes of Health.
(10) Graduate research assistant on Grant GP 27742X supported by the National Science Foundation.

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