Chemical Communications

NUMBER 15/1965 11 AUGUST

Monohydroboration of *N*-Alkenylcarbamates: Preparation of Aminoalkylboronic Acids

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THE reaction of diborane with *N*-alkenylcarbamates follows a similar course to that described for *N*-alkenylureas.[1] Hydrolysis of the monohydroborated products then affords aminoalkylboronic acids. By this method the boron analogues of β-alanine and γ-aminobutyric acid have been prepared, namely 2-aminoethylboronic acid (Ib) and 3-aminopropylboronic acid (IIb).

Thus, hydroboration of ethyl and benzyl *N*-vinylcarbamate gave 2-(ethoxycarbonylamido)-ethylboronic acid and 2-(benzyloxycarbonylamido)-ethylboronic acid respectively, while ethyl- and benzyl-*N*-allylcarbamates yielded mixtures with the boronic acid function in both the 2- and 3-positions to the carbamate moiety. 3-Benzoxycarbonylamido)propylboronic acid could be obtained pure from these mixtures.

While the ethylcarbamates could not be cleanly hydrolysed, the benzyl compounds afforded the corresponding aminoalkylboronic acid hydrobromides (Ia) and (IIa) after treatment with 10% hydrogen bromide in acetic acid. The free aminoalkylboronic acids (Ib) and (IIb) were obtained as dihydrates by ion-exchange and proved to be strong bases, indicating the possible quaternization of both the boron and nitrogen atoms.

The introduction of the boron atom in the non-terminal position of these allylamine derivatives, and the high yields of substituted ethylboronic acids available from the vinyl compounds, indicates preferred ring size of four or six atoms for the internally-stabilized borane intermediates[1] involved. Since the yield of substituted butylboronic acids from hydroboration of ethyl *N*-3-butenylcarbamate (where a six-centred intermediate is possible) was less than 15% (unpublished results) a four-centred reaction intermediate may be more likely. Similar four-centred transition states have been involved to account for the *cis*-eliminations of the organoboranes obtained by hydroboration of vinyl chloride, and vinyl ethers and thioethers.[2]

$$(HO)_2B\cdot CH_2CH_2NH_2\cdot X$$

(I) a. $X = HBr$

b. $X = 2H_2O$

$$(HO)_2B\cdot CH_2CH_2CH_2NH_2\cdot X$$

(II) a. $X = HBr$

b. $X = 2H_2O$

(*Received, May* 31*st*, 1965; *Com.* 352.)

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[1] D. N. Butler and A. H. Soloway, *J. Amer. Chem. Soc.*, **1964**, **86**, **2961**.

[2] H. C. Brown and O. J. Cope, *J. Amer. Chem. Soc.*, **1964**, **86**, **1801**; D. J. Pasto and C. C. Cumbo, *ibid*, **1964**, **86**, **4343**.