A Rapid Rearrangement of α-Bromoethylborane Induced by Electrophilic Reagents

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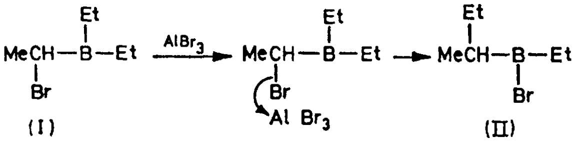
Summary α-Bromoethyldiethylborane undergoes rapid almost instantaneous, rearrangement at 25 °C to s-butyl ethylboron bromide under the influence of aluminium bromide and related electrophilic catalysts.

α-BROMOETHYLDIETHYLBORANE (I) undergoes nucleophilic induced rearrangement to derivatives of s-butylethylborane, whose rearrangement must involve co-ordination of the nucleophile with the boron atom followed by the migration of an alkyl group from boron to carbon.[1]

We report that treatment of (I) with an equivalent quantity of aluminium bromide in carbon disulphide at



(1)

(I) (II)

25 °C results in an almost instantaneous isomerization of (I) into s-butylethylboron bromide (II) (equation 1). The rearrangement is readily followed by changes in the ^{1}H n.m.r. spectra. Rapid isomerization of (I) to (II) was also observed with a catalytic quantity of aluminium bromide (5 mole %).

The following procedure is representative. Aluminium bromide (0·13 g, 0·5 mmol) was dissolved in carbon disulphide (20 ml) and α-bromoethyldiethylborane (1·77 g, 10 mmol) was added to it at 25 °C. The resultant mixture was stirred for 10 min. The ^{1}H n.m.r. spectrum revealed complete isomerization to (II). Distillation gave 1·65 g (9·3 mmol) of pure (II).

The effectiveness of a number of Lewis acid catalysts was explored by adding a number of metal halides to (I) in carbon tetrachloride and following the change in the ^{1}H n.m.r. spectra with time. When the rearrangement was complete, the reaction mixture was treated with water, the organic layer was separated, and the product was isolated and identified as the 8-hydroxyquinolinate. In addition, the reaction mixture was oxidized with alkaline hydrogen peroxide and the products, butan-2-ol and ethanol, determined by g.l.c.

The data are summarized in the Table.

The results reveal that the catalysts listed in Group I are the most effective, causing almost instantaneous rearrangement. However, sulphuric acid gives a relatively low yield of product, presumably the result of side-reactions. Although aluminium isopropoxide, which shows only weak Lewis acidity, causes a rapid rearrangement, it is not possible to state at this time whether the activity of this reagent is a reflection of its electrophilic or nucleophilic character. The catalysts in Group II, which are generally less effective for Friedel–Crafts reactions,[2] are also less effective here. The reaction induced by silver fluoride is sluggish, possibly a consequence of its low solubility in the reaction mixture.

TABLE

Rearrangement of α-bromoethyldiethylborane with various electrophiles[a]

Electrophile	Half-life of rearrangement[b] (min)	Yield of s-butylethylborinic acid[c] (%)	Oxidation[d] Bu^{s}OH	EtOH
Group I				
$AlCl_3$	0—5[e]	96	96	98
$AlBr_3$	0—5[e,f]	95	98	98
$Al(OPr^i)_3$	0—5[e]	90	90	92
$ZrCl_4$	0—5[e]	90	91	95
$ZnCl_2$	0—5[e]	88	90	95
$AgBF_4$	0—5[e]	95	98	99
H_2SO_4	0—5[e]	58	60	72
Group II				
$HgCl_2$	10	88	88	93
$SnCl_4$	10	90	88	92
$SbCl_3$	15	91	93[g]	93[g]
$TiCl_4$	20	85	92[g]	95[g]
AgF	180	89	85	90

[a] Solutions of α-bromoethyldiethylborane (0·87 M) in carbon tetrachloride, except where otherwise indicated, were treated with an equimolar quantity of the electrophile at 25 °C. [b] Time of the disappearance of the ^{1}H n.m.r. signals at δ 4·13 and 1·73. [c] As the 8-hydroxyquinolinate, determined by ^{1}H n.m.r. [d] Determined by g.l.c., using diethyl ether as a solvent, except where otherwise indicated. [e] Very fast, almost instantaneous. [f] Carbon disulphide used as solvent. [g] Methylene chloride used as solvent.

Previously it was reported that the bromination of triethylborane in the presence of nucleophilic reagents, such as water, involves predominantly a double migration.[3]

However, bromination in the presence of an electrophilic reagent, such as tin(IV) bromide, permits control of the reaction to achieve a single migration.

This development provides a simple new route to dialkylboron bromides, R^1R^2BBr, and greatly enhances the possibilities of this versatile route to carbon structures *via* the bromination of organoboranes.

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