

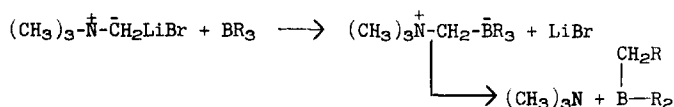
NITROGEN YLIDS II¹ ATTEMPTED STABILIZATION OF TRIMETHYLAMMONIUM METHYLIDE WITH ORGANOBORANES

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(Received 21 November 1966; in revised form 27 December 1966)

A recent report by Tufariello and Lee² concerning the reaction of trialkylboranes with sulfur ylids prompted us to report our observations of a similar rearrangement involving organoboranes and nitrogen ylids. Phosphorus ylids formed stable adducts with triphenylborane and borane although the trimethylborane adduct was not isolated.³ In an attempt to form adducts of trimethylammonium methylide with triphenylborane, we noted that trimethylamine was rapidly evolved from the reaction mixture. In view of the facile elimination of trimethylamine and the report⁴ that trimethylamine oxide can be used to oxidize organoboranes - a process which involves the migration of a boron substituent to oxygen - we suspected that a migration of a boron substituent to carbon had occurred with the isoelectronic nitrogen ylid.⁵ Although this migration adequately accounts for the observed products of this reaction, an alternative pathway involving a carbene mechanism cannot be ruled out entirely.



The nitrogen ylid was prepared from tetramethylammonium bromide and phenyllithium in ether and the solvent was removed on the vacuum line. Equimolar amounts of the solid ylid were added to a cooled solution (-78°C) of the organoborane in tetrahydrofuran. An equal volume of dimethoxyethane was added and the reaction mixture was allowed to warm slowly to room temperature and then heated to reflux until trimethylamine was no longer evolved. The reaction mixture was treated with alkaline hydrogen peroxide and the products formed were examined by gas chromatography. The results are summarized in Table I.

The reaction of symmetrical trisubstituted organoboranes, trinexylborane and triphenylborane, with tetramethylammonium methylide followed by oxidation gave good yields of the

Table I
Rearrangement Products Resulting from the Reaction
of Organoboranes with Trimethylammonium Methylide^a

Borane	Rearrangement Products, % ^b
Triphenylborane	Benzyl alcohol (46%)
Trihexylborane	1-Heptanol (63%)
Bis(3-methyl-2-butyl)- hexylborane	1-Heptanol (6%) 2,3-Dimethyl-1-butanol (60%)
Bis(3-methyl-2-butyl)- borane	2,3-Dimethyl-1-butanol (22%) Methanol ^c
Borane (BH ₃)	Methanol ^c

^a Equimolar amounts of the organoborane and ylid were used.

^b Yield based on a theoretical 100% rearrangement. The products were determined by vpc and the yield determined by the use of an internal standard.

^c Trace.

alcohol corresponding to the migration of one of the boron substituents to carbon.

In order to determine the migration aptitude of various boron substituents, organoboranes containing two different ligands were synthesized. A comparison of the yield of the rearranged alcohols obtained from bis(3-methyl-2-butyl)-hexylborane showed that secondary alkyl groups migrated more readily than primary alkyl groups. In the reactions of trisubstituted organoboranes, trimethylamine was rapidly evolved as the reaction mixture was warmed to room temperature. An estimation of the difference in migration aptitude between secondary alkyl groups and hydrogen was made by reacting bis(3-methyl-2-butyl)borane with the nitrogen ylid. In this case the rate of evolution of trimethylamine was reduced and the yield of 2,3-dimethyl-1-butanol was lowered when compared with the yield of this alcohol obtained from bis(3-methyl-2-butyl)hexylborane. The detection and measurement of methanol formed by hydrogen migration was complicated by the formation of formaldehyde from the oxidation of ylid with hydrogen peroxide.⁶ An estimation of methanol from hydrogen evolution and integration of the methanol-formaldehyde peak on gas chromatographic analysis showed that little, if any, was formed. When the ylid was reacted with diborane the rate of trimethylamine evolution was reduced further and corresponded closely to the rate of decomposition of the ylid. No significant amount of methanol was detected from this reaction. Apparently the presence of a B-H bond in the Lewis acid caused either a marked decrease in the ease of complexation of the borane with the ylid or a decrease in the ease of migration. Further work on the stabilization of nitrogen ylids is in progress.

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7. This work was supported by the National Institutes of Health (GM-14062).