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REACTION OF PHENYLISOCYANIDE WITH DIBORANE-6

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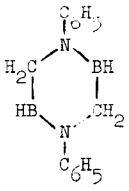
The reactions of isocyanides with trialkyl boranes have recently been reported. (1,2,3) We wish to report preliminary results from our study of the interaction of phenylisocyanide and diborane-6.

The product $(C_6H_5NCBH_3)_2$ was isolated when C_6H_5NC and B_2H_6 were allowed to react in either methyl ether or ethyl ether at -111° C. The compound is a white solid and the stoichiometry was determined by measuring the diborane absorbed by weighed amounts of phenylisocyanide. The $(C_6H_5NCBH_3)_2$ is soluble in methyl ether, ethyl ether, benzene and acetone. It is insoluble in water but reacts slowly with this solvent. The compound was shown to be dimeric by its molecular weight in benzene and its proposed structure is I. The proposed structure (I) has only one hydrogen attached to each boron and is supported by the fact that acid hydrolysis liberates only one mole of hydrogen per $C_6H_5NCBH_3$ unit. To demonstrate that the production of only one mole of hydrogen per boron was not caused by a slow hydrolysis reaction, samples of $(C_6H_5NCBH_3)_2$ were hydrolyzed in concentrated HCl in sealed tubes at 95°C. for periods of one

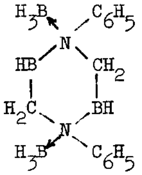


I

and four weeks. In each case, only one hydridic hydrogen was found per boron. The infrared spectrum is in agreement with the proposed structure having bands that have tentatively been assigned to ν(C-H)[2920 cm^{-1}] and ν(B-H)[2360 cm^{-1}] in addition to bands expected for a phenyl group. No absorption bands are found in the 2100-2150 cm^{-1} region characteristic of RN≡C and no bands that could be attributed to B-H-B bridging hydrogens are observed.

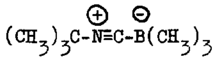
Compound I does not have a sharp melting point but decomposes over the range of 80-120°C.

It was interesting to note that I reacts further with diborane at 0°C. to produce $[C_6H_5NC(BH_3)_2]_2$. The formula was determined by measuring the quantity of diborane absorbed by I using ethyl ether as the reaction medium. The proposed structure of the diadduct is the Lewis salt II. The molecular weight of II as determined by freezing point depression in benzene is in agreement with the proposed structure. It must be noted, however, that experimental difficulties encountered in preparing solutions of the air sensitive II and measuring their freezing point in the vacuum line, along with the ready loss of diborane from II result in a relatively high degree of uncertainty in the molecular weight measurement. The infrared spectrum of the diadduct, II, differs from that of the monoadduct, I, primarily in having two distinct (B-H) bands.



II

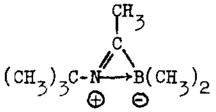
The reaction of phenylisocyanide and diborane is quite different from the reactions of alkyl isocyanide and alkyl boranes. No products analogous to III, IV, V or VI have been isolated.



$$(CH_3)_3C-\overset{\oplus}{N}\equiv C-\overset{\ominus}{B}(CH_3)_3$$

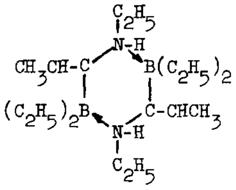
(2)

III



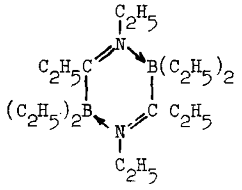
(2)

IV



(3)

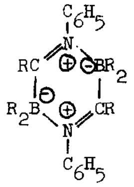
V



(3)

VI

The hydrogen analog of the initial product obtained from phenylisocyanide and BR_3, VII, has also not been observed. The proposed structure I is



(1)

VII

analogous to the product obtained when VII is heated to 200°C. (1)

We are currently continuing our investigations of the reactions of isocyanides with boron hydrides and other Lewis acids.

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