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# THE PHENYL-ISOCYANIDE REACTION WITH DIBORANE

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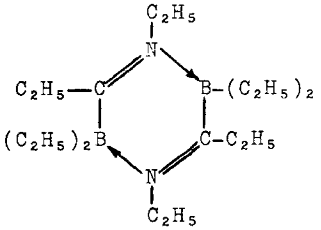
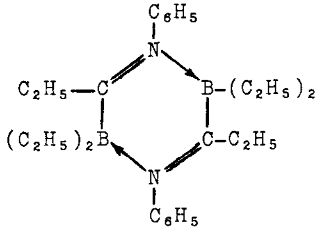
We have previously reported the preparation and characterisation of the compound I which was obtained by reaction of ethylisocyanide with triethylboron (1). This compound is structurally analogous to the phenyl derivative II reported by Hesse and Witte (2).



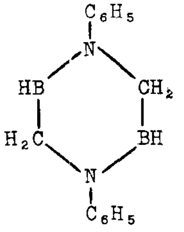
I



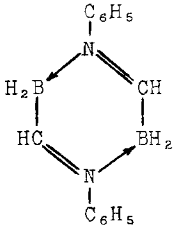
II

In view of the existence of these two compounds, investigations have been now extended to the reaction products of isocyanides with diborane. Contrary to the observation of Casanova (3) we reported (1) that the reaction of isocyanides with $B_2H_6$ can be carried out without great difficulty under controlled conditions. Indeed, the extreme versatility of these reactions makes complicate this study owing the difficulty in the separation of the reaction products. Work is in progress on the reactions of some aliphatic and aromatic isocyanides with diborane.

Recently, J.Tanaka has reported (4) the preparation of the derivative III. In this comunication we report part of the results of investigations concerning the existence a new type of ring IV, isomeric with III.



III



IV

The procedure followed in the preparation of IV is different in some details from that of Tanaka (4) leading to III. The method of preparation of IV gives reproducible results. However, following Tanaka's procedure, we were unable to obtain III as a pure compound.

Compound IV can be prepared reacting phenylisocyanide with diborane with the following method. A stoichiometric amount of diborane was slowly added to a 5% solution of phenylisocyanide in anhydrous petroleum ether (b.p.: 30--50°C) with vigorous stirring and the temperature of the mixture was maintained at-68°C. A white solid cristalline product was immediately formed. The mixture after addition of the diborane was allowed to stir for three hours. Hence, always at the temperature of -68°C, the mixture was concentrated in vacuum. Filtration under nitrogen gave a homogeneus white cristalline product, air sensitive and soluble in $C_6H_6$, $CHCl_3$ and $CH_2Cl_2$. The compound slowly decomposes in alcohols, ketons, pyridine, dimethylsulfoxide and has not a sharp melting point but starts decomposing at 135°C. Quantitative elementary analysis indicates that this compound is a 1:1 adduct. Found B, 9,00%; N, 12,25%. $C_6H_5NC \longrightarrow BH_3$ requires: B, 9,23%; N, 11,98%.

By solvolysis of the product with methyl alcohol two hidrydic hydrogens for boron atom have been found. The same result have been obtained by acid hydrolysis, as suggested by Tanaka (4). The molecular weight (Mechrolab Vapor Pressure Osmometer Type 301 A) found at 25°C is 232. This value shows that the molecular weight of the compound under investigation is twice the value of the 1:1 adduct (M.W. calculated for $(C_6H_5NCBH_3)_2$ = 234). The infrared spectra in nujol and hexachlorobutadiene have no absorption bands in the 1650-2250 $cm^{-1}$ range. This shows that $-N\equiv C$ groups are not present, and rules out the possibility that this substance is a simple coordinative compound of the type $RNC \longrightarrow B$ [illegible]e infrared spectrum shows in addition to bands expected for a phenyl group, two bands of strong absorption intensity at 1589 $cm^{-1}$ and 2360 $cm^{-1}$ and bands of medium intensity at 2260, 1140 and 968 $cm^{-1}$. While the former strong band is assigned to a $-C{=}N-$ stretching mode, the other bands can be assigned to $-BH_2$ groups. We assign the band at 2360 and 2260 $cm^{-1}$ to the B-H stretching mode of $BH_2$ groups. This assignement is confirmed by the absorption bands at 1140 $cm^{-1}$, typical of the in-plane deformation mode, and by that at 968 $cm^{-1}$, typical of the out-of-plane deformation mode, of the $BH_2$ groups (5). Also the proton resonance spectra (5% $CH_2Cl_2$ and 5% $CDCl_3$ solutions, 37°C, Varian A 60) have been recorded at 60 Mc relative to tetramethylsilane as internal standard. At cause of the poor solubility of the product under investigation, from these spectra it is not possible to obtain good resolution in the 6,5-7,5 p.p.m. range from which to identify separately the signals of aromatic protons and protons of the -CH=N- groups. However, from the N.M.R. data it is possible to conclude that aliphatic $-CH_2$ groups are not present in this molecule. In fact, no signals are found in the 1,5-4,5 p.p.m. range, typical of $-CH_2$ aliphatic groups. Hence, one can conclude that following the procedure above reported the compound with structure IV is obtained, as analytical, spectroscopic and molecular data show.

The analogy of structure existing between compounds I, II and IV clearly shows that they are all members of the same type of heterocyclic ring containing carbon, nitrogen and 4-coordinated boron atoms.

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