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THE REACTIONS OF ALKYLISOCYANIDES WITH TRIALKYLBORONS

Silvano Bresadola, Giorgio Carraro, Cesare Pecile and Aldo Turco
Edison S.p.A., Laboratorio Ricerche, Bollate, Milano;
Department of Chemistry, University of Padova, Italy.

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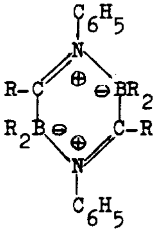
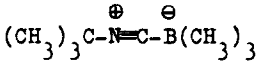
The reactions of trialkylborons with isocyanides have been the object of recent interest because they lead to the formation of new classes of compounds.

The reaction of phenylisocyanide with BR_3 ($R=C_2H_5-$, $n-C_4H_9-$) gives a compound for which the cyclic structure (a) has been proposed (1). On the other hand the reaction of ter-butyl-isocyanide with $B(CH_3)_3$ gives the adducts (b) and (c) (2).

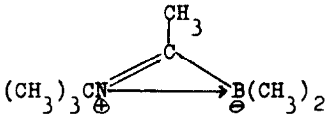


(a)



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

(b)



(c)

We have studied the reaction of C_2H_5-NC with $B(C_2H_5)_3$ and have isolated two different reaction products. The properties of one are consistent with a cyclic structure of type (a), the other product we believe is a member of a hitherto unreported type of heterocyclic ring.

Triethylboron (3) was slowly added to a solution of C_2H_5NC (4) in anhydrous ethyl ether at 20°C. The solution was left standing for 24 hr. at 20°C. Concentration of the solution by distillation in a current of nitrogen gave a thermally stable white crystalline product (I), m.p. 95-97°C. Further evaporation of the solvent gave a white solid (II) which was purified by recrystallization from benzene; m.p. > 200°C with decomposition. Both solids are air-insensitive and soluble in C_6H_6, $CHCl_3$, CCl_4, CH_2Cl_2, and in other common organic solvents. Solid (I) slowly decomposes in chloroform. Quantitative elementary analysis indicates that both compounds are 1:1 adducts. Found: (I), B, 7.15; C, 70.5; H, 13.2. (II), B, 7.20; C, 70.7; H, 13.15. $C_2H_5NC\rightarrow B(C_2H_5)_3$ requires: B, 7.07; C, 70.65; H, 13.09.

The molecular weight (Mechrolab Vapor Pressure Osmometer type 301A) found in CCl_4 at 25°C is (I) 310, (II) 306. These values show that the molecular weight of each compound is twice the value of the 1:1 adduct (M.W. calculated for $[C_2H_5NCB(C_2H_5)_3]_2$: 306).

The infrared spectra of (I) and (II) in KBr pellets and in CCl_4 solution do not have absorption bands in the 1650-2500 cm^{-1} range. This shows that $-N\equiv C$ groups are not present, and rules out the possibility that (I) and (II) are simple coordinative compounds of the type $R\text{-}NC\rightarrow BR_3$.

The infrared spectrum of (I) shows two bands of medium intensity at 3250 cm^{-1} and 1645 cm^{-1}. The former band is assigned to a N-H stretching mode. The band at 1645 cm^{-1} can be assigned to a C=C stretching mode of a trisubstituted ethylenic group. This assignement is confirmed by a strong absorption at 785 cm^{-1} which is typical of the C-H out of plan bending of trisubstituted ethylenic groups (5).

The infrared spectrum of compound (II) has a strong absorption at 1594 cm^{-1}, which we assign to a -C=N- stretching mode (5).

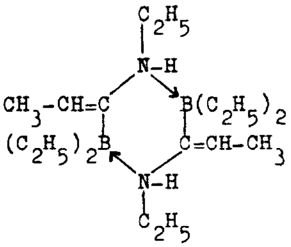
The proton resonance spectra (15% CCl_4 solution, 37°C, Varian A 60) have been recorded at 60 Mc relative to tetramethyl silane as internal standard. The spectrum of compound (I) consists of the following signals.

The quartet at δ = 5.45 ppm. with intensity of two protons, is assigned to the CH proton of the $=CH-CH_3$ group. The doublet at 1.59 ppm. with intensity of six is assigned to the methyl protons of the same group. A very broad peak with intensity of two appears at 4.15 ppm. and can be assigned to the N-H group. A signal with a multiplicity of five and intensity of four is observed at 2.95 ppm. It can be assigned to methylenic protons of the $-HN-CH_2-CH_3$ group. A slight difference between $J_{NH.CH_2}$ and $J_{CH_2.CH_3}$ may be responsible for the imperfect simmetry of the observed quintuplet. Attempts to remove $J_{NH.CH_2}$ coupling by deuteration were unsuccessful. The observed triplet at 1.08 ppm. with intensity of six is assigned to the methyl protons of the same group. The complex pattern with intensity of twenty observed from 0.75 ppm. to 0.25 ppm. is assigned to the CH_3 and CH_2 protons of the group $> B-CH_2-CH_3$ (6).

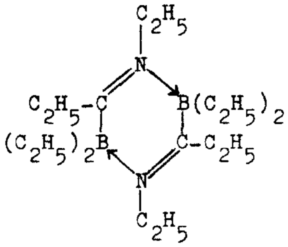
The proton resonance spectrum of compound (II) consists of two quartets each with intensity of four, centered at 3.45 ppm. ($-CH_2-N <$), and 2.47 ppm. ($-CH_2-C=$); two partially overlapping triplets with intensity of twelve at 1.22 ppm. ($>N-CH_2-CH_3$) and 1.14 ppm. ($=C-CH_2-CH_3$). A broad band with a complex structure is observed at 0.55 ppm. This signal with intensity of twenty, is assigned to the residual ethyl groups bonded to the boron atoms. The evidence reported here leaves little doubt the compound (II) can be formulated as a derivative of the 2,5-diboro-2,5-dihydropyrazine, thus confirming the correctness of the structure recently proposed by other authors (1).

The combined analytical, spectroscopic and molecular weight data obtained for compound (I) are strongly in favour of a heterocyclic structure of the type of 2,5-diboropiperazine.

If our interpretation is correct adduct (I) is a derivative of a new class of compounds, previously unreported.



(I)



(II)

Contrary to the observation of other authors (2) we have found that the reaction of isocyanides with boron hydrides can be carried out without great difficulty under controlled conditions. The products of this reaction are under investigation.

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