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# REACTIONS OF TRICYCLOHEXYLBORON WITH NITROSYL COMPOUNDS.

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Very few works (1) have been reported on the reactions of trialkylborons with nitrosylcompounds, details of which are, therefore still unknown.

We now report the reactions of tricyclohexylboron with nitrosylsulfuric acid and nitrosylchloride in sulfuric acid.

In this reaction several kinds of products, which may be explicable in terms of prior nitrosation at the α-carbon of the cyclohexyl group and subsequent reactions, were obtained, e.g., ε-caprolactam, cyclohexanone oxime, cyclohexylhydroxylamine, etc. As a typical example, nitrosylsulfuric acid (14.7 g) was added to a mixture of tricyclohexylboron (10.0 g) (2) and sulfuric acid (60 ml.) at room temperature with stirring and in an atmosphere of nitrogen. The temperature was gradually raised to 50°, and kept for five hours at this temperature. After the end of the reaction, the product was cooled to room temperature and filtered under nitrogen. White crystals of unreacted tricyclohexylboron (2.45 g) were recovered. The filtrate was poured into ice water with sufficient stirring. In a couple of minutes brown crystals (3.25 g) came out, and were identified to be dicyclohexylborinic acid (m.p. 53-54.5°) (3).

After separation of the acid, the filtrate was carefully neutralized below 10° with an aqueous solution (50 %) of sodium hydroxide and then made slightly alcaline. This solution was extracted with chloroform, which on evaporation gave a brown liquid of high boiling point.

It was found by VPC analysis that the liquid contained cyclohexyl hydroxylamine (0.24 g), cyclohexanone oxime (0.36 g), ε-caprolactam (0.99 g), and small amounts of dicyclohexylamine and dicyclohexyl. (Fractional distillation of the liquid gave cyclohexanone oxime and ε-caprolactam.)

In another experiment at 80°, ether was used as an extracting solvent in place of chloroform. After evaporation of the ether, there was also obtained yellow liquid of high boiling point. On cooling the liquid separated cyclohexylhydroxylamine (0.1 g) as crystals, and the liquid portion was submitted to VPC analysis. In addition to cyclohexylhydroxylamine (0.8 g), small amounts of cyclohexanone oxime, dicyclohexylamine and dicyclohexyl were obtained. In comparison with the result in the reaction at 50° the amount of cyclohexylhydroxylamine was increased while that of dicyclohexylamine decreased. The yield of ε-caprolactam was very low. Since it is already known by our own experiments (4) that dicyclohexylamine can be obtained by the reaction of tricyclohexylboron with nitrosocyclohexane in tetrahydrofuran at 50° for 5 hours, while, if this reaction is carried out in n-hexane, both cyclohexylhydroxylamine and cyclohexene are obtained, the formation of dicyclohexylamine and cyclohexylhydroxylamine in the present reaction may be interpreted as follows:

$$\mathrm{NOHSO_4 + (C_6H_{11})_3B \longrightarrow C_6H_{11}NO + (C_6H_{11})_2BHSO_4} \qquad \mathrm{(I)}$$

$$\mathrm{C_6H_{11}NO + (C_6H_{11})_3B \longrightarrow C_6H_{11}NHOB(C_6H_{11})_2 + C_6H_{10}} \qquad \mathrm{(II)}$$

$$\big\downarrow \mathrm{H_2O}$$

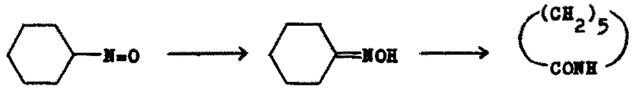
$$\mathrm{C_6H_{11}NHOH + (C_6H_{11})_2BOH}$$

$$\mathrm{C_6H_{11}NO + (C_6H_{11})_3B \longrightarrow (C_6H_{11})_2NOB(C_6H_{11})_2} \qquad \mathrm{(III)}$$

$$\big\downarrow \mathrm{2(C_6H_{11})_3B,\ H_2O}$$

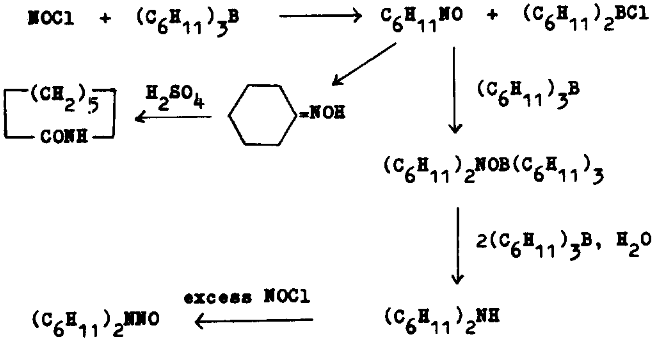
$$\mathrm{(C_6H_{11})_2NH + 3(C_6H_{11})_2BOH + C_6H_{11}\text{-}C_6H_{11}}$$

In sulfuric acid as solvent, both reactions (II, III) occured, concurrently, and high temperatures (80°, 90°) may be favorable to the reaction (II). The formation of ε-caprolactam is very easy to understand. Nitrosocyclohexane produced may be converted to the corresponding oxime, which then undergoes Beckmann rearrangement to give the lactam.



(IV)

With the use of nitrosylchloride as nitrosyl compound, tricyclohexylboron gave N-nitrosodicyclohexylamine and ε-caprolactam. Formation of these compounds may be explained as follows:



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