Tetrahedron Letters No.16, pp. 1097-1100, 1971. Pergamon Press. Printed in Great Britain.

THE REACTIONS OF THIOBORONITE

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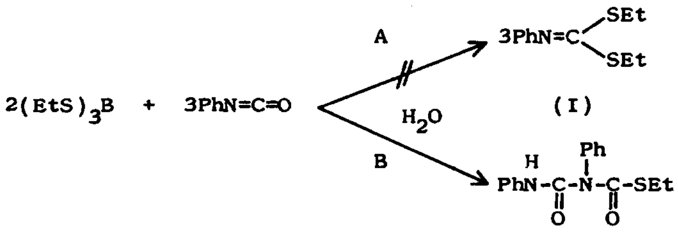
(Received in Japan 13 February 1971; received in UK for publication 19 March 1971)

It is known that various thioboronites or thioborates react with carbonyl compounds to give the corresponding mercaptals or mercaptols[1]. These results indicate that the boron-sulphur bond cleavage takes place easily probably through co-ordination complexes of the carbonyl compounds and the boron compounds.

Based on these facts, the reaction of triethyl orthothioborate with phenylisocyanate was examined with the assumption that the corresponding mercaptol(I) would result according to the route A. However, it was found that N-ethylthiocarbonyl-N,N'-diphenylurea(II) was obtained in 94% yield by refluxing them in benzene.



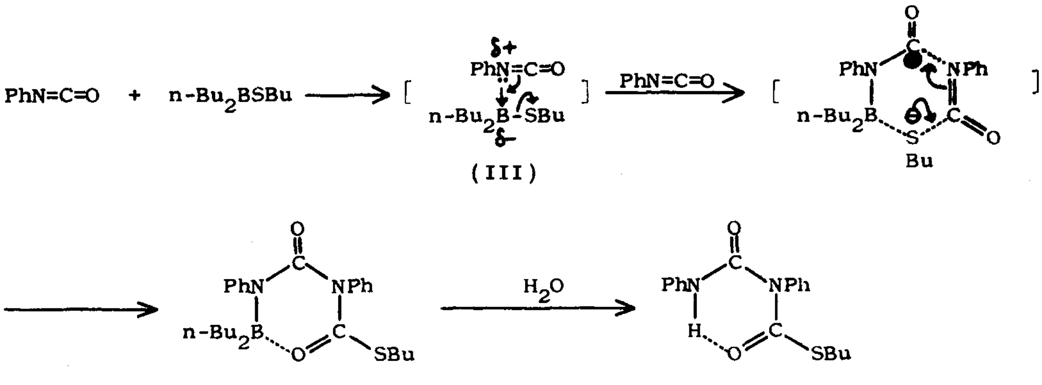
(I)

(II)

Next, the reactions of thioboronite with isocyanates, isothiocyanate, carbodiimide and nitriles were tried with the expectation that these compounds would afford active intermediates, co-ordinated complexes. When a mixture of n-butyl di-n-butylthioboronite (0.01 M) and phenylisocyanate (0.02 M) in carbon tetrachloride was allowed to react under nitrogen atmosphere for 20 min, it was observed that the infrared spectrum of the oily substance, obtained by evaporating the solvent *in vacuo*, has not peaks at 2250 cm^{-1} (ν N=C=O) and 1110 cm^{-1}

attributable to B-S but new peaks at about 1700 cm^{-1} (ν C=O) and at 1330-1320 cm^{-1} attributable to ν B-N. From this spectroscopic data, it can be assumed that phenylisocyanate and n-butyl di-n-butylthioboronite formed a 2:1 adduct. It was further confirmed by the isolation of N-n-butylthiocarbonyl-N,N'-diphenylurea(V) by hydrolysis of this adduct 95% yield as white needles (purified with silica gel column chromatography and recrystallized from 95% ethyl alcohol. m.p. 90.0-90.5°C). The structure of V was made clear by elemental analysis and compared with authentic compound prepared separately from phenylisocyanate and S-n-butyl thiocarbanilate.

The reaction is considered to proceed as follows; in the first stage of

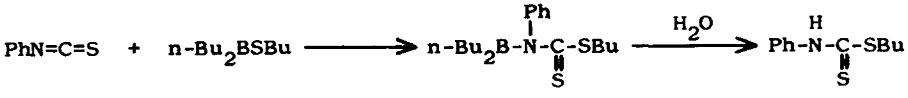

(III)
(IV)
(V)

this reaction, one mole of isocyanate co-ordinates to thioboronite to form an intermediate(III), which is facile to produce mercapto anion by the influence of $\overset{\delta-}{B}\leftarrow:\overset{\delta+}{N}$ polarization. Then, another isocyanate pulls out the mercapto anion from III accompanied with a nucleophilic attack of the nitrogen atom on the carbon atom of the initially co-ordinated isocyanate to result in the formation of an adduct(IV).

In a similar way, N-n-butylthiocarbonyl-N,N'-dicyclohexylurea (100%, m.p. 65-66°C) or N-n-butylthiocarbonyl-N,N'-diethylurea (95%, b.p. 136-140°C/7mmHg) was obtained by the reaction of cyclohexylisocyanate or ethylisocyanate with n-butyl di-n-butylthioboronite.

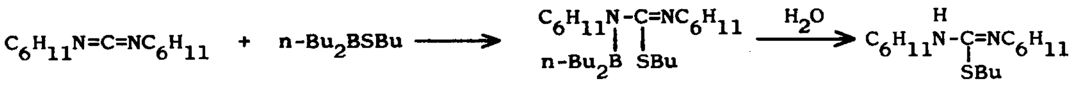
Further, it was found that n-butyl di-n-butylthioboronite reacts with phenylisothiocyanate and dicyclohexylcarbodiimide to give the corresponding 1:1

adducts which are converted to n-butyl dithiocarbanilate(VI, 45%) and S-n-butyl-N,N'-dicyclohexylisothiourea(VII, 83%), respectively, by hydrolysis.



$$PhN{=}C{=}S \;+\; n\text{-}Bu_2BSBu \longrightarrow n\text{-}Bu_2B\text{-}\overset{\overset{\displaystyle Ph}{|}}{N}\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}SBu \xrightarrow{H_2O} Ph\text{-}\overset{H}{N}\text{-}\underset{\underset{\displaystyle S}{\|}}{C}\text{-}SBu$$

(VI)



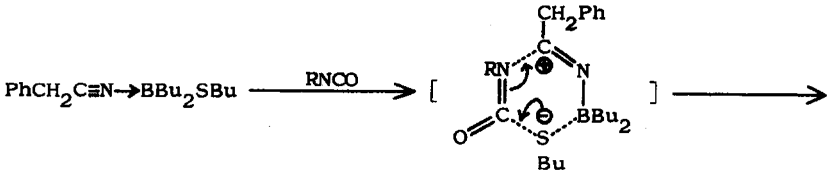
$$C_6H_{11}N{=}C{=}NC_6H_{11} \;+\; n\text{-}Bu_2BSBu \longrightarrow \begin{array}{c} C_6H_{11}N\text{-}C{=}NC_6H_{11} \\ |\quad\;\; | \\ n\text{-}Bu_2B\;\; SBu \end{array} \xrightarrow{H_2O} C_6H_{11}\overset{H}{N}\text{-}\underset{\underset{\displaystyle SBu}{|}}{C}{=}NC_6H_{11}$$

(VII)

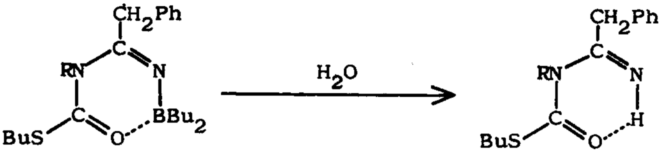
The formation of 2:1 adducts in the cases of isocyanates different from isothiocyanate and carbodiimide may depend on the strong abilities of isocyanates to pull out mercapto group from initially formed 1:1 adducts.

Next, the reactions of n-butyl di-n-butylthioboronite with nitriles were tried. B. M. Mikhailov and his co-worker reported that thioboronite reacted with acetonitrile in carbon tetrachloride to afford the stable dimerized adduct $(R_2BN{=}CMeSR)_2$ on standing over night$^{2)}$. Actually, this adduct (R=n-Bu) did not further react with mercuric cyanide, sodium borohydride, lithium aluminum hydride and diborane.

An attempt to synthesize an analogous adduct of n-butyl di-n-butylthioboronite with benzyl cyanide failed, but the infrared spectrum of the oily substance, obtained by evaporating the reaction mixture, showed the shift of absorption band of nitrile group from 2246 cm^{-1} to 1810 cm^{-1} attributable to the co-ordinated nitrile group $\nu C{\equiv}N$. Then, the nitrile-thioboronite co-ordination complex(VIII) thus obtained was treated at 0^oC with an equimolar amount of phenylisocyanate in ether with the expectation that it might pull out mercapto group from VIII. In the presence of a catalytic amount of $Et_2O{\cdot}BF_3$ under dry air, disappearance of the absorption at 1810 cm^{-1} was observed after stirring for about 10 hr. at 0^oC. Phenylacetamidine derivative (IX, R=Ph, m.p. 69.5-70.5^oC) was obtained by hydrolysis of the reaction mixture, expectively, as shown in the following scheme.



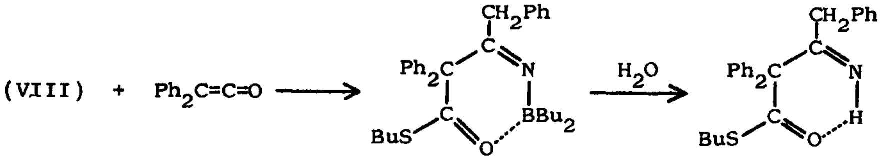
(VIII)



(IX)

In a similar way, the reactions of VIII with another isocyanates gave the corresponding acetamidine derivatives(IX) in fairly good yields.

Further, it was found that VIII reacts with diphenylketene to afford phenylacetaldimine derivative(X, m.p. 151°C) in 49% yield.



(X)

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2) B. M. Mikhailov, V. A. Dorokhov and I. P. Yakovlev, Izv. Akad. Nauk SSSR., Ser. Khim., 1966 (2); 332-4 [C. A. 64, 17623g (1966)].