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The Reactions of Complexes of Thioboronite with Compounds Containing Carbon-Nitrogen Multiple Bond

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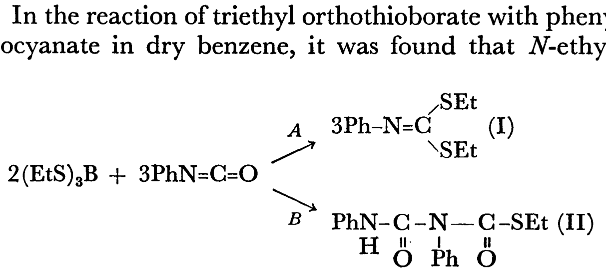
n-Butyl di-*n*-butylthioboronite reacts with isocyanates to give 1 : 2 adducts, and with isothiocyanate or carbodiimide to give a 1 : 1 adduct. It was found that thioboronite forms a 1 : 1 co-ordinated complex with benzyl cyanide, and that the complex reacts with isocyanates to give the corresponding acetamidine derivatives in good yields.

It has been reported by Mikhailov and his co-workers[1] that various thioboronites or thioborates react with carbonyl compounds to give the corresponding mercaptols or mercaptals. The results indicate that the boron-sulphur bond cleavage takes place easily through co-ordinated complexes of carbonyl compounds and boron compounds. The reactions of thioboronites with compounds containing the carbon-nitrogen multiple bond, such as isocyanates, carbodiimide and nitriles, were studied in order to examine the chemical behavior of the boron-sulfur bond.

In the reaction of triethyl orthothioborate with phenyl isocyanate in dry benzene, it was found that *N*-ethylthiocarbonyl-*N*,*N'*-diphenylurea (II) is obtained in a 94% yield (route *B*) instead of the expected mercaptol (I) (route *A*).



$$2(EtS)_3B + 3PhN{=}C{=}O \xrightarrow{A} 3Ph\text{-}N{=}C(SEt)_2 \ \text{(I)}$$

$$2(EtS)_3B + 3PhN{=}C{=}O \xrightarrow{B} PhN(H)\text{-}C(=O)\text{-}N(Ph)\text{-}C(=O)\text{-}SEt \ \text{(II)}$$

n-Butyl di-*n*-butylthioboronite (0.01 M) in carbon tetrachloride was treated with phenyl isocyanate (0.02 M) in the same solvent under nitrogen atmosphere at room temperature. After stirring for 20 min, it was observed that the infrared spectra of the oily substance obtained by evaporating the solvent *in vacuo* showed no bands at 2250 cm^{-1} ($\nu_{N=C=O}$) and 1110 cm^{-1} assignable to *B–S* bond, but new bands at about 1700 cm^{-1} ($\nu_{C=O}$) and 1330—1320 cm^{-1} assignable to *B–N* bond. It can be assumed that *n*-butyl di-*n*-butylthioboronite and phenyl isocyanate forms an 1 : 2 adduct. This was further confirmed by the fact that *N*-*n*-butylthiocarbonyl-*N*,*N'*-diphenylurea (V) was isolated as white crystal in a 95% yield by hydrolysis of this adduct. The structure was established by elemental analysis and comparison with the authentic compound prepared from phenyl isocyanate and *S*-*n*-butyl thiocarbanilate according to the method of Lakra *et al.*[2]

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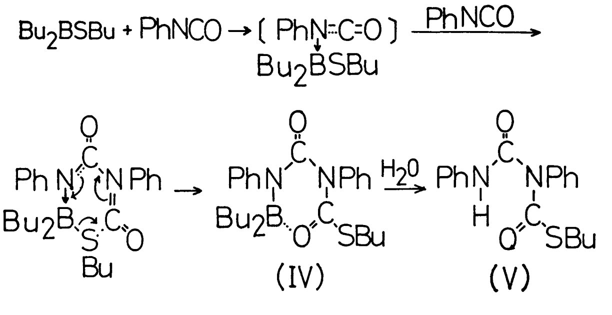
[1] B. M. Mikhailov and N. S. Fedotov, *Izv. Akad. Nauk SSSR., Otdel. Khim. Nauk*, 999-1000 (1961); *Chem. Abstr.* **57**, 16643 (1962).

[2] H. Lakra and F. B. Pains, *J. Amer. Chem. Soc.*, **51**, 2220 (1929).

TABLE 1. REACTION OF THIOBORONITE WITH ISOCYANATES.

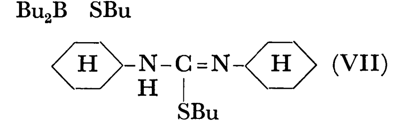
R-N=C=O	Product yield (%)	Product mp (bp) (°C)	Formula	Calcd (%) C	Calcd (%) H	Calcd (%) N	Calcd (%) S	Found (%) C	Found (%) H	Found (%) N	Found (%) S
C_6H_5	95	90.0—90.5	$C_{18}H_{20}O_2N_2S$	65.84	6.14	8.53	9.82	65.58	6.18	8.29	9.96
p-$O_2NC_6H_4$	98	128 (decomp.)	$C_{18}H_{20}O_2N_2S$	51.67	4.34	13.39	7.65	51.39	4.06	13.59	7.83
⟨H⟩	quant.	65.0—66.0	$C_{18}H_{32}O_2N_2S$	63.50	9.47	8.23	9.40	63.69	9.22	8.53	9.51
C_2H_5	95	(136—140/7 mmHg)	$C_{14}H_{20}O_2N_2S$	51.70	8.68	12.06	13.78	52.04	8.28	12.20	14.64

The reaction is considered to proceed as follows; initially one mole of isocyanate co-ordinates to thioboronite to form a 1:1 complex (III).[3] Then another isocyanate abstracts the mercapto group, activated by the influence of $\overset{\delta-}{B}\leftarrow\overset{\delta+}{N}$ polarization and accompanied by a nucleophilic attack of the nitrogen atom on the carbon atom of initially co-ordinated isocyanate to form (VI).

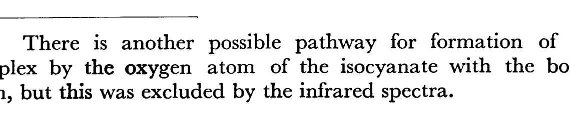


In a similar way, p-nitrophenyl isocyanate, cyclohexyl isocyanate and ethyl isocyanate gave the corresponding ureas in almost quantitative yields. The results are summarized in Table 1.

The reaction of n-butyl di-n-butylthioboronite with phenyl isothiocyanate and with dicyclohexylcarbodiimide was tried. In both cases, formation of the corresponding 1:1 adducts was confirmed by infrared spectra. The adducts were in turn converted into n-butyl dithiocarbanilate (VI 45%) and S-n-butyl-N,N'-dicyclohexylisothiourea (VII 83%) by hydrolysis, respectively.



$$Bu_2BSBu + Ph\text{-}N{=}C{=}S \longrightarrow [Bu_2B\text{-}\overset{Ph}{N}\text{-}\underset{S}{\overset{}{C}}\text{-}SBu] \xrightarrow{H_2O} Ph\text{-}\underset{H}{N}\text{-}\underset{S}{C}\text{-}SBu \text{ (VI)}$$



$$Bu_2BSBu + \langle H\rangle\text{-}N{=}C{=}N\text{-}\langle H\rangle \longrightarrow [\langle H\rangle\text{-}\underset{Bu_2B}{N}\text{-}C{=}N\text{-}\langle H\rangle] \xrightarrow{H_2O} \langle H\rangle\text{-}\underset{H}{N}\text{-}\underset{SBu}{C}{=}N\text{-}\langle H\rangle \text{ (VII)}$$

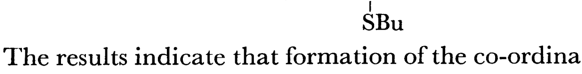
Differing from isothiocyanate and carbodiimide, the formation of the 1:2 adduct in the case of isocyanate, might depend on its strong electrophilic character, which abstracts the mercapto group from the 1:1 complex initially formed.

An attempt to synthesize an analogous adduct of n-butyl di-n-butylthioboronite and benzyl cyanide was made according to the report by Mikhailov *et al.*[4] showing that the stable dimerized adduct ($(R_2BN{=}CMeSR')_2$) is obtained by the reaction of acetonitrile with thioboronite (R_2BSR'). Unexpectedly, it was found that a 1:1 complex is produced instead of the dimerized adduct when n-butyl di-n-butylthioboronite (0.01 M) was allowed to react with benzyl cyanide (0.01 M) under nitrogen atmosphere at room temperature for 20 min. After removal of the solvent, the band at 2150 cm^{-1} ($\nu_{C\equiv N}$) disappeared and a new strong band appeared at 1810 cm^{-1} in the infrared spectra of the resulting oily substance. With the addition of ethanol amine, the band at 2150 cm^{-1} reappeared and the band at 1810 cm^{-1} disappeared. It is thus clear that thioboronite and benzyl cyanide form a 1:1 co-ordinated complex, and that the band at 1810 cm^{-1} is assignable to the nitrile group shifted greatly to lower frequency by co-ordination. It was found that the 1:1 complex exists in ether and dioxane, but it dissociates into nitrile with the addition of tetrahydrofuran, amines (pyridine, triethylamine) dimethyl sulfide as shown in the following equation.

$$[PhCH_2C\overset{..}{=}N\rightarrow BBu_2SBu] + :L \rightleftharpoons PhCH_2CN + L:BBu_2SBu$$

L: THF, pyridine, triethylamine, dimethylsulfide

When the co-ordinated complex obtained by evaporating the solvent *in vacuo* was stirred for a few days, the band at 1810 cm^{-1} in the infrared spectra disappeared and a new band at 1610 cm^{-1} ($\nu_{C=N}$) appeared, the stable adduct (VIII) being obtained as a white crystal in a 40—50% yield. It was also observed that dry air is effective to accelerate the transfer of mercapto group, but the detailed mechanism is not yet clear.



$$[PhCH_2CN\rightarrow BBu_2SBu] \longrightarrow (PhCH_2\underset{SBu}{C}{=}N\text{-}BBu_2)_n \text{ (VIII)}$$

The results indicate that formation of the co-ordinated complex of thioboronite and benzyl cyanide facilitates the formation of mercapto anion due to the influence of $\overset{\delta-}{B}\leftarrow\overset{\delta+}{N}$ polarization.

Thus, it is expected that an abstraction of the mercapto group from the complex would occur by the use of isocyanates. An equimolar amount of phenyl isocyanate was added to the 1:1 complex in the presence of a catalytic amount of boron trifluoride etherate in the

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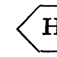
[3] There is another possible pathway for formation of the complex by the oxygen atom of the isocyanate with the boron atom, but this was excluded by the infrared spectra.

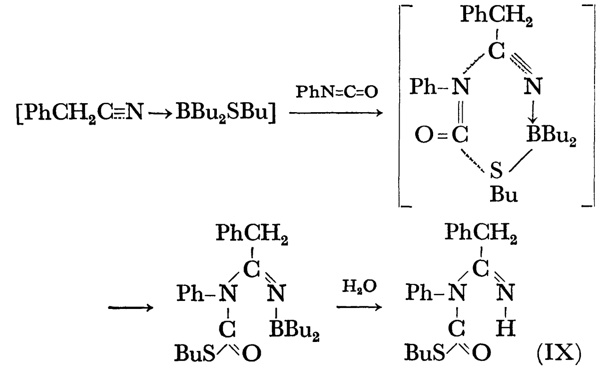
[4] B. M. Mikhailov, V. A. Dorokhov and I. P. Yakovlev, *Izv. Akad. Nauk SSSR., Ser. Khim.*, **1966** (2) 332; *Chem. Abstr.*, **64**, 17623 g (1966).

TABLE 2. REACTION OF ISOCYANATES WITH 1:1 COMPLEX OF THIOBORONITE AND BENZYL CYANIDE

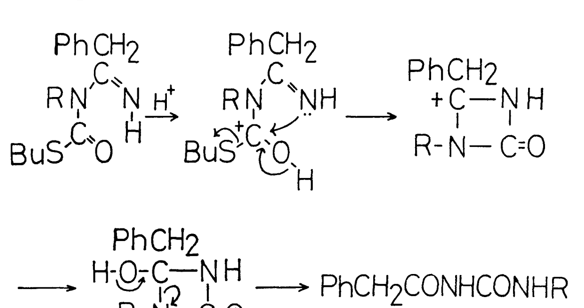
R-N=C=O	Product		Foumula	Calcd (%)				Found (%)			
	Yield (%)	mp (°C)		C	H	N	S	C	H	N	S
p-$O_2NC_6H_4$	83	149.0—149.5	$C_{19}H_{21}O_3N_3S$	61.44	5.70	11.32	8.66	61.14	5.48	11.16	8.96
C_6H_5	74	69.5— 70.5	$C_{19}H_{22}ON_2S$	69.94	6.75	8.59	9.86	69.83	6.74	8.78	9.65
α-$C_{10}H_7$	70	110.5—111.0	$C_{23}H_{24}ON_2S$	73.38	6.43	7.44	8.50	73.08	6.29	7.55	8.24
p-$CH_3OC_6H_4$	69	99.5—100.0	$C_{20}H_{24}O_2N_2S$	67.39	6.79	7.86	8.98	67.31	6.75	7.99	9.24
p-$CH_3C_6H_4$	61	111.0—111.5	$C_{20}H_{24}ON_2S$	70.56	7.11	8.23	9.40	70.42	6.94	8.20	9.34
m-$CH_3C_6H_4$	46	a)									
o-$CH_3C_6H_4$	49	83.0	$C_{20}H_{24}ON_2S$	70.56	7.11	8.23	9.40	70.25	6.96	8.02	9.44
	67	101.0—102.0	$C_{19}H_{28}ON_2S$	68.63	8.49	8.43	9.64	68.38	8.21	8.41	9.94
C_2H_5	59	a)									
t-C_4H_9	35	a)									

a) Oily substances which undergo decomposition during the course of vacuum distillation. This was confirmed by means of infrared spectra and the hydrolysis to acylurea.

minimum amount of ether at 0°C under dry air⁵⁾. After stirring the mixture for 10 hr, the infrared spectra of the oily substance obtained by evaporating the solvent showed the diappearance of the band at 1810 cm^{-1} and 2150 cm^{-1} ($\nu_{N=C=O}$) and the appearance of a new band at 1605 cm^{-1} ($\nu_{C=N}$). By hydrolysis of the reaction mixture, *N*-*n*-butylthiocarbonyl *N*-phenyl phenylacetamidine (IX) was obtained in a 74% yield as expected. The reaction is considered to proceed as shown below.



The structure was established by elemental analysis, infrared spectra and NMR spectra. In the case of various isocyanates, a similar reaction took place to give the corresponding acetamidine derivatives. The results are shown in Table II.



It was found that acetamidine derivatives thus obtained give the corresponding acylureas (X) quantitatively by acidic hydrolysis as shown in the above scheme.

Experimental

Reaction of n-*Butyl Di*-n-*butylthioboronite and Phenyl Isocyanate.* A solution of phenyl isocyanate (2.38 g, 0.02 mol) in carbon tetrachloride was added dropwise with strirring to a solution of *n*-butyl di-*n*-butylthioboronite (2.20 g, 0.01 mol) in the same solvent at room temperature under nitrogen atmosphere. After stirring for 20 min, the oily substance obtained by evaporating the solvent was hydrolyzed in THF-water for 3 hr at room temperature, and saturated with sodium chloride. The THF layer was then separated and the water layer was extracted with ether three times. The THF layer and the ether layer were combined and dried with sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel. From the elute of benzene a white crystal was obtained. Recrystallization from 95% ethanol gave *N*-*n*-butylthiocarbonyl-*N*,*N'*-diphenylurea, 3.02 g (95%), mp 90—90.5°C.

In a similar way, the corresponding *N*-*n*-butylthiocarbonylurea derivatives were obtained by the reaction of *n*-butyl di-*n*-butylthioboronite with *p*-nitrophenyl isocyanate, cyclohexyl isocyanate, or ethyl isocyanate, respectively. The results are listed in Table 1.

Reaction of n-*Butyl Di*-n-*butylthioboronite and Phenyl Isothiocyanate.* A mixture of phenyl isothiocyanate (1.35 g, 0.01 mol) and *n*-butyl di-*n*-butylthioboronite (2.23 g, 0.01 mol) in carbon tetrachloride was stirred for 3 days at room temperature under nitrogen atmosphere. The oily substance obtained by evaporating the solvent was hydrolyzed in THF-water for 3 hr at room temperature and saturated with sodium chloride. The THF layer was then separated and the water layer was extracted with ether three times. The THF layer and the ether layer were combined and dried with sodium sulfate. After removal of the solvent the residue was chromatographed on silica gel. From the elute of benzene a white crystal was obtained. Recrystallization from petroleum ether gave *n*-butyl dithiocarbanilate, 1.02 g (45%) mp 55.5—56.0°C.

Found: C, 63.43; H, 7.46; N, 6.69; S, 15.18%. Calcd for $C_{11}H_{15}NS_2$: C, 63.14; H, 7.23; N, 6.69; S, 15.29%.

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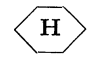
5) When a large amount of ether is used as solvent, free thioboronite liberated from the complex reacts with isocyanate to give the 1:2 adduct (IV) as shown below.

$$PhCH_2CN + Bu_2BSBu \rightleftharpoons PhCH_2CN \rightarrow BBu_2SBu$$

$$\downarrow 2RNCO$$

$$1:2 \text{ adduct (IV)}$$

TABLE 3. HYDROLYSIS OF PHENYLACETAMIDINE DERIVATIVES. $PhCH_2CONHCONHR$

R	mp (°C)	Fromula	Calcd (%)			Found (%)		
			C	H	N	C	H	N
p-$O_2NC_6H_4$	189.0	$C_{15}H_{13}O_4N_3$	60.19	4.38	14.08	59.94	4.24	14.28
C_6H_5	147.5—148.5	$C_{15}H_{14}O_2N_2$	70.85	5.55	11.02	70.61	5.49	11.11
α-$C_{10}H_7$	202.0	$C_{19}H_{16}O_2N_2$	74.98	5.30	9.21	74.79	5.00	9.40
p-$CH_3OC_6H_4$	165.0—166.0	$C_{16}H_{16}O_3N_2$	67.59	5.67	9·85	67.89	5.96	9.89
p-$CH_3C_6H_4$	186.0—186.5	$C_{16}H_{16}O_2N_2$	71.62	6.01	10.44	71.35	6.05	10.51
m-$CH_3C_6H_4$	154.0—155.0	$C_{16}H_{16}O_2N_2$	71.62	6.01	10.44	71.86	6.26	10.70
o-$CH_3C_6H_4$	159.0—160.0	$C_{16}H_{16}O_2N_2$	71.62	6.01	10.44	71.69	5.74	10.50
	126.0—126.5	$C_{15}H_{20}O_2N_2$	69.20	7.44	10.76	69.35	7.49	10.49
C_2H_5	155.0—156.0	$C_{11}H_{14}O_2N_2$	64.06	6.84	13.58	63.77	6.62	13.41
t-C_4H_9	157.5—158.5	$C_{13}H_{18}O_2N_2$	66.64	7.74	11.96	66.83	7.85	11.68

Reaction of n-*Butyl Di*-n-*butylthioboronite with Dicyclohexylcarbodiimide.* A mixture of n-butyl di-n-butylthioboronite (2.14 g, 0.01 mol) and dicyclohexylcarbodiimide (2.06 g, 0.01 mol) in methylene chloride was stirred for 1 hr at room temperature under nitrogen atmosphere. By treating the mixture with water, S-n-butyl-N,N'-dicyclohexyl isothiourea was obtained in an 85% yield as an oily substance which undergoes decomposition during the course of vacuum distillation to give dicyclohexylcarbodiimide.

Reaction of n-*Butyl Di*-n-*butylthioboronite and Benzyl Cyanide.* A solution of benzyl cyanide (0.61 g, 0.005 mol) in methylene chloride was added with stirring to a solution of n-butyl di-n-butylthioboronite (1.11 g, 0.005 mol) in methylene chloride at room temperature under nitrogen atmosphere. After stirring for 20 min, the 1:1 complex of n-butyl di-n-butylthioboronite and benzyl cyanide was obtained as a yellow oily substance by evaporating the solvent *in vacuo*. After stirring the complex under dry air for a few days, dimerized adduct was obtained as a white precipitate by adding 95% ethanol.

Recrystallization from acetonitrile at a temperature below 50°C gave a white needle 0.77 g (45%), mp 66.0—66.5°C.

Found: C, 72.25; H, 10.31; N, 4.53; S, 9.85%. Calcd for $C_{20}H_{34}NBS$: C, 72.48; H, 10.36; N, 4.23; S, 9.67%.

Reaction of 1:1 Complex between n-*Butyl Di*-n-*butylthioboronite and Benzyl Cyanide with Phenyl Isocyanate.* The 1:1 complex obtained from n-butyl di-n-butylthioboronite (1.42 g) and benzyl cyanide (0.78 g) was stirred for 1 hr at room temperature under dry air. A solution of phenyl isocyanate (0.79 g) in 3 ml ether was then added all at once to the complex in the presence of a catalytic amount of boron trifluoride etherate at 0°C. After stirring for 10 hr at 0°C, the reaction mixture was dissolved in dry THF. The THF solution was added with vigorous stirring to the mixture of THF and pH 7 buffer (9.10 g, KH_2PO_4+18.90 g Na_2HPO_4/l). After stirring 3 hr at 25—30°C, the THF layer was separated and the water layer was extracted with ether three times. Both layers were combined and dried with sodium sulfate. The yellow oily substance obtained by evaporating the solvent *in vacuo* was crystallized in a small amount of petroleum ether at −78°C. The crystal was filtered. The filtrate was concentrated by evaporation and the residue was chromatographed on silica gel. From the elute of benzene a white crystal was obtained. Recrystallization from petroleum ether gave N-n-butylthiocarbonyl N-phenyl phenylacetamidine, 1.57 g (74%) mp 69.5—70.5°C.

The corresponding phenyl acetamidine derivatives were obtained in a similar way. The results are listed in Table 2.

Hydrolysis of N-n-*Butylthiocarbonyl* N-*Phenylacetamidine.* Dilute hydrochloric acid solution was added to a solution of N-n-butylthiocarbonyl N-phenyl phenylacetamidine (0.41 g) in THF at room temperature. After removal of the solvent, the acylurea was obtained as a white crystal (0.32 g). The yield of acylurea was quantitative.

In a similar way, various acylureas were obtained in quantitative yields. The results are listed in Table 3.