CHARACTERISTICS OF REDUCTIVE CLEAVAGE OF (B-CARBORANYL)-

## THIOCYANATES

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Previously it was established [1] that under homogeneous reduction conditions the SCN group in aryl thiocyanates is cleaved at the S-C bond, and here diaryl disulfides are formed in good yield. Carborane represents an electron-deficient molecule, in which the B atoms are connected by tricenter bonds [2]. Consequently, previously it was not clear whether the B-S or the S-C bond is more sensitive toward a reducing agent. For the B-T1-SCN fragment it is even more difficult to predict the sequence of bond cleavage.

We ran the homogeneous reduction of a series of (B-carboranyl) thiocyanates using the dipotassium salt of cyclooctatetraene and the  $HSiCl_3 + Bu_3N$  system. The composition of the products is given in Table 1. It proved that the reduction of (B-m-carboranyl)thiocyanate by the  $HSiCl_3 + Bu_3N$  system leads to a mixture of (B-carboranyl)mercaptan and di(B-carboranyl)-disulfide, but here the conversion is a total of 10%. The conversion increases to 90% when  $C_8H_8K_2$  is used.

 $\begin{array}{l} \text{RCB}_{10}\text{H}_{9}(\text{SCN})\text{CR} \xrightarrow[2.H_{2}\text{O}]{} \text{RCB}_{10}\text{H}_{9}(\text{SH})\text{CR} + [\text{RCB}_{10}\text{H}_{9}(\text{S})\text{CR}] \\ \text{R} = o\text{-H}, \ p\text{-H} \end{array}$ 

The m-carborane fragment is not isomerized to the o-carborane fragment during reaction; reaction is exclusively at the SCN group. An increase in the conversion of the substrate is explained by the greater reductive capacity of  $C_8H_8K_2$  when compared with the HSiCl<sub>3</sub> + Bu<sub>3</sub>N system [3]. The formation of two products in the studied reactions can be caused either by the reaction of the obtained (B-carboranyl)thallium mercaptide with the starting (B-carboranyl)thiocyanate or by the greater tendency of the formed di(B-carboranyl)disulfide to be reduced when compared with the starting thiocyanate. The first assumption is supported by the formation of a mixture of (9-carboranyl)mercaptan and di(9-carboranyl)disulfide when a 1:1 reducing agent-substrate ratio is used, and also by the quantitative formation of dithenyl disulfide when potassium thienyl mercaptide is reacted with thienyl thiocyanate [4].

The reduction of (B-carborany1)thallium dithiocyanates, containing B-T1-S-CN fragments, proceeds exclusively at the B-T1 bond and leads only to the corresponding o- or m-carboranes

# $HCB_{10}H_{9}Tl(SCN)CH \xrightarrow{C_{2}H_{9}K_{2}} HCB_{10}H_{10}CH_{9}$

Substrate	C <sub>8</sub> H <sub>8</sub> K <sub>2</sub> : sub- strate mole ratio	Degree of sub- strate conver- sion, %	Yield of products, %	
			di(B-carboranyl) disulfide	(B-Carboranyl)- mercaptan
m-HCB <sub>10</sub> H <sub>9</sub> (SCN) CH m-HCB <sub>10</sub> H <sub>9</sub> (SCN) CH n-HCB <sub>10</sub> H <sub>9</sub> (SCN) CH	1:2 1:1 1:2	90 85 95	<b>25</b> 15 20	65 70 75

TABLE 1. Reduction of Carbonyl Thiocyanates Using  $C_8H_8K_2$  in THF Solution

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 7, pp. 1640-1642, July, 1983. Original article submitted November 17, 1982. probably formed by reaction of the intermediately formed B-carboranyl radical with the solvent. The pyrolysis of (B-carboranyl)thallium dithiocyanates without a solvent leads to (B-carboranyl)thiocyanates [5]. To ascertain the effect of the anion on the course of the reductive cleavage of the B-T1 bond we ran the homogeneous reduction of (1,7-dimethyl-m-carboran-9-yl)thallium bis(trifluoroacetate). It proved that the reduction product is a mixture of dimethyl-m-carborane and bis(dimethyl-m-carbonate). The biscarborane is probably formed

 $\mathrm{HCCB_{10}H_{9}[Tl(OCOCF_{3})_{2}]CH} \xrightarrow{C_{9}H_{8}K_{2}} \mathrm{H_{3}CCB_{10}H_{10}CCH_{3}} + (\mathrm{H_{3}CCB_{10}H_{9}CCH_{3}})_{2}$ 

by the recombination of the carboranyl radicals that are formed in the process of reducing the B-Tl bond, analogous to the radical dimerization of 1,2-diphenyl-o-carborane [6].

### EXPERIMENTAL

The dipotassium salt of cyclooctatetraene was obtained as described in [4], and the carboranyl thiocyanates and (B-carboranyl)thallium dithiocyanates were obtained as described in [5]. The chromato-mass spectrometric analysis was run on an LKB-9000 instrument, and the quantitative composition of the mixtures was determined on a Chrom-4 instrument equipped with a flame-ionization detector and a Kent-Chromalog-2 integrator. For the separation by GLC we used glass columns packed with 2% Dexil-200 deposited on Chromosorb W (100/120 mesh). The samples were inserted directly into the column. The temperature program ranged from 90 to 300°C. We used helium as the carrier gas at a flow rate of 35 ml/min.

<u>Reaction of (m-Carboran-9-y1)thiocyanate with the HSiCl<sub>3</sub> + Bu<sub>3</sub>N System. To 1 mmole of (m-carboran-9-y1)thiocyanate in abs. benzene was added a mixture of HSiCl<sub>3</sub> and Bu<sub>3</sub>N (0.5 mmole each) in benzene and the mixture was stirred for 2 h at ~20° in an argon atmosphere. Then the reaction mixture was diluted with water and extracted with hexane. The GLC analysis disclosed that the hexane solution contains the starting (m-carboran-9-y1)thiocyanate (90%), (m-carboran-9-y1)mercaptan (6%), and di(m-carboran-9-y1)disulfide (4%).</u>

Reaction of (B-Carboranyl) thiocyanates with  $C_8H_8K_2$ . To a solution of the substrate in abs. THF was added  $C_8H_8K_2$  in THF (see Table 1 for ratio of reactants) and the mixture was stirred for 2 h in an argon atmosphere. Then the reaction mixture was treated in succession with aqueous AcOH and water, and then extracted with ether. The ether extract was washed with NaHCO<sub>3</sub> solution, dried, and analyzed employing chromato-mass spectrometry.

Reaction of (o-Carboran-9-y1)thallium Dithiocyanate with  $C_8H_8K_2$ . To a solution of 1.15 g (2.5 mmoles) of (o-carboran-9-y1)thallium dithiocyanate in THF was added 0.5 g (2.5 mmoles) of  $C_8H_8K_2$  and the mixture was stirred for 2 h at ~20° in an argon atmosphere. Then the reaction mixture was treated in succession with aqueous AcOH and water, and then extracted with ether. The ether extract was evaporated, and the solid residue was recrystallized from hexane to give 0.2 g (60%) of o-carborane.

Reaction of (1.7-Dimethyl-m-carboran-9-yl) thallium Bis(trifluoroacetate) with  $C_8H_8K_2$ . To 2.5 mmoles of the bis(trifluoroacetate) in THF was added 0.5 g (2.5 mmoles) of  $C_8H_8K_2$ in THF and the mixture was stirred for 2 h at ~20° in an argon atmosphere. Then the reaction mixture was treated in succession with aqueous AcOH and water, and then extracted with ether. The ether extract was washed with aqueous NaHCO<sub>3</sub> solution, dried over CaCl<sub>2</sub>, and analyzed employing chromato-mass spectrometry. It was found that the reaction products represent a mixture of the 1,7-dimethyl-m- (75%) and bis(1,7-dimethyl-m-) carboranes (25%).

#### CONCLUSION S

1. (B-Carboranyl)thiocyanates are reduced by the dipotassium salt of cyclooctatetraene at the S-C bond.

2. Borothallated carboranes are reduced by  $C_8H_8K_2$  at the B-Tl bond, in which connection the composition of the reaction products depends on the nature of the anion attached to the metal atom.

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ELUTION CHROMATOGRAPHY OF REACTING TWO-COMPONENT

## MIXTURES UNDER LONGITUDINAL MIXING

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(2)

Most of the theories for the chromatographic separation of mixtures fail to take into account reaction between the components being separated. However, in a number of cases such reaction is not negligibly small. Its effect on the chromatographic separation process can be taken into account as a first approximation by solving the problem of elution of the zones of a two-component reacting mixture under nonequilibrium conditions in the absence of absorption of one of the components. An analysis of the solution discloses that the number of peaks and their shape depends on the conditions of running the chromatographic experiment, and also on the equilibrium and kinetic characteristics of the system.

If the reaction has the form  $A + B \underset{k_{-1}}{\overset{k_1}{\underset{k_{-1}}{\rightarrow}}} AB$ , then the problem can be described by the

following system of equations

$$D_{l} \frac{\partial^{2}C_{i}}{\partial x^{2}} - v \frac{\partial C_{i}}{\partial x} - \alpha \frac{\partial C_{i}}{\partial t} - (1 - \alpha) \frac{\partial \langle \overline{C}_{i} \rangle}{\partial t} = f_{i} (C_{A}, C_{B}, C_{AB})$$
(1)

where i = A, AB;  $\alpha$  is the fraction of the mobile phase;  $(1 - \alpha)$  is the fraction of the stationary phase;  $C_i$  is the concentration of the i-th substance in the mobile phase;  $\overline{C_i}$  is the average concentration of the i-th substance in the stationary phase;  $D_{\chi}$  is the effective longitudinal mixing coefficient (it is assumed that  $D_{\chi}$  is the same for all of the components of the mixture);  $f_i$  is the contribution of chemical reaction to the material balance.

If an excess of reactant B is fed continuously into the column during the entire experiment it can be assumed that  $C_{\rm R}$  = const, and then

$$f_{\mathbf{AB}} = -f_{\mathbf{A}} = k_{-1}C_{\mathbf{AB}} - k_{1}C_{\mathbf{A}} \tag{2}$$

where  $k_1 = k_1'/C_R$ .

As a result, a linearization of the system of material balance equations is obtained. We will assume that only substance A is absorbed by the sorbent, in which connection  $\langle \overline{C}_A \rangle = \langle K_d \rangle C_A$ , where  $\langle K_d \rangle$  is the bulk distribution coefficient between the mobile and stationary phases (Henry constant). The problem is solved using the following initial and limiting conditions:

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