



Soviet-era science, translated into English

B. M. MIKHAILOV, V. F. POZDNEV

1963

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196301.44962>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

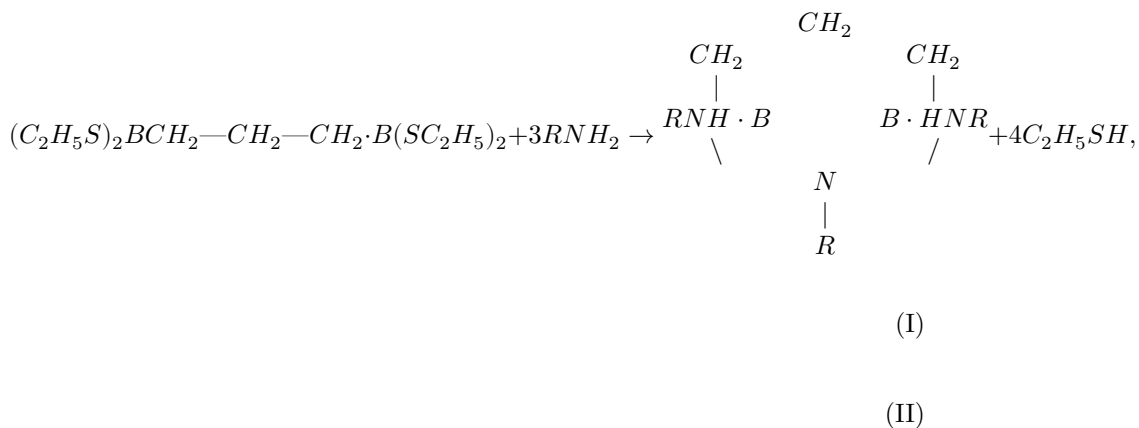
B. M. MIKHAILOV, V. F. POZDNEV

REACTIONS OF 1,1,5,5-TETRAETHYLMERCAPTO-1,5-DIBORAPENTANE WITH AMMONIA AND AMINES

(Presented by Academician B. A. Kazanskii, January 2, 1963)

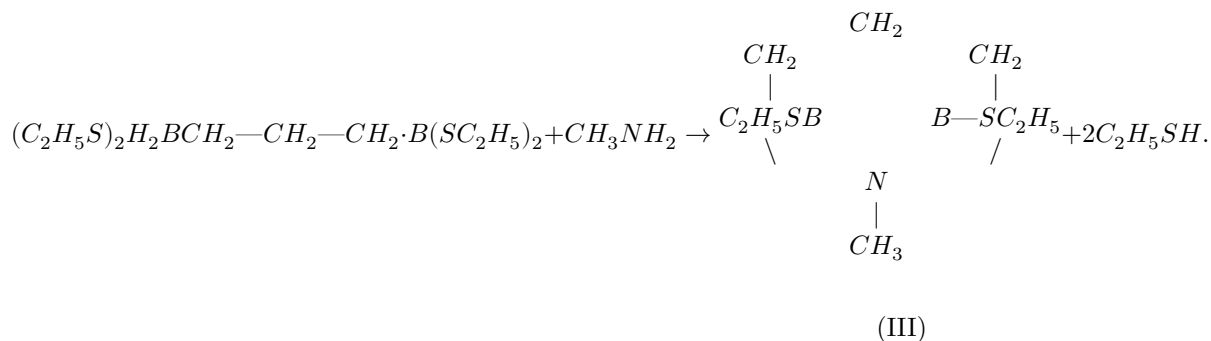
The previously obtained by us ⁽¹⁾ esters of propanedithioboric acid (1,1,5,5-tetraalkylmercapto-1,5-diborapentanes) are unusual compounds containing in the molecule two boron atoms and four reactive functional groups. We investigated their behavior toward ammonia and primary and secondary amines. Since these compounds contain groupings of alkylthioboric acid esters, it could be expected that their reactions with the indicated reagents would proceed analogously to the reactions of alkylthioboric acid esters ⁽²⁾: with ammonia, derivatives of borazole, probably of polymeric type, would be obtained, and with amines—tetraalkylamino- or bis-dialkylamino derivatives.

However, in the reaction with ammonia and primary amines, specific structural features of 1,1,5,5-tetraalkylmercapto-1,5-diborapentanes appeared. When ammonia acts on 1,1,5,5-tetraethylmercapto-1,5-diborapentane (I), instead of a borazole derivative a crystalline substance was obtained, which proved to be 2,5-diamino-1-aza-2,5-diboracyclohexane (II, $R = H$). With primary amines (methylamine or ethylamine), I also reacts with formation of cyclic compounds—respectively, 1-methyl-2,5-di-(methylamino)-1-aza-2,5-diboracyclohexane (II, $R = CH_3$) and 1-ethyl-2,5-di-(ethylamino)-1-aza-2,5-diboracyclohexane (II, $R = C_2H_5$).

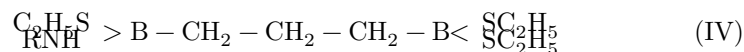




To elucidate the mechanism of formation of the cyclic compounds II, the reaction of I with methylamine was carried out at a reagent ratio of 1 : 1. It turned out that under these conditions 1-methyl-2,5-diethylmercapto-1-aza-2,5-diboracyclohexane (III) is obtained:



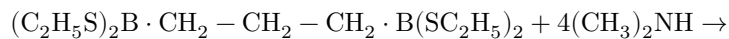
These data indicate that at the first stage of the formation of the cyclic compounds II, in the thioester one alkylmercapto group is initially replaced by an amino or alkylamino group. Then the resulting compound IV cyclizes with elimination of mercaptan into a compound of type III, which subsequently, by exchanging alkylmercapto groups for amino- or alkylaminogroup, is converted into II

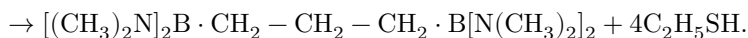


Heterocyclic compounds II and III, which are unstable in air, are readily hydrolyzed by water, being converted into propane-1,3-diboronic acid and an amine.

The reactions of 1,1,5,5-tetraethylmercapto-1,5-diborapentane with secondary amines were investigated using dimethylamine and diethylamine as examples.

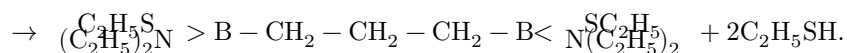
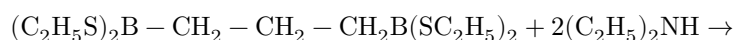
When I is mixed with an excess of dimethylamine in a solvent, the reaction proceeds with heating; however, as a result, a mixture of substances with different degrees of substitution of ethylmercapto groups by dimethylamino groups is obtained. If, however, the reaction is carried out by passing a stream of gaseous dimethylamine through ether I heated to 90-95°, distilling off the ethylmercaptan in the stream of amine, it is possible to obtain 1,1,5,5-tetra-(dimethylamino)-1,5-diborapentane (V) in 75% yield.





(V)

1,1,5,5-Tetraethylmercapto-1,5-diborapentane reacts with diethylamine similarly to the esters of alkylthioboronic acids (2), with formation of the mixed mercapto-amino derivative—1,5-bis-(diethylamino)-1,5-diethylmercapto-1,5-diborapentane (VI)



(VI)

Experimental Part

2,5-Diamino-1-aza-2,5-diboracyclohexane (II, R = H).

5.7 g (0.018 M) of 1,1,5,5-tetraethylmercapto-1,5-diborapentane was dissolved in 20 ml of chloroform, and a stream of ammonia was passed into the solution heated to 60–70°, while the ethylmercaptan formed was distilled off. The solution was filtered from turbidity, the solvent was distilled off in vacuo, and the crystalline residue (1.8 g, m.p. 43–48°) was sublimed in vacuo. 2,5-Diamino-1-aza-2,5-diboracyclohexane was obtained (0.86 g, 44.5%) with m.p. 63–66°.

Found, %: C 32.79; 32.68; H 10.31; 10.00; B 19.67; 19.65
 $\text{C}_3\text{H}_{11}\text{B}_2\text{N}_3$. Calculated, %: C 32.52; H 10.01; B 19.53

Molecular weight found 114.3, calculated 110.7.

1-Methyl-2,5-di-(methylamino)-1-aza-2,5-diboracyclohexane (II, R = CH₃).

Into a solution of 8.7 g (0.028 mole) of 1,1,5,5-tetraethylmercapto-1,5-diborapentane in 25 ml of benzene, 8 g of methylamine was introduced. Then the ethylmercaptan and benzene were removed in vacuo, and the residue (4.3 g) was distilled. 3 g (70.1%) of 1-methyl-2,5-bis-(methylamino)-1-aza-2,5-diboracyclohexane was obtained, b.p. 87–91° at 7 mm.

On repeated distillation the substance had b.p. 90–91° at 7 mm, n_D^{20} 1.4895, d_4^{20} 0.9328; *MR* found 47.74, calculated 47.33.

Found, %: C 46.92; 46.93; H 10.88; 11.04; B 14.09; 14.05
 $C_6H_{17}B_2N_3$. Calculated, %: C 47.14; H 11.21; B 14.15

Molecular weight found 145.6, calculated 152.8.

1-Ethyl-2,5-di-(ethylamino)-1-aza-2,5-diboracyclohexane (II, R = C_2H_5).

To a solution of 17.5 g (0.057 mole) of 1,1,5,5-tetraethylmercapto-1,5-diborapentane in 20 ml of chloroform, 14 g of ethylamine was added. Then the ethylmercaptan was distilled off on a water bath, the solvent was removed in vacuo, and the residue was distilled.

10.3 g (93%) of 1-ethyl-2,5-di-(ethylamino)-1-aza-2,5-diboracyclohexane was obtained, b.p. 62–66° at 1 mm. After repeated distillation the substance had b.p. 120–121° at 15 mm, n_D^{20} 1.4740, d_4^{20} 0.8892. *MR* found 61.60, calculated 61.68.

Found, %: C 55.63; 55.44; H 11.80, 11.68; B 10.99; 11.16
 $C_9H_{23}N_3B_2$. Calculated, %: C 55.45; H 11.89; B 11.10

1-Methyl-2,5-diethylmercapto-1-aza-2,5-diboracyclohexane (III). To a solution of 16.2 g (0.052 M) of 1,1,5,5-tetraethylmercapto-1,5-diboracyclohexane in 100 ml of diethyl ether, with stirring, a solution of 1.6 g (0.052 M) of methylamine in 50 ml of diethyl ether was added dropwise over 40 min. The mixture was left at room temperature for half an hour, and then the solvent and mercaptan were distilled off in vacuum.

By fractional distillation, 4.3 g (0.020 M) of 1-methyl-2,5-diethylmercapto-1-aza-2,5-diboracyclohexane was obtained with b.p. 124–126° at 3 mm; n_D^{20} 1.5440, d_4^{20} 1.0175; *MR* found 66.66, calculated 66.71. Molecular weight found 209.6, calculated 214.9.

Found, %: C 45.06; 45.16; H 8.71; 8.74; B 9.93; 9.75
 $C_8H_{19}B_2S_2N$. Calculated, %: C 44.70; H 8.90; B 10.05

In addition, 4.8 g of the starting 1,1,5,5-tetraethylmercapto-1,5-diborapentane was isolated from the distillation residue. After recrystallization from diethyl ether, the substance had m.p. 62–64°. Literature data ⁽¹⁾ 63–66°. Molecular weight found 304, 284, calculated 307.6.

Found, %: C 42.69; 42.75; H 8.49; 8.27
 $C_{11}H_{26}B_2S_4$. Calculated, %: C 42.91; H 8.45

The yield of 1-methyl-2,5-diethylmercapto-1-aza-2,5-diborahexane, calculated on the reacted 1,1,5,5-tetraethylmercapto-1,5-diborapentane, is 54%.

1,1,5,5-Tetra-(dimethylamino)-1,5-diborapentane (IV). 9.4 g (0.03 M) of 1,1,5,5-tetraethylmercapto-1,5-diborapentane was melted, and a stream of dimethylamine was passed through the melt at 90–95° until ethyl mercaptan ceased to distill off.

The residue (7.2 g) was distilled in vacuum. 5.4 g (75.1%) of 1,1,5,5-tetra-(dimethylamino)-1,5-diborapentane was obtained with b.p. 95–97° at 2 mm. After additional distillation, the substance had b.p. 97° at 2 mm, n_D^{20} 1.4775, d_4^{20} 0.8841; *MR* found 77.12, calculated 77.21.

Found, %: C 55.31; 55.25; H 12.40; 12.33; B 9.11; 8.86
 $C_{11}H_{30}B_2N_4$. Calculated, %: C 55.04; H 12.59; B 9.01

1,5-Bis-(diethylamino)-1,5-diethylmercapto-1,5-diborapentane (VI).

To 10 g (0.032 M) of 1,5-diethylmercapto-1,5-diborapentane, 25 ml (0.24 mole) of diethylamine was added, and after 20 min a mixture of ethyl mercaptan with diethylamine was distilled off at 42–54°. The residue was distilled in vacuum. 8.4 g (0.025 mole, 79.5%) of 1,5-bis-(diethylamino)-1,5-diethylmercapto-1,5-diborapentane was obtained with b.p. 130–135° at 1 mm.

The substance, distilled once more, had b.p. 133–134° at 1 mm, n_D^{20} 1.4973, d_4^{20} 0.9202; *MR* found 105.05, calculated 105.19.

Found, %: C 55.53; 55.72; H 11.29; 11.10; B 6.62; 6.85; N 8.72; 8.75; S 19.65; 19.75

$C_{15}H_{36}B_2N_2S_2$. Calculated, %: C 54.55; H 10.98; B 6.55; N 8.48; S 19.42

Thus, it has been established that 1,1,5,5-tetraethylmercapto-1,5-diborapentane with ammonia or primary amines forms amino derivatives of 1-aza-2,5-diboracyclohexane. 1,1,5,5-Tetraethylmercapto-1,5-diborapentane gives 1,1,5,5-tetra-(dimethylamino)-1,5-diborapentane with dimethylamine. 1,1,5,5-Tetraethylmercapto-1,5-diborapentane reacts with diethylamine to form 1,5-bis-(diethylamino)-1,5-diethylmercapto-1,5-diborapentane.

Institute of Organic Chemistry named after N. D. Zelinsky
 Academy of Sciences of the USSR

Received
 18 XII 1962

CITED LITERATURE

1. B. M. Mikhailov, V. F. Pozdnev, *Izv. AN SSSR, OKhN*, 1962, No. 10, 1861.
2. B. M. Mikhailov, T. K. Kozminskaya, *ZhOKh*, **11**, 3619 (1960).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.