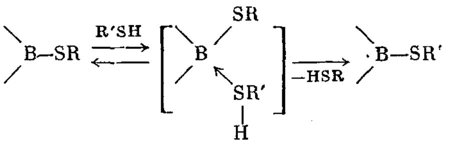
EXCHANGE REACTIONS OF B-TRIALKYLMERCAPTOBORAZOLES

B. M. Mikhailov and A. F. Galkin

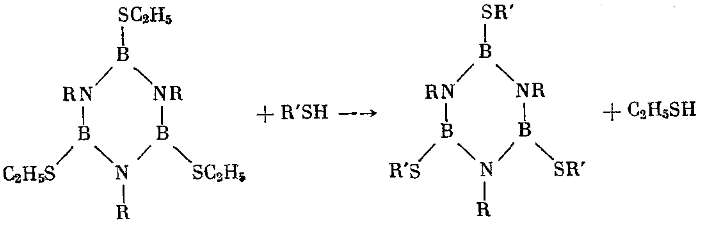
UDC 542.91 + 547.77

Exchange reactions of B-trifunctional derivatives of borazole known in the literature include transamination [1], transhalogenation [2-4], and the exchange reactions of hexaalkylborazoles with B-trichloroborazoles leading to unsymmetrical functional derivatives of borazole [5].

Continuing a study of the properties of B-trialkylmercaptoborazoles obtained by the method described previously [6], we have found that on being heated to 120-200°C with higher mercaptans they undergo a "transmercaptanation" reaction. Esters of dialkylthioboric acids possess similar properties [7]. The transmercaptanation of B-trialkylmercaptoborazoles with higher thiols, like other exchange reactions, apparently takes place through a stage of the formation of an unstable complex which is in equilibrium with the starting materials. When the low-boiling thiol is removed from the medium, the equilibrium is shifted to the right:



Thus, from B-triethylthio-N-trimethylborazole (I) (R = CH_3) we have obtained B-tri-n-amylthio-N-trimethylborazole (II) (R = CH_3, R' = n-C_5H_{11}) and B-tri-n-hexylthio-N-trimethylborazole (II) (R = CH_3, R' = n-C_6H_{13}) with yields of 54-66%



(I) (II)

R=CH_3, C_2H_5; R' = n-C_4H_9, n-C_5H_{11}, n-C_6H_{13}

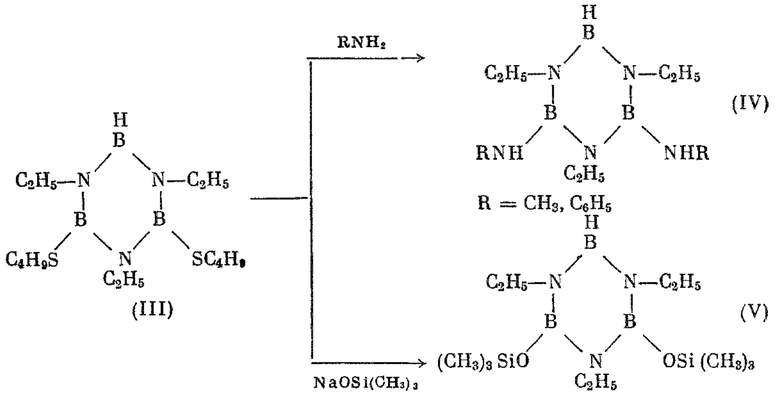
and from B-triethylthio-N-triethylborazole (I) (R = C_2H_5) by the action of n-butyl mercaptan we have obtained the known [6] B-tri-n-butylthio-N-triethylborazole (II) (R = C_2H_5, R' = n-C_4H_9) with a yield of 71%.

We have previously shown that B-trialkylthio-N-trialkylborazoles are capable on reacting with tetraalkyldiborane, of replacing one alkylthio group by a hydrogen atom with the formation of B-dialkylthio-N-trialkylborazoles [8]. In the present work we have carried out some reactions of the B-di-n-butylthio-N-triethylborazole (III) obtained in this way with nucleophilic reagents (methylamine, aniline, sodium trimethylsilanolate). The yield of the corresponding B-disubstituted borazoles (IV) (R = CH_3, C_6H_5) and B-di(trimethylsiloxy)-N-triethylborazole (V) were 50-62% of theoretical (see scheme on following page). The reaction of B-di-n-butylthio-N-trimethylborazole (VI) with dimethylamine gave B-bis(dimethylamino)-N-trimethylborazole (VII) with a yield of 60.5%.

The IR spectra of (IV) (R = CH_3) and (VII) have absorption bands in the regions of the stretching vibrations of the B—H bond at 2465 and 2560 cm^{-1}: (IV) (R = C_6H_5) — 2480, 2540 cm^{-1}; (V) — ν_{BH} — 2475, 2560 cm^{-1}, $\nu_{B-O(Si)}$ — 1385 cm^{-1}.

The NMR spectra of compounds (VI) and (VII) were recorded using B-proton double resonance and the chemical shifts of the proton attached to the boron atom were determined (δ = 4.40 p.p.m.). Hexamethyldisiloxane was used as internal standard.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskiya, No. 2, pp. 407-409, February, 1968. Original article submitted July 12, 1967.



EXPERIMENTAL

All the operations were carried out in an atmosphere of nitrogen. The B-triethylthio-N-trialkylborazoles (I) were obtained by the reaction of B-trichloro-N-trialkylborazoles with lead ethyl mercaptide in benzene, as described previously [6].

B-Triethylthio-N-trimethylborazole (I) (R = CH_3). With stirring, 157.0 g of lead ethyl mercaptide was added to a solution of 71.6 g of B-trichloro-N-trimethylborazole in 650 ml of absolute benzene, and the mixture was boiled for 2 h. The precipitate of lead chloride that deposited was filtered off and washed with benzene. After the benzene had been distilled off, distillation of the residue in vacuum gave 67.3 g (~70%) of (I) (R = CH_3) with bp 145-150°C (0.1 mm); d_4^{20} 1.1187; n_D^{20} 1.5348. Found %: C 35.77; H 7.61; B 10.65. $C_9H_{24}B_3N_3S_3$. Calculated %: C 35.68; H 7.98; B 10.72.

B-Triethylthio-N-triethylborazole (I) (R = C_2H_5). Similarly, 40.0 g of B-trichloro-N-triethylborazole and 73.0 g of lead ethyl mercaptide gave 31.7 g (61.7%) of B-triethylthio-N-triethylborazole with bp 108-110°C (0.07 mm); d_4^{20} 1.0700; n_D^{20} 1.5205. Found %: C 41.54; H 8.38; B 9.65. $C_{12}H_{30}B_3N_3S_3$. Calculated %: C 41.80; H 8.74; B 9.44.

B-Tri-n-amylthio-N-trimethylborazole (II) (R = CH_3, R' = n-C_5H_{11}). A mixture of 15.1 g of B-triethylthio-N-trimethylborazole (I) (R = CH_3) and 19.5 g (25% excess) of n-amyl mercaptan was heated with a Hempel column from 120 to 200°C over 4 h, the ethyl mercaptan liberated being distilled off. The amount collected was 8 ml (73% of theoretical). Then the excess of n-amyl mercaptan was distilled off and the residue was fractionated in vacuum. This gave 14.1 g (66%) of B-tri-n-amylthio-N-trimethylborazole with bp 165-170°C (0.03 mm); d_4^{20} 1.0197; n_D^{20} 1.5310. Found %: C 50.38; H 9.78; B 7.55. $C_{18}H_{42}B_3N_3S_3$. Calculated %: C 50.37; H 9.86; B 7.58.

B-Tri-n-hexylthio-N-trimethylborazole (II) (R = CH_3, R' = n-C_6H_{13}). Similarly, by heating a mixture of 16.2 g of B-triethylthio-N-trimethylborazole and 30.0 g (25% excess) of n-hexyl mercaptan at 120-200°C for 3 h, with subsequent fractionation of the reaction mixture, we obtained 13.5 g (54%) of B-tri-n-hexylthio-N-trimethylborazole with bp 195-200°C (0.05 mm); d_4^{20} 1.0304; n_D^{20} 1.5220. Found %: C 53.05; H 10.10; B 7.20. $C_{21}H_{48}B_3N_3S_3$. Calculated %: C 53.48; H 10.26; B 6.88.

B-Tri-n-butylthio-N-triethylborazole (II) (R = C_2H_5, R' = n-C_4H_8). This was obtained under similar conditions from B-triethylthio-N-triethylborazole with a yield of 71%, bp 130-135°C (0.1 mm); n_D^{20} 1.5225. Literature data [6]: bp 130-135°C (0.1 mm); n_D^{20} 1.5228.

B-Tri(methylamino)-N-triethylborazole (IV) (R = CH_3). Through a bubbler, 2.0 g (40% excess) of methylamine was passed into a solution of 7.6 g of B-di-n-butylthio-N-triethylborazole in 25 ml of benzene. The solvent and the n-butyl mercaptan liberated in the reaction were distilled off. The residue (4.7 g) was distilled in vacuum to give 3.0 g (60.5%) of B-di(methylamino)-N-triethylborazole with bp 140-142°C (15 mm); d_4^{20} 0.9470; n_D^{20} 1.4870. Found %: C 43.96; H 10.80; B 14.26. $C_8H_{24}B_2N_5$. Calculated %: C 43.14; H 10.85; B 14.55.

The IR spectrum had absorption bands at 2465 and 2560 cm^{-1} (stretching vibrations of the B—H bond).

B-Tris(trimethylsiloxy)-N-triethylborazole (V). With stirring, 5.3 g (10% excess) of sodium trimethylsilanolate in 30 ml of ether was added to a solution of 7.25 g of B-di-n-butylthio-N-triethylborazole in 20 ml of ether. The precipitate of sodium mercaptide that deposited was filtered off, and the solvent was driven off. Distillation of the residue (6.7 g) in vacuum gave 4.5 g (62%) of B-di(trimethylsiloxy)-N-triethylborazole with bp 73-75°C (0.07 mm); d_4^{20} 0.9524; n_D^{20} 1.4438. Found %: C 43.15; H 10.16; B 9.58; Si 16.34. $C_{12}H_{34}B_3N_3O_2Si_2$. Calculated %: C 42.30; H 10.05; B 9.52; Si 16.42.

The IR spectrum had absorption bands at 2475 and 2560 cm^{-1} (stretching vibrations of the B—H bond) and 1385 cm^{-1}, $\nu_{B-O(Si)}$.

B-Di(phenylamino)-N-triethylborazole (IV) (R = C_6H_5). With stirring, 10.0 g of freshly-distilled aniline was added to a solution of 17.8 g of B-di-n-butylthio-N-triethylborazole (III) in 70 ml of ether. The temperature of the reaction mixture rose slightly. After 1 h's stirring, the solvent and the n-butyl mercaptan liberated in the reaction were distilled off. The fractionation of 18.6 g of the residue in vacuum with subsequent recrystallization from hexane gave: 1) 8.8 g (50%) of B-di(phenylamino)-N-triethylborazole with bp 150-160°C (0.1 mm); mp 106-107°C. Found %: C 62.08; H 8.16; B 9.40. $C_{18}H_{28}B_3N_5$. Calculated %: C 62.30; H 8.13; B 9.33. 2) 3.5 g of a substance with bp 135-140°C (0.05 mm); n_D^{20} 1.5440, consisting of a mixture of B-di(phenylamino)-N-triethylborazole and the starting material.

The IR spectrum had absorption bands at 2480 and 2540 cm^{-1} (stretching vibrations of the B—H bond).

B-bis(Dimethylamino)-N-trimethylborazole (VII). From 8.3 g of B-di-n-butylthio-N-trimethylborazole (VI) and 3.0 g of dimethylamine in 30 ml of benzene was obtained 3.5 g (60.5%) of B-bis(dimethylamino)-N-trimethylborazole with bp 65-68°C (0.08 mm); n_D^{20} 1.4872. Found %: B 15.30, 15.20. $C_7H_{22}B_3N_5$. Calculated %: B 15.33.

CONCLUSIONS

1. B-Tri-n-amylthio- and B-tri-n-hexylthio-N-trimethylborazoles have been synthesized by the transmercaptanation of B-triethylmercapto derivatives of borazole with higher thiols.

2. The reaction of B-di-n-butylthio-N-trialkylborazoles with nucleophilic reagents (methylamine, dimethylamine, aniline, sodium trimethylsilanolate) has given the corresponding B-disubstituted N-trialkylborazoles with one B—H bond.

LITERATURE CITED

1. W. Gerrard, H. R. Hudson, and E. F. Mooney, J. Chem. Soc., 1962, 113.
2. K. A. Muszdat, L. Hill, and B. Kirson, Israel J. Chem., 1, 27 (1963).
3. K. Niedenzu, H. Beyer, and H. Jenne, Ber., 96, No. 10, 2649 (1963).
4. K. Niedenzu, Inorg. Chem., 1, 943 (1962).
5. H. C. Newson, W. G. Woods, and A. L. McCloskay, Inorg. Chem., 2, 36 (1963).
6. B. M. Mikhailov and A. F. Galkin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1961, 371.
7. B. M. Mikhailov and Yu. N. Bubnov, Izv. Obshch. Khim., 31, 160 (1961).
8. B. M. Mikhailov and A. F. Galkin, Dokl. Akad. Nauk SSSR, 176, 1078 (1967).