ACTION OF HYDRAZINE AND PHENYLHYDRAZINE ON DIALKYLTHIOBORINIC ESTERS

B. M. Mikhailov and Yu. N. Bubnov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 2, pp. 368-370, February, 1960
Original article submitted July 7, 1959

We have recently found that butyl dibutylthioborinate reacts with hydrazine and with phenylhydrazine with formation respectively of 1,2-bisdibutylborinohydrazine and 1-dibutylborino-2-phenylhydrazine [1]. In the present paper, we report the results of a further study of the reactions of dialkylthioborinic esters with hydrazine and phenylhydrazine.

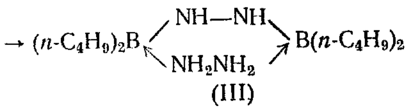
When a mixture of two equivalents of butyl dipropylthioborinate and one equivalent of hydrazine is heated to 50-110°, 1,2-bisdipropylborinohydrazine (II) is obtained in 89% yield. The reaction clearly passes through the stage of (dipropylborino)hydrazine (I), which is more active towards the dialkylthioborinic ester than hydrazine.

$$2\,(n\text{-}C_3H_7)_2BSC_4H_9\text{-}n + NH_2NH_2 \rightarrow \underset{(I)}{[(n\text{-}C_3H_7)_2BNHNH_2]} \rightarrow$$

$$\xrightarrow{(n\text{-}C_3H_7)_2BSC_4H_9\text{-}n} \underset{(II)}{(n\text{-}C_3H_7)_2BNH{-}NHB(n\text{-}C_3H_7)_2}$$

Compounds of type (I) are not obtained by reaction of a 1,2-bisdialkylborinohydrazine with excess of hydrazine. Thus, mixture of the previously obtained 1,2-bisdibutylborinohydrazine [1] with hydrazine gives a crystalline complex (III) which decomposes to its components when warmed:

$$(n\text{-}C_4H_9)_2BNH{-}NHB(n\text{-}C_4H_9)_2 + NH_2NH_2 \rightarrow$$



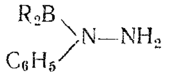
(III)

We did not succeed in effecting further replacement of hydrogen atoms by dialkylborino groups in the compound (II): When (II) was heated with a dialkylthioborinic ester, it was unaffected.

At 100° dialkylthioborinic esters react with phenylhydrazine with formation of 1-dialkylborino-2-phenylhydrazines (IV):

$$R_2BSC_4H_9\text{-}n + NH_2{-}NHC_6H_5 \rightarrow \underset{(IV)}{R_2BNH{-}NHC_6H_5} + n\text{-}C_4H_9SH$$

$$R = n\text{-}C_3H_7;\quad i\text{-}C_3H_7.$$

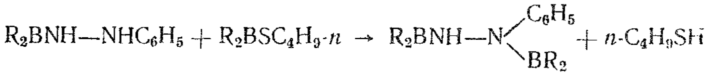


$$R_2B(C_6H_5)N{-}NH_2$$

(V)

The compounds obtained are assigned the structure (IV) rather than (V) on the basis of their reaction with the thio ester which requires a higher temperature than hydrazine, phenylhydrazine, or a (dialkylborino)hydrazine (I), which contain unsubstituted amino groups.

As the experiments showed, a 1-dialkylborino-2-phenylhydrazine (IV) will react with a dialkylthioborinic ester only at 150-200° with formation of a 1,2-bisdialkylborino-1-phenylhydrazine (VI). The resulting compounds are assigned the structure (VI) on the basis of the observation referred to previously, according to which hydrogen atoms attached to nitrogen which is also attached to a dialkylborino group are not further substituted under the action of dialkylthioborinic esters.



$$R_2BNH{-}NHC_6H_5 + R_2BSC_4H_9\text{-}n \rightarrow R_2BNH{-}N(C_6H_5)(BR_2) + n\text{-}C_4H_9SH$$

(VI)

$R = n\text{-}C_3H_7;\quad n\text{-}C_4H_9$

When solutions of 1-dialkylborino-2-phenylhydrazines in carbon tetrachloride or methyl iodide are allowed to stand, they acquire an intense blue or green color, respectively, and give precipitates.

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen.

Butyl Diisopropylthioborinate [2]. 1-Butanethiol (14 ml, 0.134 mole) was added to triisopropylborine (18.5 g, 0.132 mole), and a considerable rise in temperature occurred. The reaction mixture was heated at 150° for 15 minutes. Gas amounting to 3100 ml was liberated, and this contained 132 millimoles of propane, 0.38 millimoles of propene, and 0.38 millimoles of hydrogen. Distillation gave 17.5 g (76.9%) of butyl disisopropylthioborinate: b.p. 83-84° (8 mm); n_D^{20} 1.4582; d_4^{20} 0.8253. Found: C 64.22; 64.59; H 12.58; 12.55; B 5.91; 5.96%. $C_{10}H_{23}BS$. Calculated: C 64.51; H 12.45; B 5.81%.

1,2-Bisdipropylborinohydrazine (II, R = n-C_3H_7). A mixture of 12.6 g (0.068 mole) of butyl dipropylthioborinate [2] and 1.1 ml (0.034 mole) of hydrazine was heated in a vacuum (34 mm) for 15 minutes with simultaneous distillation of the thiol (the bath temperature was raised gradually from 50° to 100°). We obtained 6 g (89%) of 1-butanethiol and 6.05 g (79.1%) of 1,2-bisdipropylborinohydrazine; b.p. 121-122° (9 mm); n_D^{20} 1.4421; d_4^{20} 0.7966. Found: C 64.56; H 13.32; 13.28; B 9.37; 9.42%. $C_{12}H_{30}B_2N_2$. Calculated: C 64.33; H 13.50; B 9.66%.

1-Diisopropylborino-2-phenylhydrazine (IV, R = i-C_3H_7). A mixture of 13.9 g (0.075 mole) of butyl diisopropylthioborinate and 7.4 ml (0.07 mole) of phenylhydrazine was heated for 25 minutes in a vacuum (150 mm) at 100-105°. We obtained 6.72 g (90%) of 1-butanethiol and 13.4 g (87.6%) of 1-diisopropylborino-2-phenylhydrazine; b.p. 89-90° (0.035 mm); n_D^{20} 1.5151; d_4^{20} 0.9181. Found: C 70.93; 70.92; H 10.45; 10.53; B 5.15; 5.17%. $C_{12}H_{21}BH_2$. Calculated: C 70.60; H 10.37; B 5.30%.

1-Dipropylborino-2-phenylhydrazine (IV, R = n-C_3H_7). From 13.9 g (0.074 mole) of butyl dipropylthioborinate and 7.4 ml (0.07 mole) of phenylhydrazine, we similarly obtained 6.98 g (93.4%) of 1-butanethiol and 13.8 g (90.8%) of 1-dipropylborino-2-phenylhydrazine; b.p. 94-95° (0.03 mm); n_D^{20} 1.5165; d_4^{20} 0.9196. Found: C 70.98; 70.90; H 10.69; 10.70; B 5.54%. $C_{12}H_{21}BN_2$. Calculated: C 70.61; H 10.37; B 5.30%.

1,2-Bisdipropylborino-1-phenylhydrazine (VI, R = n-C_3H_7). A mixture of 7.15 g (0.036 mole) of 1-dipropylborino-2-phenylhydrazine and 9.9 ml (0.042 mole) of butyl dipropylthioborinate was heated for one hour in a vacuum (160 mm) at 180-190° (bath temperature); 2.65 g of 1-butanethiol was liberated. Vacuum fractionation gave 7.12 g (68.5%) of 1,2-bisdipropylborino-1-phenylhydrazine, b.p. 115-116° (0.08 mm). After refractionation the substance had: b.p. 105-106° (0.04 mm); $n_D^{21.5}$ 1.4901; $d_4^{21.5}$ 0.872. Found: C 71.79; 71.93; H 11.61; 11.57; B 6.99; 7.55%. $C_{18}H_{34}B_2N_2$. Calculated: C 72.03; H 11.42; B 7.21%.

1,2-Bisdibutylborino-1-phenylhydrazine (VI, R = n-C_4H_9). A mixture of 10.8 g (0.047 mole) of 1-dibutylborino-2-phenylhydrazine [1] and 12.1 g (0.057 mole) of butyl dibutylthioborinate was heated for 30 minutes in a vacuum (25 mm) at a bath temperature of 100-200° with simultaneous distillation of the thiol formed. We obtained 4.31 g of 1-butanethiol and 13.04 g (78.9%) of 1,2-bisdibutylborino-1-phenylhydrazine; b.p. 132-133.5° (0.03 mm); n_D^{20} 1.4883; d_4^{20} 0.8678. Found: C 73.86; 74.19; H 11.95; 11.78; B 6.15; 6.08%. $C_{22}H_{42}B_2N_2$. Calculated: C 74.17; H 11.88; B 6.07%.

All organoboron derivatives of hydrazine are colorless liquids, soluble in organic solvents and readily hydrolyzed and oxidized.

Hydrazine Complex of 1,2-Bisdibutylborinohydrazine (III, R = n-C_4H_9). A mixture of 2.37 g of 1,2-bisdibutylborinohydrazine and 0.28 g of hydrazine was found to crystallize out completely in the course of one week. The product was washed with isopentane and vacuum-dried. We obtained 2.42 g (88%) of the hydrazine complex of 1,2-bisdibutylborinohydrazine in the form of colorless crystals, m.p. 39-40.5°. Found: C 61.18; 60.78; H 13.71; 13.91; B 7.23; 6.49%. $C_{16}H_{42}B_2N_4$. Calculated: C 61.55; H 13.56; B 6.93%. The substance is readily oxidized by atmospheric oxygen.

SUMMARY

1. Dialkylthioborinic esters react with hydrazine and with phenylhydrazine with formation, respectively, of 1,2-bisdialkylborinohydrazines and 1-dialkylborino-2-phenylhydrazines.

2. When heated with dialkylthioborinic esters, 1-dialkylborino-2-phenylhydrazines react with formation of 1,2-bisdialkylborino-1-phenylhydrazines.

3. With hydrazine, 1,2-bisdialkylborinohydrazines form crystalline complexes which decompose when heated.

LITERATURE CITED

1. B. M. Mikhailov and Yu. N. Bubnov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 172 (1959).*
2. B. M. Mikhailov, V. A. Vaver, and Yu. N. Bubnov, Doklady Akad. Nauk SSSR 126, 579 (1959).*

---

* Original Russian pagination. See C. B. translation.