Soviet-era science, translated into English

CHEMISTRY

Ya. M. Paushkin, I. S. Panidi, L. A. Platonova

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.00941

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

SovietRxiv

Abstract

Full Text

CHEMISTRY

Ya. M. Paushkin, I. S. Panidi, L. A. Platonova

SYNTHESIS OF SEMISYMMETRIC TRIS-AMIDES OF BORIC ACID

(Presented by Academician A. N. Nesmeyanov, 15 VI 1964)

By semisymmetric tris-amides of boric acid we mean compounds of the type $\begin{matrix} R_2N \\ R_2N \end{matrix} > B - NR'_2$, in which one amine residue differs from the other two.

Accordingly, tris-amides in which all amine residues differ from one another may be called unsymmetric tris-amides of boric acid.

Semisymmetric tris-amides of boric acid are fairly stable compounds (^{1}); however, attempts to prepare the lower analog—dimethylamino-bis(ethylamino)boron—by the transamination reaction

$$[(CH_3)_2N]_3B + 2C_2H_5NH_2 \rightarrow (CH_3)_2NB(NHC_2H_5)_2 + 2(CH_3)_2NH$$

and by ammonolysis of $[(CH_3)_2N]BCl_2$ were not successful, although the IR spectra of the undistilled product indicate the presence of the desired compound in a mixture with disproportionation products (^{2}).

The first method likewise gave no results in the case of tert-butylamine, in the authors' opinion (^{3}), because of steric hindrance to transamination.

It is evident that, in the transamination of the lower homolog of boric acid tris-amides, $B[N(CH_3)_2]_3$, in addition to other considerations, its high reactivity must also be taken into account. The transamination reaction with this compound can be carried out quite smoothly with such amines in which the reactivity of the amino group is lowered in comparison with lower aliphatic amines.

Thus, from the products of the interaction of aniline and *m*-toluidine with tris(dimethylamino)boron, the corresponding aryl-aminobis(dialkylamino)borons can be isolated:

$$C_6H_5{-}NHB[N(CH_3)_2]_2$$

$$m\text{-}CH_3C_6H_4{-}NHB[N(CH_3)_2]_2$$

SovietRxiv

Di-*n*-butylamine reacts similarly. At the same time, from *o*-toluidine, products of deep substitution, evidently borazoles, can be obtained; and in the transamination of tris(diethylamino)boron, the product of double substitution is readily isolated.

Tris(diethylamino)boron is a less reactive compound than tris(dimethylamino)boron. Evidently, therefore, it reacts fairly calmly not only with aromatic but also with aliphatic amines, with formation of the corresponding semisymmetric tris-amides of boric acid.

The reaction can be carried out either by boiling equimolecular quantities of the starting reagents with a reflux condenser, or under conditions in which the amine evolved is removed from the reaction sphere:

$$B(NR_2)_3 + H_2NR' \rightarrow R'NHB(NR_2)_2 + R_2NH.$$

By this reaction we obtained semisymmetrical tris-amides of boric acid, the physicochemical properties of which are given in Table 1. The aliphatic tris-amides described are colorless, and the aromatic derivatives are faintly colored liquids with a characteristic musty odor; they are decomposed by water to boric acid and the corresponding amines, and undergo alcoholysis with alcohols. The molecular refraction for the synthesized compounds was calculated from the data of Mikhailov and co-workers (4), who calculated the refraction of the B–N bond in boron-nitrogen compounds.

Table 1

Physicochemical properties of semisymmetrical tris-amides of boric acid

No.	Compound	B.p., °C/mm Hg	n_D^{20}	ρ_4^{20}	Molecular refraction, found	Molecular refraction, calculated	Boron content, %, found	Boron content, %, calculated	Yield, % of theory
I	n-$C_3H_7NHB[N(C_2H_5)_2]_2$	74/2	1,4434	0,8273	68,44	68,578	5,0	5,07	70
II	iso-$C_4H_9NHB[N(C_2H_5)_2]_2$	99/4	1,4419	0,8202	73,400	73,226	4,91	4,76	50
III	iso-$C_3H_7NHB[N(C_2H_5)_2]_2$	95/12	1,4441	0,8226	68,855	68,578	4,92	5,07	20
IV	$(n$-$C_4H_9)_2NB[N(C_2H_5)_2]_2$	130–135/6	1,4518	0,8303	91,95	92,008	3,88	3,68	52
V	$C_6H_5NHB[N(C_2H_5)_2]_2$	128–132/3	1,5176	0,9272	80,738	80,422	–	–	13

SovietRxiv

No.	Compound	B.p., °C/mm Hg	n_D^{20}	ρ_4^{20}	Molecular refraction, found	Molecular refraction, calculated	Boron content, %, found	Boron content, %, calculated	Yield, % of theory
VI	*m*-$CH_3C_6H_4NHB[N(C_2H_5)_2]_2$	125–126/2	1,5158	0,9243	85,345	85,070	–	–	19
VII	(*n*-$C_4H_9)_2NB[N(CH_3)_2]_2$	98–100/2	1,4515	0,8403	72,99	73,416	4,51	4,76	24
VIII	$C_6H_5NHB[N(CH_3)_2]_2$	98/2	1,5409*	0,9681	62,02	61,830	–	–	32
IX	*m*-$CH_3C_6H_4NHB[N(CH_3)_2]_2$	106–106,5/2	1,5358	0,9677	66,075	66,478	–	–	28

* Literature data: $n_D^{24,5} = 1,5353$ (6).

The boron contents found, given in Table 1, were determined by the method of neutron absorptiometry developed by us jointly with the A. A. Skochinskii Institute of Mining for boron–nitrogen compounds (5). The data of the elemental analysis* of the compounds obtained are given in Table 2.

Table 2

Results of elemental analysis of semisymmetrical tris-amides of boric acid

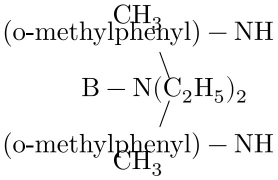
No.	Empirical formula	Found, % C	Found, % H	Found, % N	Found, % B	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % B
I	$C_{11}H_{28}N_3B$	62,77	13,31	19,01	4,75	62,44	13,23	19,26	5,07
I	$C_{11}H_{28}N_3B$	62,30	13,30	19,20	4,62	62,44	13,23	19,26	5,07
II	$C_{12}H_{30}N_3B$	62,34	13,42	18,13	4,81	63,43	13,30	18,49	4,76
II	$C_{12}H_{30}N_3B$	63,03	13,47	18,40	4,70	63,43	13,30	18,49	4,76
III	$C_{11}H_{28}N_3B$	62,25	13,34	19,10	5,06	62,44	13,23	19,26	5,07
III	$C_{11}H_{28}N_3B$	62,42	13,40	19,32	4,79	62,44	13,23	19,26	5,07
IV	–	–	–	–	–	–	–	–	–
V	$C_{14}H_{26}N_3B$	67,30	10,93	16,95	4,19	68,02	10,60	17,00	4,38
V	$C_{14}H_{26}N_3B$	67,49	10,81	16,80	4,17	68,02	10,60	17,00	4,38
VI	$C_{15}H_{26}N_3B$	69,28	11,20	16,13	3,83	68,96	10,80	16,09	4,14
VI	$C_{15}H_{26}N_3B$	68,50	10,90	16,30	4,41	68,96	10,80	16,09	4,14
VII	–	–	–	–	–	–	–	–	–
VIII	$C_{10}H_{18}N_3B$	62,04	9,70	21,71	5,64	62,85	9,49	21,99	5,66
VIII	$C_{10}H_{18}N_3B$	62,42	9,68	21,90	5,72	62,85	9,49	21,99	5,66
IX	$C_{11}H_{20}N_3B$	64,13	10,03	20,11	5,19	64,41	9,83	20,49	5,27
IX	$C_{11}H_{20}N_3B$	64,27	10,06	20,32	4,87	64,41	9,83	20,49	5,27

The comparatively low yields of semisymmetrical tris-amides of boric acid are explained by the formation of products of double substitution, as well as of polymers in the form of the residue after vacuum distillation.

In one of the experiments, when boiling *o*-toluidine with tris-(diethylamino)boron, the reaction mass, left overnight, crystallized.

* A. I. Korosteleva took part in the work.

After two recrystallizations from cyclohexane, the crystals had an elemental composition corresponding to diethylamino-bis-(*o*-methylphenylamino)boron:



$$\begin{array}{l} \overset{CH_3}{(\text{o-methylphenyl})} - NH \\ \qquad\qquad \diagdown \\ \qquad\qquad\quad B - N(C_2H_5)_2 \\ \qquad\qquad \diagup \\ \underset{CH_3}{(\text{o-methylphenyl})} - NH \end{array}$$

Experimental Part

1. *n*-Propylamino-bis-(diethylamino)boron. *n*-Propylamine (5.2 g) and tris-(diethylamino)boron (20 g) were refluxed for 9 h under a weak stream of argon. After removal of the low-boiling products, the reaction mass was distilled under vacuum. This gave 13.1 g (70% yield) of a product boiling at 73-76°/2 mm; repeated distillation of it afforded analytically pure *n*-propylamino-bis-(diethylamino)boron, b.p. 74°/2 mm Hg, n_D^{20} 1.4432; ρ_4^{20} 0.8273.

Found, %: C 62.77, 62.80; H 13.31, 13.30; N 19.01, 19.20;
B 4.75, 4.62

$C_{11}H_{28}N_3B$. Calculated, %: C 62.44; H 13.23; N 19.26;
B 5.07

2. Phenylamino-bis-(diethylamino)boron. Aniline (8.2 g) and tris-(diethylamino)boron (20 g) were refluxed for 30 min, after which the reflux condenser was replaced by a descending condenser and diethylamine was distilled off (5.1 g; n_D^{20} 1.3860). Twofold distillation in vacuo gave a fraction boiling at 128-132°/3 mm Hg; n_D^{20} 1.5176; ρ_4^{20} 70.922.

Found, %: C 67.30, 67.49; H 10.93, 10.81; N 16.95, 16.80;
B 4.19, 4.17

$C_{14}H_{26}N_3B$. Calculated, %: C 68.02; H 10.60; N 17.00;
B 4.38

3. Diethylamino-bis-(*o*-methylphenylamino)boron. *o*-Toluidine (9.4 g) and tris-(diethylamino)boron (20 g) were refluxed for two hours, after which diethylamine was distilled off. The mixture left overnight crystallized. Analytically pure crystals were isolated by two recrystallizations from cyclohexane.

Found, %: C 75.70, 75.81; H 7.78, 7.93; N 12.11, 12.38;
B 3.65, 3.60

$C_8H_{26}N_3B$. Calculated, %: C 76.13; H 7.91; N 12.69;
B 3.27

All the remaining semisymmetric tris-amides of boric acid were obtained by the above-described procedures 1 and 2.

Institute of the Petrochemical and Gas Industry
named after I. M. Gubkin

Received
1 VI 1964

References Cited

1. D. W. Aubrey, W. Gerrard, E. F. Mooney, *J. Chem. Soc.*, **1962**, 1786.
2. D. W. Aubrey, M. F. Lappert, H. Pyszora, *J. Chem. Soc.*, **1960**, 5239.
3. D. W. Aubrey, M. F. Lappert, *Proc. Chem. Soc.*, **1960**, 148.
4. B. M. Mikhailov, T. A. Shchegoleva, Yu. N. Bubnov, *Izv. AN SSSR, OKhN*, **1962**, No. 3, 413.
5. N. G. Malysheva, L. P. Starchik et al., *ZhAKh*, **18**, No. 11, 1367 (1963).
6. R. J. Brotherton, T. Buckmann, *Inorg. Chem.*, **2**, No. 2, 424 (1963).

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

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