Transamination of Boron–Nitrogen Compounds[1,2]

By W. D. English, A. L. McCloskey and H. Steinberg

Tris-(alkylamino)-boranes, bis-(alkylamino)-arylboranes and borazoles undergo a general transamination reaction with primary or secondary mono- and polyamines: $>BN + >N'H \rightarrow >BN' + >NH$. The reaction provides a convenient synthesis of aminoboranes.

The reaction of n-butoxybis-(diethylamino)-borane with di-n-butylamine has been briefly mentioned in the literature[3]; however, transamination in general has been overlooked as a preparative method. Analogous reactions such as trans-esterification,[4] transacylation[5] and transalkylation[6] are common in boron chemistry, and transamination has been used with other elements such as silicon[7] and sodium.[8]

Previously recorded methods for synthesizing aminoboranes, the reaction of amines with boron hydrides,[9] boron–oxygen compounds[10] and boron halides[11] have certain inherent drawbacks. Boron hydrides require special apparatus and precautions; the displacement of alkoxide residues from boron with amines is not general but takes place only in special cases and the formation of hydrogen halides in the reaction of boron halides with amines often interferes with progress of the reaction or purification of the products.[12]

It has been found that amines effect a facile displacement of organic substituted nitrogen atoms bonded to boron to form new aminoboranes. The transamination reaction is general and can be used to prepare both monomeric and polymeric species. Results of the transamination reaction of various boron compounds are collected in Table I. Several new alkylaminoboranes were obtained by this synthetic route and their physical properties and analytical data are included in Table I.

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(2) A portion of this research was supported by Wright Air Development Center of the U. S. Air Force under Contract AF 33(616)5931, Project No. 8-(8-7340), Task No. 73404.

(3) W. Gerrard, M. F. Lappert and C. R. Pearce, J. Chem. Soc., 381 (1957); Chemistry & Industry, 292 (1958).

(4) P. D. George and J. R. Ladd, J. Am. Chem. Soc., 77, 1900 (1955).

(5) A. Pictet and A. Geleznoff, Ber., 36, 2219 (1903).

(6) H. C. Brown and B. C. Subba Rao, J. Org. Chem., 22, 1137 (1957).

(7) R. Larson and O. Mjorne, Svensk. Kem. Tidskr., 61, 59 (1949).

(8) M. Picon, Compt. rend., 175, 1213 (1922).

(9) A. B. Burg and C. L. Randolph, Jr., J. Am. Chem. Soc., 71, 3451 (1949).

(10) A. L. McCloskey, H. Goldsmith, R. J. Brotherton, H. Steinberg and G. W. Willcockson, Paper presented at 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959; Abstracts of Papers, p. 34-M.

(11) A. R. Johnson, J. Phys. Chem., 16, 1 (1912); H. A. Skinner and N. B. Smith, J. Chem. Soc., 2324 (1954); D. W. Aubrey and M. F. Lappert, ibid., 2927 (1959).

(12) The presence of a protonic acid catalyzes the decomposition of many aminoboranes when they are heated.[14] When hydrogen halides are generated in the formation of aminoboranes, it is usually difficult to remove them completely. Apparently either amine hydrohalides or aminoborane–hydrohalide complexes[14] are appreciably soluble in aminoboranes.

(13) W. D. English and A. L. McCloskey, unpublished results.

(14) E. Wiberg and K. Schuster, Z. anorg. Chem., 213, 77 (1933).
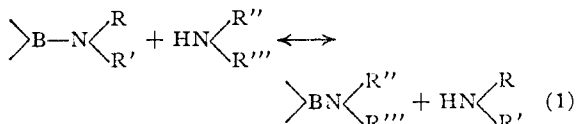
Experimental

Since most of the reactions were carried out in similar fashion, only one of the standard type is described in detail. Minor variations are indicated in Table I. The preparation of tris-(methylamino)-borane from tris-(sec-butylamino)-borane was sufficiently different so that it is described separately.

Synthesis of Tris-(sec-butylamino)-borane from sec-Butylamine and Tris-(isopropylamino)-borane.—A mixture of 50 g. (0.68 mole) of sec-butylamine and 42 g. (0.22 mole) of tris-(isopropylamino)-borane was placed in a 500-ml. round-bottomed flask. The flask was attached to a short fractionating column and the contents were heated to boiling. Isopropylamine, b.p. 32–33°, distilled at a 1:10 reflux ratio. The temperature of the reaction gradually increased from 65 to 205°, at which point heating was terminated. The isopropylamine which had distilled, $n^{24}D$ 1.3725, weighed 33 g., (82.5% yield). The residue in the reaction flask was distilled through a short Vigreux column at reduced pressure to yield 39.0 g. (75% yield) of colorless tris-(sec-butylamino)-borane, b.p. 134–136° (47 mm.), $n^{24}D$ 1.4324.

Preparation Tris-(methylamino)-borane from Methylamine and Tris-(sec-butylamino)-borane.—A 300-ml. three-necked flask containing 32 g. (0.14 mole) of tris-(sec-butylamino)-borane was connected to a steam-heated reflux condenser and heated on a steam-bath. When the temperature of the liquid in the flask reached 80°, excess methylamine was passed through the liquid for 2.5 hr. The excess methylamine was allowed to escape through a water-cooled still-head at the top of the reflux condenser. Distillate collected in the receiver attached to the still-head. Methylamine addition was terminated when distillate was no longer collected. The reaction mixture was distilled at reduced pressure to give 5.9 g. (40% yield) of tris-(methylamino)-borane, b.p. 70–80° (48 mm.), $n^{25}D$ 1.4432. There remained 9.6 g. of polymeric residue in the flask, presumably a polyborazole such as described by Lappert.[15]

Discussion of Results

The transamination reactions of aminoboranes collected in Table I can be summarized by the equation

$$>B-N\begin{matrix}R\\R'\end{matrix} + HN\begin{matrix}R''\\R'''\end{matrix} \longleftrightarrow$$

$$>BN\begin{matrix}R''\\R'''\end{matrix} + HN\begin{matrix}R\\R'\end{matrix} \quad (1)$$

The reaction is general and the products usually are formed in good yield. Among the types of amines which react are primary and secondary mono-, di- and triamines with normal, branched, aromatic and heterocyclic radicals on the nitrogen. The polyamines yield co-polymeric products with di- or trifunctional boron compounds, i.e.

$$RB(NHR')_2 + NH_2R''NH_2 \longrightarrow$$
$$\left(\begin{matrix}R\\|\\-B-NH-R''-NH-\end{matrix}\right)_n + 2R'NH_2 \quad (2)$$
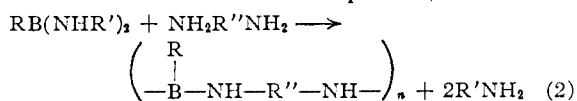
It was found that high boiling amines normally displaced lower boiling amines, but the technique could be varied so that the opposite reaction would

(15) M. F. Lappert, Proc. Chem. Soc., 59 (1959).

TABLE I

TRANSAMINATION OF BORON–NITROGEN COMPOUNDS

Boron compound	Wt., g.	Amine	Wt., g.	Reaction conditions	Name	B.p., °C.	Wt., g.	Yield, %	Name	B.p., °C. (mm.)	n^tD / t, °C.	Wt., g.	Yield, %	Lit. ref.	Boron, Calcd. Found	Nitrogen, % Calcd. Found
Tris-(isopropylamino)-borane	42	n-Butyl	50	14 hr. refl.	Isopropyl	32–33	33.9	84	Tris-(n-butylamino)-borane	105–106 (1)	1.4438 25	5.4	10	b	4.76 4.74	... ...
Tris-(isopropylamino)-borane	42	sec-Butyl	50	5 hr. refl.	Isopropyl	32–33 (n^{24}D 1.3725)	32	82	Tris-(sec-butylamino)-borane	134–136 (47)	1.4324 24	39.0	75	b	4.76 4.78	... ...
Tris-(isopropylamino)-borane	36	Piperidine	75	3 hr. refl.	Isopropyl	33–38	32.7	95	Tris-(piperidino)-borane	132–149 (1)	....	45.5	89	..	4.12 4.49	16.0 15.7
Tris-(isopropylamino)-borane	30	N-Methyl-aniline	60	24 hr. refl.	Not coll.	...	..	..	Tris-(N-methylanilino)-borane	M.p. 211–212	....	30	53	c	.. ..	... ...
Tris-(isopropylamino)-borane	34	Melamine	50	30 hr. refl.	Isopropyl	33	30	62	Sol. polymer, stable to low red heat	....	....	..	..	..	.. 6.68	... ...
Tris-(sec-butylamino)-borane	32	Methyl	Exc.	See text	sec-Butyl	...	..	..	Tris-(methylamino)-borane	70–80 (48)	1.4432 25	5.9	41	b	.. ..	... ...
Tris-(t-butylamino)-borane	40	Aniline	60	3 hr. refl.	t-Butyl	42–46 (n^{24}D 1.3750)	30	78	Tris-(anilino)-borane	M.p. 164–167	....	46.1	91	d	.. ..	... ...
Tris-(diethylamino)-borane	30	n-Hexyl	50	3 hr. refl.	Diethyl	55–56	27	94	Tris-(n-hexylamino)-borane	Dec. at >150 (0.1)	1.4549 25	31.3	74	..	3.86 3.48	13.51 13.37
Tris-(diethylamino)-borane	30	Diphenyl	100	26 hr. heat.	Diethyl	...	40 (ml.)	84	Tris-(diphenylamino)-borane^a	M.p. 247–248	....	47	69	..	2.12 e	8.15 9.26
Bis-(t-butylamino)-phenylborane	5.6	Hexamethyl-enediamine	2.8	50 ml. xylene 6 hr. refl.	t-Butyl	...	2.3	65	Waxy, thermoplastic resin	....	....	4.3	83	..	5.79 5.77	... ...
Hexamethylborazole	20	n-Butyl	30	28 hr. refl.	Not coll.	...	..	..	Bis-(n-butylamino)-methylborane	80–85 (1) 110–123 (30)	....	25.2	41	..	6.49 6.53	16.45 16.61
B-Tris-(isopropyl-amino)-N-triisopropyl-borazole	14	Piperidine	15 16 add. 31 tot.	24 hr. refl. 3 hr. refl.	None evolved Isopropyl	... 32–35	.. ..	.. 71	.... Tris-(piperdino)-borane	.... 133–147 (1)	....	.. 20.1	.. 69	.. ..	.. .. ..	... ...

a Calcd. for C₂₆H₃₀N₃B: C, 83.8; H, 5.83. Found: C, 83.91; H, 5.99.   b D. W. Aubrey and M. F. Lappert. *J. Chem. Soc.*, 2927 (1959).   c A. Dornow and H. H. Gehrt. *Angew. Chem.*, **68**, 619 (1956).   d R. C. Jones and C. R. Kinney, *J. Am. Chem. Soc.*, **61**, 1378 (1939).   e Found: B, 2.15, 2.13.

TABLE II

EFFECT OF STRUCTURE AND BASICITY[17] ON RATE OF TRANSAMINATION

Entering amine	K	Leaving amine	K	Conversion %	Time, hr.
N-Methylaniline	2.5×10^{-10}	Isopropylamine	5.3×10^{-4}	53	24
n-Butylamine	$\sim 10^{-4}$			84	14
sec-Butylamine	4.4×10^{-4}			82	5
Piperidine	1.6×10^{-3}			95	3
Diphenylamine	$\sim 10^{-10}$	Diethylamine	1.3×10^{-3}	84	26
n-Hexylamine	$\sim 10^{-4}$			94	3
Aniline	4.6×10^{-10}	t-Butylamine	3.4×10^{-4}	91	3
Hexamethylenediamine	$\sim 10^{-4}$			83	6

take place (see preparation of tris-(methylamino)-borane in Experimental section).

Table II compares the percentage conversion of some selected transamination reactions with the basicities of the entering and leaving amine. It is seen that when isopropylamine or diethylamine are the leaving groups, in general the reaction rates increase with increasing basicity of the entering amine which is consistent with a mechanism of simple nucleophilic displacement on boron of one amine by a second amine. However, it also is seen that in general the steric requirements of the entering amine are decreasing with increasing basicity which makes it impossible to separate the relative importance of the amine basicities and steric effects on the reaction rates.

Our findings disagree with those reported by Aubry and Lappert[16] in a paper which appeared since presentation[17] of this work at Cleveland. These workers stated that a primary amine will displace a secondary amine but that the reverse reaction will not occur. However, we observed that both piperidine and N-methylaniline displaced isopropylamine.

In general, secondary amines reacted more slowly than primary amines or piperidine, a secondary amine with the alkyl groups "tied back." The only amine which failed to react was diisopropylamine, which would displace neither isopropylamine nor diethylamine from boron. This might be due to prohibitive steric requirements of a tetrahedral transition state or of the final product. Examination of Fisher–Hirschfelder–Taylor models indicates that the sterically-hindered trigonal coplanar tris-(diisopropylamino)-borane, a compound unsuccessfully sought in this Laboratory, could not be assembled which indicates the impossibility of forming the quadricovalent tetrahedral intermediate or transition state.

Boron–nitrogen compounds which can be transaminated include tris-(alkylamino)-boranes, bis-

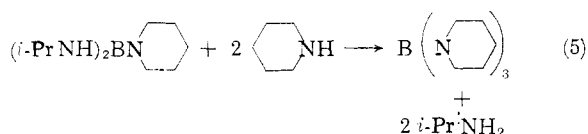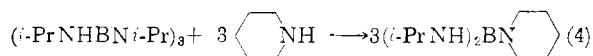(16) D. W. Aubry and M. F. Lappert, *Pro. Chem. Soc.*, 148 (1960).

(17) 1. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., revised edition, 1953.

(alkylamino)-arylboranes, B-trialkyl-N-trialkylborazoles and B-tris-(alkylamino)-N-trialkylborazoles. There have been previous observations[18] that amines and borazoles will react; however. the nature of the reaction and the identity of the products were not elucidated.

It was found in this work that hexaalkylborazoles undergo a reaction

$$3RB(NHR')_2 + 3RNH_2 \quad (3)$$
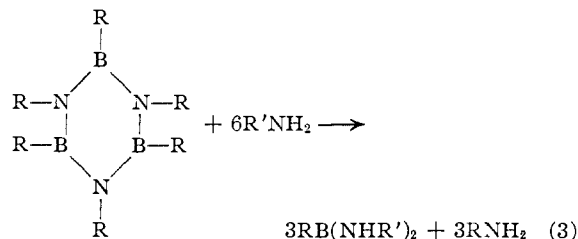
In the aminolysis of B-tris-(isopropylamino)-N-triisopropylborazole with piperidine there was some evidence that the ring B–N bonds were opened before reaction of the exocyclic B–N bonds,[19] since no trace of isopropylamine was evidenced until piperidine in excess of three moles per mole of borazole had been added. It is likely that an intermediate compound such as bis-(isopropyl-amino)-piperidinoborane was formed, although this was not isolated.

$$(i\text{-PrNHBN}i\text{-Pr})_3 + 3 \bigcirc\!\!\text{NH} \longrightarrow 3(i\text{-PrNH})_2\text{BN}\bigcirc \quad (4)$$

$$(i\text{-PrNH})_2\text{BN}\bigcirc + 2 \bigcirc\!\!\text{NH} \longrightarrow \text{B}\left(\text{N}\bigcirc\right)_3 \quad (5)$$
$$+$$
$$2\ i\text{-Pr NH}_2$$

Since the transamination of boron–nitrogen compounds takes place readily with a wide variety of reactants, it appears to be a reaction of significant preparative value.

(18) (a) A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926); (b) E. Wiberg and A. Bolz, *ibid.*, **73**, 209 (1940).

(19) The hydrolysis of B-aminoborazoles was reported [K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 3561 (1959)] to cause initial rupture of the exocyclic B–N bond.

Derivatives of Aromatic Sulfinic Acids. IV. The Absolute Configurations of Asymmetric Sulfur in Epimeric Sulfinic Esters[1]

BY HARRY F. HERBRANDSON AND CARMEN M. CUSANO

Equilibration of (−)-menthyl (+)-p-iodobenzenesulfinate and (−)-menthyl (−)-p-iodobenzenesulfinate in nitrobenzene at 25° gives a mixture which contains 59 ± 3% of the (+)-epimer. To ethoxide-ion catalyzed ethanolysis, the (+)-epimer is more reactive by a factor of about two. These facts have been interpreted in terms of a tentative assignment of absolute configurations to the asymmetric sulfurs and of conformations to the two esters.

Epimeric sulfinic esters which differ only in the configuration of the sulfur previously have not been obtained in a pure form, although Phillips[2] was able to obtain pure (−)-menthyl (−)-p-toluenesulfinate and its impure epimer (−)-

(1) This work was supported in part by the Office of Naval Research.
(2) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

menthyl (+)-and (±)-p-toluenesulfinate. p-Iodo-benzenesulfinic acid has been found to give (−)-menthyl esters of sufficiently high melting points that the two diastereoisomers can be separated by fractional crystallization. This has permitted a study of the differences in reactivity of the two epimers, and we wish to report on the determina-