J. inorg. nucl. Chem., 1974, Vol. 36, pp. 1465–1468. Pergamon Press. Printed in Great Britain.

IMPROVED PREPARATION OF TRIS(ORGANOAMINO)BORANES

WILLIAM R. PURDUM* and EDWIN M. KAISER†
Department of Chemistry, University of Missouri, Columbia, Columbia, Missouri 65201

(*Received* 2 *July* 1973)

Abstract—Tris(organoamino)boranes may be rapidly and conveniently prepared by the interaction of boron trifluoride diethyl etherate and N-lithiodialkyl-, diaryl-, and alkylarylamides in tetrahydrofuran. The procedure is more general and is less sensitive to steric effects than older ones and affords previously described as well as new tris(organoamino)boranes in high yields.

INTRODUCTION

TRIS(ORGANOAMINO)BORANES have previously been prepared by a variety of methods, only two of which appear to be somewhat general. The first, and the most general involves the aminolysis of various boron substrates by amines (Eqn 1). Most commonly, boron trichloride[1] has been interacted with primary and secondary aliphatic and aromatic amines though certain borate esters[2] and diboron trisulfide[3] have occasionally been employed as the boron substrate. The reaction was originally conducted in the gas phase [1b] but has been modified so that it may be effected in the liquid phase[1c] with or without an inert solvent. Although the procedure affords the lower molecular weight tris(organoamino)boranes in high yield, it possesses certain inherent drawbacks, viz. extended reaction periods required for the preparation of the higher molecular weight derivatives, possible steric requirements which inhibit the formation of certain bulky derivatives[1e, 1k, 4], and *in situ* decomposition of the desired products (when liquid) during their purification by distillation by the amine hydrochloride co-product[5].

$$6RR'NH + BX_3 \rightarrow (RR'N)_3B + 3RR'NH \cdot HX. \quad (1)$$

An extension of the above aminolysis procedure has been reported which involves the transamination of a previously prepared tris(organoamino)borane by either a primary or secondary amine (Eqn 2)[5, 6]. Of course, a disadvantage of this method is that a tris-compound, prepared by another route, must be on hand.

$$(RR'N)_3B + 3R''R'''NH \rightarrow (R''R'''N)_3B + 3RR'NH. \quad (2)$$

A second general method involves the treatment of boron trifluoride dimethyl- or diethyl etherate with three equivalents of an amine in an inert solvent such as benzene or tetrahydrofuran (THF) followed by the addition of three equivalents of methylmagnesium iodide or ethylmagnesium bromide[7, 8]. Like the one above, this method is usually not suitable for the preparation of tris(organoamino)boranes derived from sterically hindered or bulkier amines [1k, 7, 8].

Several other less general methods for the preparation of tris(organoamino)boranes also involve organometallic reagents. For example, interaction of N-potassio-N-methylaniline with boron trifluoride dimethyl etherate[8] and of N-lithiodiisopropylamine with bis(diisopropylamino) chloroborane[9, 10] give the expected tris-compounds, respectively. The latter reaction is poor unless rather vigorous conditions are employed[10]. Finally, treatment of ethylamine–boron trifluoride complex in excess ethylamine with three equivalents of lithium metal gives the expected tris-compound[11]. These three techniques have apparently not been extended to amines other than those listed.

The current paper describes a convenient, general method for the preparation of tris(organoamino)-boranes involving various N-lithioamines and boron trifluoride diethyl etherate.

DISCUSSION

The synthetic approach to the tris(organoamino)-boranes developed in this investigation involves the following general procedure (Scheme I): (1) the formation of the organoaminolithium reagent at 0° by the addition of the appropriate amount of *n*-butyllithium in hexane to the desired amine in THF; (2) the addition of boron trifluoride diethyl etherate at 0–25°; (3) refluxing the resulting mixture for three

*Shell Oil Company Fellow, 1972–1973.
†Author to whom correspondence should be directed.

Table 1. Comparison of general methods for effecting the preparation of tris(organoamino) boranes

Amines ($RR'NH$)		General methods* Yields (%)†					b.p. (mm) or (mp)
R	R'	A	B	C	D	E	(°C)
CH_3	CH_3	92	69	67	—	92‡	145–151 (760)
CH_3CH_2	CH_3CH_2	92	93	62	—	—	100 (15)
$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	94	92	—	—	—	85–88 (0·05)
$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	61	90	50	—	—	130–135 (0.10)
$(CH_3)_2CHCH_2CH_2$	$(CH_3)_2CHCH_2CH_2$	85	—	—	—	—	134–136 (0·025)
pyrrolidine		89	—	45	—	—	120–123 (1·0)
piperidine		89	94	—	89	—	168–178 (10·0) (68–70)
morpholine		66	—	—	—	—	(72–75)§, ‖
C_6H_5	CH_3	83	97	80	53	34¶	(211–213)‖, **
C_6H_5	CH_3CH_2	84	—	25	—	33¶	(164–165)§, ‖
C_6H_5	C_6H_5	83	††	††	69	—	(245–247‖, ‡‡
$C_6H_5CH_2$	C_6H_5	71	—	—	—	40¶	(199–201)§, ‖
$C_6H_5CH_2$	$C_6H_5CH_2$	75	76	—	—	—	(271–273)‖, §§
$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2$	41	—	—	—	—	(269–271)‖, ‖‖
1,2,3,4-tetrahydrocarbazole		70	—	94	—	—	(335–337)‖, §§
$(CH_3)_2CH$	$(CH_3)_2CH$	—	—	—	—	¶¶	—

*Method A: current method—three equivalents of organoaminolithium reagent and one equivalent of boron trifluoride diethyl etherate; the physical constants of the tris-compounds agreed with those previously published; the new compounds were identified by spectral methods; Method B: amination of boron trichloride using excess amine (reference [1]); Method C: amine plus boron trifluoride etherate plus added Grignard reagent (references [7] and [8]; Method D: transamination of a tris(organoamino)borane (references [5] and [6]; Method E: miscellaneous.

†The dashes indicate that the reaction was not attempted with a specific amine unless otherwise noted.

‡Amination of boron trifluoride diethyl etherate by dimethylaminotrimethylstannane (reference [12]).

§Recrystallized from cyclohexane.

‖In the purification of all solid derivatives by recrystallization, a hot vacuum filtration should be employed to remove the lithium fluoride co-product.

¶Reduction of the corresponding anilide ($RCONHC_6H_5$) with sodium borohydride (reference [13]).

**Recrystallized from toluene.

††Tris(diphenylamino)borane apparently cannot be prepared by this method.

‡‡Recrystallized from petroleum ether (bp 60–70°).

§§Recrystallized from benzene.

‖‖Recrystallized from 1,4-dioxane.

¶¶Has been prepared in unspecified yield via bis(diisopropylamino)chloroborane and excess lithium diisopropylamide in refluxing decalin for ten hours (reference [10]).

hours. Table 1 lists the amines utilized and the percent conversions to tris-compounds realized by this procedure. Also listed in Table 1 for comparison are the previously reported results obtained by utilizing those methods which have received the most discussion in the earlier literature.

Scheme I

$$RR'NH + n\text{-}C_4H_9Li \xrightarrow[0°]{\text{THF-hexane}} RR'NLi + n\text{-}C_4H_{10}$$

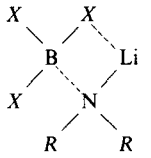
$$3RR'NLi + BF_3 \cdot O(C_2H_5)_2 \xrightarrow[3\ hr]{\text{THF-hexane}} (RR'N)_3B + (CH_3CH_2)_2O + LiF$$

As shown in Table 1, the linear secondary aliphatic amines (dimethyl-, diethyl, di-*n*-propyl-, and di-*n*-butylamine) were readily converted to the corresponding tris(organoamino)boranes in relatively high yields. In addition, the previously unreported tris(di-(3-methylbutyl)amino)borane was also realized in good yield. The cyclic secondary aliphatic amines (pyrrolidine, piperidine, and morpholine) also afforded the corresponding tris-compounds in reasonably high yields.

The steric requirements of the current method are presumably less than the aminolysis[1], Grignard[7, 8], and transamination[4, 5, 6] procedures since tris-(organoamino)boranes were also derived from certain rather bulky amines. Thus, diphenyl-, dibenzyl-, diphenethyl-, di(3-methylbutyl)-, and N-benzylphenylamines as well as 1,2,3,4-tetrahydrocarbazole and N-ethylaniline were all converted to their corresponding tris-compounds. On the other hand, the application of this technique to the synthesis of tris(diisopropylamino)borane afforded only bis(diisopropylamino)-fluoroborane even after refluxing for an extended period in heptane using excess N-lithiodiisopropylamine. This latter result suggests a possible steric limit for the present rather mild reaction conditions since tris(diisopropylamino)borane has been prepared under much more vigorous conditions[10].

Some justification for the choice of reagents and

conditions is in order. Thus, lithioorganoamino reagents rather than the corresponding sodio- or potassio compounds were employed because of the ease of their preparation due to the ready availability of *n*-butyllithium in hexane; also, the need to handle bulk metals was not necessary. Moreover, even though the more ionic organoaminosodium and potassium derivatives are generally considered to be more reactive than the corresponding more covalent lithium compounds, the ability of the lithium cation to better coordinate with the available electron density of a species might compensate for this reactivity imbalance if the current reactions proceed via a concerted four-centered transition state I. Incidentally, this latter pathway is commonly observed in reactions at a trigonally substituted boron atom[1e, 4]. Similarly, because of its ease of handling, boron trifluoride etherate was employed as the boron substrate rather than boron trichloride even though the latter compound as its tetrahydrofuranate afforded tris(N-methylanilino)borane in a yield comparable to that obtained with the former reagent.



I

With regard to experimental conditions, the application of heat was observed to be necessary for the reaction to occur since, in general, the percent conversions of desired products were less at room temperature than at reflux. It should be mentioned that the 3 hr time period is arbitrary and is probably longer than necessary to effect these transformations. Interestingly, it was not necessary to remove the lithium fluoride co-product before distillation of the liquid tris-compounds. This is in marked contrast to the above-mentioned difficulties experienced with by-product amine hydrohalides in the earlier amination procedure[5].

It is anticipated that the currently described preparation of tris(organoamino) boranes will encourage additional studies into their synthetic utility as aminating agents in organic chemistry[14].

EXPERIMENTAL

Boron trifluoride diethyl etherate was purchased from Eastman Organic Chemicals and distilled from calcium hydride. *n*-Butyllithium was purchased as a 15 per cent solution in hexane from Foote Mineral Co., Exton, Pa. and from Apache Chemical Co., Rockford, Ill. Aliphatic amines were distilled from barium oxide and liquid aromatic amines were distilled from zinc dust and barium oxide. Commercial anhydrous THF (Mallinckrodt Chemical Works) was distilled from solutions containing excess *n*-butyllithium and stored over type 5-A molecular sieves. Melting points were obtained on a Thomas–Hoover melting point apparatus and are uncorrected. I.R. spectra were recorded on a Perkin–Elmer 237B Spectrophotometer and only those vibrations are reported which were considered necessary for structural confirmations. PMR spectra were obtained at 60 mc on a Varian A-60 spectrometer using tetramethylsilane as external standard. Unless otherwise stated, the standard apparatus for the preparation of the tris-compounds consisted of a 500 ml., three-necked, round-bottomed flask equipped with a mechanical stirrer, Friedrichs condenser, helium inlet, and addition funnel.

General procedure for the preparation of tris(organoamino)-boranes; tris(diethylamino)borane

The following procedure for the preparation of tris-(diethylamino)borane may be considered general; details are listed in Table 1. A solution of 11·0 g (0·15 mole) of freshly distilled diethylamine in 125 ml of anhydrous THF at 0° was treated with 90 ml (0·15 mole) of 1·6 M *n*-butyllithium in hexane. After stirring at 0° for 30 min, the pale-yellow solution was treated with 7·1 g (0·05 mole) of boron trifluoride diethyl etherate and then refluxed for 3 hr. After removal of the solvent by distillation, the resulting gel-like solution was transferred to a smaller apparatus and distilled under reduced pressure to yield 10·4 g (92 per cent) of the desired product: b.p. 100° (15 mm) ([8] b.p. 95° (11 mm)); i.r. NH absent, 1414 cm^{-1} (^{11}BN), 1267 cm^{-1} (possibly CN) ([15] 1414 cm^{-1} (^{11}BN)); PMR (CCl_4) δ 2·82 (*q*, J = 7·0 cycles/sec, 12, CH_2), 0·93 (*t*, J = 7·0 cycles/sec, 18, CH_3).

When the tris-products were solid rather than liquid, they were, upon removal of the solvent, recrystallized from a suitable solvent (see Table 1).

Preparation of tris(dimethylamino)borane

Due to the low boiling point of dimethylamine, the preparation of its N-lithio derivative was conducted at −78°. Thus, a solution of 10·8 g (0·24 mole) of dimethylamine in 100 ml of anhydrous THF at this temperature was treated with 160 ml (0·25 mole) of 1·6 M *n*-butyllithium in hexane added dropwise via a hypodermic syringe. After 30 min, the white slurry was treated with 11·4 g (0·08 mole) of boron trifluoride diethyl etherate while the reaction mixture was slowly warming to room temperature. The mixture was then refluxed for three hours and worked-up as above to afford 10·4 g (92 per cent) of tris(dimethylamino)borane: b.p. 145–151° ([8] b.p. 146°); n_D^{22} 1·4420 ([1e] n_D^{20} 1·4462); i.r. NH absent, 1506, 1411 and 1380 cm^{-1} (CH_3), 1444 cm^{-1} (^{11}BN), 1467 cm^{-1} (^{10}BN) ([15] 1449 cm^{-1} (^{11}BN), 1471 cm^{-1} (^{10}BN)); PMR (CCl_4) δ 2·39 (*s*, CH_3).

Attempted preparation of tris(diisopropylamino)borane in refluxing heptane

A solution of 21·3 g (0·21 mole) of freshly distilled diisopropylamine in 125 ml of anhydrous heptane at 0° was treated with 150 ml (0·23 mole) of 1·6 M *n*-butyllithium in hexane. After 60 min at 0°, the N-lithiodiisopropylamine solution was treated with 7·1 g (0·05 mole) of boron trifluoride diethyl etherate. This slurry was then refluxed for 12 hr and the resulting bright yellow mixture was worked-up as above to give 10·1 g (88 per cent) of bis(diisopropylamino)fluoroborane: b.p. 43–45° (0·075 mm); i.r. NH absent, 1415 cm^{-1} (^{11}BN), 1132 cm^{-1} (possibly CN), 887 cm^{-1} (possibly BF); PMR (CCl_4) δ 3·35 (*m*, 4, CH), 1·05 (*d*, 24, CH_3); mass spectrum (70 eV) m/e (relative intensity) 230 ($M^{\oplus}$) (14·1), 215 (40·5), 214 (11·7), 187 (17·6), 145 (8·8), 131 (7·6), 101 (11·1), 86 (61·1), 58 (12·9), 44 (100·0), 43 (28·8), 42 (17·6), 41 (12·3).

Other attempted preparations of tris(diisopropylamino)-

borane in refluxing heptane for 24 hr or in refluxing THF for 4 hr gave comparable yields of bis(diisopropylamino)-fluoroborane.

REFERENCES

1. (a) K. Niedenzu and J. W. Dawson, in *Inorganic Syntheses* (Edited by E. L. Muetterties) Vol. 1, p. 135. McGraw-Hill, New York (1968); (b) E. Wiberg and K. Schuster, *Z. anorg. allg. Chem.* **213**, 77 (1933); (c) G. E. Coates, *J. chem. Soc.* 3481 (1950); (d) H. Nöth and S. Lukas, *Chem. Ber.* **95**, 1505 (1962); (e) D. W. Aubrey, M. F. Lappert and M. K. Majumdar, *J. chem. Soc.* 4088 (1962); (f) H. J. Becher, *Z. anorg. allg. Chem.* **287**, 285 (1956); (g) C. R. Kenney and C. L. Mahoney, *J. org. Chem.* **8**, 526 (1943) and references cited therein; (h) D. W. Aubrey and M. F. Lappert, *J. chem. Soc.* 2927 (1959); (i) M. F. Lappert, *Proc. chem. Soc.* 59 (1959); (j) W. Gerrard, M. F. Lappert and C. A. Pearce, *J. chem. Soc.* 381 (1957); (k) D. W. Aubrey, W. Gerrard and E. F. Mooney, *J. chem. Soc.* 1786 (1962).
2. (a) U.S. Borax Chemical Corp., British Patent 859187, 1961, *Chem. Abstr.* **55**, 16391 (1961); (b) R. J. Brotherton and H. Steinberg, *J. org. Chem.* **26**, 4632 (1961); (c) B. M. Mikhailov and P. M. Aronovich, *Zh. obshch. Khim.* **29**, 3124 (1959), *Chem. Abstr.* **54**, 13035 (1960).
3. S. Jerumanis and J. M. Lalancette, *J. org. Chem.* **31**, 1531 (1966).
4. D. W. Aubrey and M. F. Lappert, *Proc. chem. Soc.* 148 (1960).
5. A. L. McCloskey, W. D. English and A. Steinberg, *J. Am. chem. Soc.* **83**, 2122 (1961).
6. R. J. Brotherton and T. Buckman, *Inorg. Chem.* **2**, 424 (1963).
7. A. Dornow and H. H. Gehrt, *Angew. Chem.* **68**, 619 (1956).
8. A. Dornow and H. H. Gehrt, *Z. anorg. allg. Chem.* **294**, 81 (1958).
9. M. F. Lappert and M. K. Majumdar, *J. organomet. Chem.* **6**, 316 (1966).
10. F. A. Davis, Private communication.
11. E. H. Brown and C. A. Kraus, *J. Am. chem. Soc.* **52**, 4414 (1930).
12. (a) M. F. Lappert and T. A. George, *Chem. Comm.* 463 (1966); (b) M. F. Lappert and T. A. George, *J. chem. Soc.* (A), 992 (1969).
13. C. H. Mack and S. E. Ellzey, Jr., U.S. Patent 3300530, 1967, *Chem. Abstr.* **66**, 115440 (1967).
14. (a) P. Nelson and A. Pelter, *J. chem. Soc.* 5142 (1965); (b) R. H. Cragg, J. P. N. Husband, G. C. H. Jones and A. F. Weston, *J. organomet. Chem.* **44**, C37 (1972).
15. D. W. Aubrey, M. F. Lappert and H. Pyszora, *J. chem. Soc.* 5239 (1960).