*Journal of Organometallic Chemistry*, 156 (1978) 95—99


# NEW REACTIONS AND REAGENTS.

# VIII. A NOVEL GENERAL SYNTHESIS OF DIALKYLBORANES AND THEIR DERIVATIVES VIA THE TRANSFORMATIONS OF DIALKYL(DIETHYLAMINO)BORANES *

SHYAM K. GUPTA **

*Armour Research Center, 15101 N. Scottsdale Road, Scottsdale, Arizona 85260 (U.S.A.)*

(Received April 4th, 1978)

## Summary

This communication describes three developments which permit convenient synthesis of dialkylboranes, dialkylborinic acids and esters, and mixed trialkylboranes from readily synthesized dialkyl(diethylamino)boranes. These reactions proceed cleanly and quantitatively. The isolation or purification of the intermediates is not necessary. These developments are: (i) the reduction of *o*-hydroxyphenyldialkylborinates with aluminum hydride to give the corresponding dialkylborane, (ii) the simple preparation of alkyl and aryl esters of dialkylborinic acids and of the parent dialkylborinic acids themselves, and, (iii) a convenient synthesis of the required dialkylamino)boranes.

---

The dialkylboranes have now become of common utility in organic syntheses [1]. We have consequently been engaged in a search for simple, easily effected syntheses of these organoboron derivatives. Our recent observation that the reaction of aryl dialkylborinates with lithium aluminum hydride provides a general route to dialkylboranes reflects such an approach (eq. 1) [2].

$$3\ R_2BOAr + LiAlH_4 \xrightarrow[0^\circ C,\ 30\ min]{hexane} 3\ R_2BH + LiAlH(OAr)_3\downarrow \qquad (1)$$

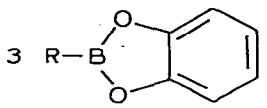
The aryl dialkylborinates have been obtained by redistribution of the trialkylboranes with aryl borates [3]. However, it proved desirable to purify the aryl dialkylborinates prior to their reaction with lithium aluminum hydride in order to obtain dialkylboranes in 95—98% purily. Unfortunately, such purification of

* Dedicated to Prof. H.C. Brown in recognition of his contributions to chemistry. (For part VII see ref. 11).

** Work performed at R.B. Wetherill Laboratory, Purdue University, W. Lafayette, Indiana, under a N1H post doctoral grant (GM-10937).

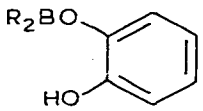
these compounds which possess low volatility may not be practical. Therefore, our efforts in the search for facile syntheses of aryl dialkylborinates and dialkylboranes continued.

We have recently disclosed a simple route to monoalkylboranes, $RBH_2$, via the reaction of alkylcatecholboranes (I) with aluminum hydride (eq. 2) [4].



$$3\ \text{(I)} + 2\ AlH_3 \xrightarrow[0\,^\circ C,\ 30\ min]{Et_2O} 3\ RBH_2 + (C_6H_4O_2)_3Al_2 \downarrow \quad (2)$$

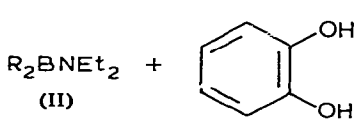
It occurred to us that a similar reaction using catechol esters of dialkylborinic acids may provide a direct route to dialkylboranes. After preliminary exploration, it was found that *o*-hydroxyphenyl dialkylborinates (II) were suitable intermediates for this synthesis. Their reduction with aluminum hydride proceeded rapidly. The aluminum aryloxide by-product precipitated concurrently, and the supernatant solutions thus obtained contained almost pure dialkylboranes (eq. 3).



$$\text{(IIa)} + 2\ AlH_3 \xrightarrow[0\,^\circ C,\ 30\ min]{pentane} 3\ R_2BH + H_2 \uparrow + \text{aluminum aryloxide} \downarrow \quad (3)$$

The synthesis of *o*-hydroxyphenyl dialkylborinates (II), and of aryl and alkyl esters of dialkylborinic acids in general, was achieved as follows. Recognizing that the reaction of boron—nitrogen bond-containing compounds with alcohols and phenols proceeds much more rapidly than the reverse reaction of alkoxyboranes with amines [5], the reaction of dialkyl(diethylamino)boranes (III) with alcohols and phenols was explored as a possible route to the alkoxy and aryloxy dialkylboranes.

The dialkyl(diethylamino)boranes (III) reacted readily with alcohols upon slight warming (60°C) to give the corresponding alkyl dialkylborinates and diethylamine. This reaction, however, gave somewhat different products when phenols were used in this synthesis instead of alcohols. In these cases, difficulty was experienced in removing the liberated diethylamine which tends to form an addition compound with the yet unreacted phenol. This difficulty was overcome by using one equivalent of sulfuric acid in these reactions. This effectively trapped diethylamine as its bisulfate. The use of catechol in this reaction (eq. 4) readily provided the desired *o*-hydroxyphenyl dialkylborinates (II).



$$R_2BNEt_2\ \text{(II)} + \text{catechol} + H_2SO_4 \xrightarrow[15\ min]{Et_2O} \text{IIa} + Et_2NH\cdot H_2SO_4 \downarrow \quad (4)$$

The synthesis of required compounds, dialkyl(diethylamino)boranes (III) *,

* The redistribution of trialkylboranes with tris(diethylamino)borane, carried out in the absence of a catalyst proceeds much more slowly even at considerably elevated temperatures [6]. For alternate syntheses of dialkyl(diethylamino)boranes, see ref. 7.

was achieved in nearly quantitative yield via diborane catalyzed redistribution of trialkylboranes with tris(diethylamino)borane (eq. 5). The selection of tris-

$$2\ R_3B + B(NC_2H_5)_3 \xrightarrow[120^\circ C]{\text{cat. } H_3B/THF} 3\ R_2BN(C_2H_5)_2 \quad (III) \qquad (5)$$

(diethylamino)borane in the above redistribution reaction was made on the basis of its easy synthesis * and its commercial availability [10].

Finally, the preparation of dialkylboranes, for example diethylborane and its pyridinate, was achieved without the necessity of isolating the intermediates (eq. 6).

$$2\ Et_3B + B(NEt_2)_3 \xrightarrow[120^\circ C]{\text{cat. } H_3B/THF} \xrightarrow[3\ H_2SO_4,\ Et_2O]{3\ \text{catechol}} \xrightarrow[0^\circ C,\ 30\ \text{min}]{2\ AlH_3} 3\ Et_2BH + 3\ H_2 + (C_6H_4O_2)_3Al_2 \qquad (6)$$

The dialkylboranes were characterized on the basis of their IR spectra, their ready transformation into pyridine-dialkylboranes, and their conversion to the mixed trialkylboranes of known structure by hydroboration with a suitable olefin [9]. These studies indicate that the dialkylborane which we prepared were practically uncontaminated by other organoboron products.

Additional transformations with representative examples are described in Table 1 **.

The present developments enable us now to prepare dialkylboranes, dialkylborinic acids and esters, and mixed trialkylboranes from readily synthesized organo-aminoboranes.

## Experimental

*Dialkyl(diethylamino)boranes (III).* The preparation of diethyl(diethylamino)-borane (IIIa) is representative. A mixture of triethylborane (9.8 g, 100 mmol), tris(diethylamino)borane (12.5 g, 55 mmol), and borane in THF (5 mmol) was stirred at 120°C for 2 h [8]. GLC monitoring of the reaction indicated quantitative conversion at this stage. The product was then kept under vacuum (150 mmHg at 25°C) for 15 min in order to remove THF solvent, then distilled to give IIIa in 94% yield.

*Alkyl-or aryl-dialkylborinates (II).* The preparation of *o*-hydroxyphenyl-diethylborinate (IIa, R = Et) is representative. A 2.9 g sample (20 mmol) of crude IIIa was dissolved in diethyl ether (20 ml). Catechol (2.4 g, 20 mmol) and sulfuric acid (100%, 1.1 ml, 20 mmol) were added to it with rapid stirring. The mixture was then refluxed gently for 15 min and cooled after the addition of pentane (10 ml). The clear supernatant solution was taken out with the aid of a

---

* Tris(diethylamino)borane was prepared by treatment of boron trichloride (1 mol) and diethylamine (6 mol) in 80% yield: (pentane, 0°C), b.p. 53—54°C/0.35 mmHg; $n_D^{20}$ 1.4434. Gerrard et al. [8] report b.p. 50—53°C/0.4 mmHg; $n_D^{20}$ 1.4450. The trialkylboranes from terminal, straight chain olefins required 2 to 4 h heating period. The trialkylboranes from terminal, α-branched olefins required 6 to 8 h, and those from internal and cyclic olefins required 12 to 16 h for equilibration.

** All products were examined by IR, NMR, and mass spectral data All new compounds also gave satisfactory (±0.4%) C, H, N analyses.

TABLE 1

THE PREPARATION OF DIALKYLBORANES AND THEIR DERIVATIVES FROM TRIALKYLBORANES VIA REDISTRIBUTION WITH TRIS(DIETHYLAMINO)BORANE

| No. | Dialkylborane derivative, $R_2BR'$ | | Yield (%) | | B.p. (°C) mmHg | $n_D^{20}$ |
|---|---|---|---|---|---|---|
| | R substituent | R' substituent | GLC | isolated | | |
| | Ethyl | H [a] | | 95 | | 1.5065 |
| | 1-Butyl | H [a] | | 95 | | 1.4890 |
| | 2-Butyl | H [a] | | 95 | | 1.4930 |
| | Isobutyl | H [a] | | 92 | | 1.4850 |
| | 1-Butyl | 1-Pentyl | 90 | 81 | 60/0.5 | 1.4270 |
| | 2-Butyl | 1-Pentyl | 92 | 83 | 49/0.4 | 1.4260 |
| | Isobutyl | 1-Pentyl | 90 | 83 | 55/0.5 | 1.4330 |
| IIIa | Ethyl | Diethylamino | 100 | 94 | 154/760 [b] | 1.4245 |
| IIIb | 1-Butyl | Diethylamino | 98 | 95 | 75—76/2.0 | 1.4371 [c] |
| IIIc | 2-Butyl | Diethylamino | 99 | 95 | 84/4.0 | 1.4430 |
| IIId | Isobutyl | Diethylamino | 100 | 93 | 67—68/2.5 | 1.4325 |
| IIIe | Cyclopentyl | Diethylamino | 96 | 90 | 85—86/0.2 | 1.4865 |
| IIb | Isobutyl | Methoxy | 98 | — | | |
| IIc | Isobutyl | o-Methylphenoxy | 99 | — | | |
| IId | Isobutyl | 8-Quinolinyl | 100 | — | | |

[a] All dialkylboranes, $R_2BH$, were isolated as their pyridine addition compounds. [b] Lit. [4] b.p. 154°C. [c] Lit. [4] b.p. 52—55°C/1.5 mmHg; $n_D^{20}$ 1.4377.

hypodermic syringe, leaving 3.5 g (102%) of diethylammonium bisulfate. The organoborane-containing supernatant liquid was used in the following preparation of diethylborane.

*Dialkylboranes and pyridine-dialkylboranes.* The preparation of diethylborane is illustrative of the general methodology. The crude *o*-hydroxyphenyl diethylborinate solution obtained above was cooled in an ice bath and then treated with aluminum hydride in THF [10] (14.7 ml of 1.5 *M*, 44 mmol, 10% excess). This resulted in the evolution of hydrogen gas (20.5 mmol) and a crystalline precipitate was formed simultaneously. After stirring for 30 min at 0°C, the mixture was diluted with pentane (20 ml) and then filtered through a glass sintered funnel packed with Celite. The filtrate on evaporation at 0°C gave 1.3 g (93%) of a clear liquid: *i*R (cyclohexane) 1580 $cm^{-1}$ (B—H—B, bridge). No other peaks in the 2800—1800 $cm^{-1}$ region were observed. This indicated the absence of any B—H (terminal) bond or Al—H bond containing impurities. Upon the addition of water, 19.0 mmol of hydrogen gas was evolved. Although these preparations of dialkylboranes are satisfactory for further use in organic synthesis, the small amounts of aluminum salts still present may conveniently be removed by dissolution of the dialkylborane in pentane, filtration, and then evaporation of the solvent.

For the preparation of pyridine-diethylborane, the following procedure was followed. Crude diethyl(diethylamino)borane (2.9 g, 20 mmol) was converted to the *o*-hydroxyphenyl diethylborinate as described above. This was treated with aluminum hydride for 15 min at 0°C. Pyridine (40 mmol) then was added to it, and after stirring for 30 min at 25°C the mixture was filtered after dilution with pentane. Removal of the solvent gave 3.2 g (105%) of the desired product. After drying at 25°C/2 mmHg for 30 min the yield was 2.85 g (95%); $n_D^{20}$ 1.5065;

IR (neat) 2320, 2250, 2200, 1620 $cm^{-1}$, NMR ($CDCl_3$, TMS) 8.61—7.43 (m, 5), 0.71 (singlet like m, 10).

*"Mixed" trialkylboranes.* The preparation of highly pure samples of mixed trialkylboranes was achieved in a similar manner. For example, (diethylamino)-di-2-butylborane (IIIc, 9.9 g, 50 mmol) was converted to *o*-hydroxyphenyldi-2-butylborinate in the usual manner. This was then reduced with aluminum hydride in THF solution (36.7 mmol, 10% excess) at 0°C for 30 min. 1-Pentene (50 mmol) was then added to it and after stirring the mixture for 30 min at 0°C it was filtered through a glass funnel. The filtrate on distillation gave 8.1 g (83%) of di-2-butyl-1-pentylborane: b.p. 49°C/0.5 mmHg, $n_D^{20}$ 1.4260. Anal. Found: C, 79.48; H, 15.02. $C_{13}H_{29}B$ calcd.: C, 79.59; H, 14.79%. The oxidation of this product with alkaline hydrogen peroxide gave, according to GLC examination, 2-butanol and 1-pentanol in a 2/1 ratio. About 2% of 2-pentanol was also produced.

## References


1 H.C. Brown, Organic Syntheses via Boranes, Wiley, New York, 1975.
2 H.C. Brown and S.K. Gupta, J. Organometal. Chem., 32 (1971) C1.
3 H.C. Brown and S.K. Gupta, J. Amer. Chem. Soc., 93 (1971) 2812.
4 H.C. Brown and S.K. Gupta, J. Amer. Chem. Soc., 93 (1971) 4062.
5 H. Steinberg and R.J. Brotherton, Organoboron Chemistry, Vol. 2, Wiley, New York, N.Y., 1966, p. 27.
6 K. Niedenzu, H. Beyer, J.W. Dawson, and H. Jenne, Chem. Ber., 96 (1963) 2653; U.S. Borax Chemical Corporation, Fr. Patent 1,324,186 (1963); Chem. Abstr., 59 (1963) 11555 g; H.K. Hofmeister and J.R. Van Wazer, J. Inorg. Nucl. Chem., 26 (1964) 1209.
7 B.M. Mikhailov and V.A. Dorokhov, Doklady Akad. Nauk SSSR, 136 (1961) 51; L.F. Hohnstedt, J.P. Brennan, and K.A. Reynard, J. Chem. Soc. A, (1970) 2455.
8 W. Gerrard, M.F. Lappert and C.A. Pearce, J. Chem. Soc., (1957) 381.
9 H.C. Brown and S.K. Gupta, J. Amer. Chem. Soc., 93 (1971) 1818.
10 Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.
11 S.K. Gupta, J. Org. Chem., in press.