Journal of Organometallic Chemistry, 329 (1987) 287–291
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Sodium hydridotrimethylboronate and its ether solvate. Study of hydridotrialkylboronates as reagents for the preparation of beryllium hydrides

Norman A. Bell *, Geoffrey E. Coates and J. Alan Heslop
Department of Chemistry, Science Laboratories, South Road, Durham, DH1 3LE (Great Britain)

(Received February 12th, 1987)

Abstract

Sodium hydridotrimethylborate is tetrameric in benzene solution and its etherate, $(NaBMe_3H)_4OEt_2$ probably also retains its solid state cubane arrangement in benzene solution. Reactions of $NaBR_3H$ ($R = Me$, Et) in a variety of ratios with halo and organoberyllium compounds have been studied. Exchange between Et_2Be and $NaBEt_3H$ does not occur to any appreciable extent beyond the EtBeH stage and reaction of equimolar EtBeCl and $NaBEt_3H$ resulted in the formation of EtBeH, isolated as its trimethylamine complex. $NaBR_3H$ and $BeCl_2$ in 1/1, 2/1 and 4/1 ratios did not yield pure beryllium hydrides.

Introduction

In 1961 Honeycutt and Riddle obtained sodium hydridotriethylboronate ($NaBEt_3H$) as a colourless oil from the reaction of sodium hydride with triethylboron in ether or hydrocarbon solvents [1]. The solubility in hydrocarbon solvents indicated a covalent constitution. Accordingly, as part of a programme of work using $NaBR_3H$ as a means of synthesising beryllium and magnesium hydrides we prepared the methyl analogue. On symmetry grounds this would be more amenable to crystallisation and would hence allow determination of its degree of association both in the solid state and in solution as well as its crystal structure. We have earlier reported the cubane structure of $(NaBMe_3H)_4OEt_2$ which contains alternate Na and H atoms at the corners of a very distorted cube with pendant BMe_3 groups attached to each of 4 hydridic hydrogens and an ether molecule, coordinated to one of the sodium atoms in the tetrameric unit [2]. Since our initial preparation of this compound and the solvent-free compound in 1967 [3], other workers have obtained

---

* To whom correspondence should be addressed at: Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB, (Great Britain).

0022-328X/87/$03.50

the solvent-free compound [4,5] and shown that compounds of the type MBR_3H (M = alkali metal, R = alkyl) are very specific reducing agents for organic substrates [6], although little is known about the nature of such reagents. Herein we report the results both of our studies on $(NaBMe_3H)_4$ and its ether solvate and of our investigations into the further usage of these reagents for the preparation of beryllium hydrides.

Experimental

Preparation of $[NaBMe_3H]_4OEt_2$

Trimethylborane, obtained from tributylborate and methylmagnesium bromide in ether, was bubbled into a vigourously stirred suspension of excess sodium hydride (7.2 g, 0.3 mol) in ether (200 cm^3) where it was immediately absorbed. Reaction was completed by gently warming the Grignard/$(BuO)_3B$ mixture to release all the borane, and finally the sodium hydride suspension was refluxed for 2 h. Excess sodium hydride was filtered off and the filtrate evaporated under reduced pressure yielding a colourless oil which was crystallised from hexane and dried briefly in vacuo, as long colourless needles, m.p. 46.5–47.0 °C. Found: B, 10.20; hydrolysable hydrogen, 1.00; Na, 23.10%; *M* (cryoscopically in 1.45; 0.71 wt% benzene) 387, 382. $C_{16}H_{50}B_4Na_4O$ calcd.: B, 10.23, hydrolysable hydrogen, 1.02; Na, 23.34%; *M*, 394.

Preparation of $[NaBMe_3H]_4$

The ether-solvate $[NaBMe_3H]_4 \cdot OEt_2$ was subjected to vacuum for several hours at room temperature yielding needles, m.p. 76–78 °C; lit. [4,5] 76 °C. Found: B, 13.50; hydrolysable hydrogen, 1.25; Na, 28.75%; *M* (cryoscopically in 1.83, 0.60 wt% benzene) 324, 323. $C_{12}H_{40}B_4Na_4$ calcd.: B, 13.53; hydrolysable hydrogen, 1.26; Na, 28.77%; *M*, 320. Infrared absorptions (cyclohexane solution): 1968m, 1876m, 1429m, 1364w, 1351w(sh), 1294s(sh), 1282s, 1176s, 1151s, 1126s, 1096s, 1064m, 1017w(sh), 1002m, 877w, 791w.

Reactions between $NaBEt_3H$ *and* Et_2Be

(i) 1/1 ratio. $NaBEt_3H$ (5 cm^3 of a 0.635 *M* ethereal solution 3.17 mmol) was added by syringe to Et_2Be (3.0 cm^3 of a 1.10 *M* solution in ether, 3.3 mmol) in ether (20 cm^3). The mixture was stirred for half an hour and then hydrolysis of an aliquot (5 cm^3) of the clear solution with water yielded ethane (14.3 Ncm^3) and hydrogen (14.2 Ncm^3).

(ii) 2/1 ratio. $NaBEt_3H$ (10.0 cm^3 of a 0.635 *M* ethereal solution, 6.35 mmol) was added by syringe to Et_2Be (3.0 cm^3 of a 1.10 *M* solution in ether, 3.3 mmol) in ether (20 cm^3). After the mixture had been stirred for 1 h at room temperature, hydrolysis of an aliquot (5 cm^3) of the clear solution with water yielded ethane (7.6 Ncm^3) and hydrogen (17.1 Ncm^3). After stirring for a further 18 h, hydrolysis of a similar aliquot of solution yielded essentially the same quantities of gases as after 1 hour.

(iii) 4/1 Ratio Et_2Be (5 cm^3 of a 1.10 *M* solution in ether, 5.5 mmol) was added to $NaBEt_3H$ (36 cm^3 of a 0.625 *M* solution in ether, 22.5 mmol) and the mixture stirred for 18 h at room temperature. Hydrolysis of an aliquot (3 cm^3) of the clear solution yielded hydrogen (38.9 Ncm^3) and ethane (6.9 Ncm^3).

Reaction between EtBeCl and $NaBEt_3H$

$NaBEt_3H$ (17.5 cm^3 of a 0.635 *M* solution in ether, 11.4 mmol) was added to an equimolar mixture of Et_2Be (5.3 cm^3 of a 1.10 *M* solution in ether, 5.83 mmol) and $BeCl_2$ (0.4617 g, 5.77 mmol) in ether resulting in the formation of an immediate white precipitate. The solution was stirred for 30 min and then the precipitate was filtered off. Volatile material was removed from the filtrate under reduced pressure and then the residue was heated at 70 ° C for 2 h. Excess Me_3N was condensed on to the viscous oily residue producing a white crystalline solid which was sublimed at 40–50 ° C under vacuum as colourless prisms m.p. 89–90 ° C lit. [7] 90–91 ° C. Found: hydrolysable hydrogen, 1.10, ethyl 30.0%. $EtBeH \cdot NMe_3$ calcd.: hydrolysable hydrogen, 1.03, ethyl 29.6%. Dissociation pressure measurements over the range 294–370 K show the enthalpy of coordination of trimethylamine to ethylberyllium hydride is about 40 kJ mol^{-1}.

Reactions between $NaBEt_3H$ and $BeCl_2$

(i) 1/1 ratio. $NaBEt_3H$ (26 cm^3 of a 0.625 *M* solution in ether, 16.3 mmol) was added to $BeCl_2$ (1.302 g, 16.4 mmol) in ether (50 cm^3). The white precipitate of salt which was immedately formed was filtered off and THF (10 cm^3) added to the filtrate. The white precipitate so formed was filtered off, dried in vacuo and identified by analysis as $BeCl_2(THF)_2$ [8]. Found: Be, 4.07; Cl, 32.2; calcd.: Be, 4.04; Cl, 31.3%.

(ii) 2/1 ratio. $BeCl_2$ (1.10 g, 13.7 mmol) in ether (40 cm^3) was added to $NaBEt_3H$ (3.50 g, 28.7 mmol) in ether (40 cm^3). The immediate white precipitate of salt was filtered off and the filtrate which contained a negligible amount of chloride was evaporated at room temperature under reduced pressure. The evolved material was collected in a liquid air trap. The colourless oil which remained was heated up slowly, and at 50–60 ° C a white solid started to form. The temperature was maintained at 90–100 ° C for 12 h resulting in a white solid residue and the material evolved throughout the heating process was collected in liquid air. Fractionation of the ethereal solution collected through a trap at −76 ° C yielded 1.0 g of Et_3B and fractionation of the material collected on heating yielded 0.9 g of Et_3B. Analysis of the white residue yielded hydrolysable hydrogen 3.28%, calculated for $H_{1.49}Be(BEt_3H)_{0.51}$, 3.30% H.

(iii) 4/1 ratio. $NaBEt_3H$ (46.8 cm^3 of a 0.625 *M* solution in ether, 29.2 mmol) was added to $BeCl_2$ (0.5846 g, 7.3 mmol) in ether (50 cm^3). The white precipitate was filtered off and ether evaporated from the filtrate leaving a viscous residue. This residue was slowly heated to 180 ° C in a vacuum and maintained at this temperature for 12 h. Finally the white solid residue was washed with ether and dried in vacuo. Analysis of the residue showed a hydrolysable H/Be/B ratio of 3.68/1/0.03.

Reaction of $NaBMe_3H$ with $BeCl_2$

$NaBMe_3H$ (62 cm^3 of a 0.982 *M* solution in ether, 61 mmol) was added with stirring to $BeCl_2$ (2.4636 g, 31 mmol) in ether (50 cm^3). After 30 minutes the precipitate was filtered off and solvent removed from the filtrate under reduced pressure over 5–6 h leaving a white residue. Fractionation of the volatile material yielded Me_3B (1.90 g, 34 mmol). Analysis of the white residue yielded hydrolysable hydrogen, 1.31; Be, 6.02; Me_3B, 35.30%. $HBe(Me_3H)(OEt_2)_{1.16}$; calculated hydrolysable hydrogen, 1.33; Be, 5.93; Me_3B, 36.7%.

Discussion

Sodium hydride readily dissolves in boiling ether containing trimethylborane from which crystals of $(NaBMe_3H)_4 \cdot OEt_2$ may be isolated. We have determined the structure of this compound earlier by X-ray methods and shown that it contains a very distorted cubane arrangement of alternating sodium and hydridic hydrogen atoms, with a BMe_3 group attached to every hydridic hydrogen atom. The sodium atom on the mirror plane, which has the fewest intramolecular interactions, is coordinated to the ether molecule [2]. Molecular weight measurements show that this tetrameric arrangement is also retained in benzene solution. On prolonged drying in a vacuum the coordinated ether is lost and the solvent-free compound is still tetrameric in benzene solution.

The ^{11}B NMR spectrum of the solvent-free compound recorded in benzene solution shows a broad singlet 234 Hz upfield from the trimethylborate external reference. The high quadrupole moment of ^{23}Na probably prevents the formation of the expected doublet by eliminating coupling between the boron and hydrogen atoms, although a rapid exchange of the methyl-boron protons with a small amount of trimethylborane would also eliminate the B–H coupling. This has been observed for $NaBEt_3H$ where the ^{11}B spectrum was initially a singlet which became a doublet with the same chemical shift on standing over sodium hydride for several months [1]. The ^1H NMR spectrum contained a single resonance at 10.30 ppm which is assigned to the $B{-}CH_3$ group. No coupling was observed between the B and CH_3 groups. There is no tetrahedral geometry about boron in the BMe_3H group, so a large effective field gradient is experienced by the central atom and the quadrupole relaxation time of the nuclear spin is large. Thus scalar coupling between the boron and methyl protons is eliminated. Infrared absorptions at 1965 and 1876 cm^{-1} in cyclohexane solution and 1968 and 1876 in Nujol are characteristic of bridging hydrogen atoms attached to boron.

The several routes available for the preparation of beryllium hydrides have recently been reviewed [9]. Alkyl–hydrogen exchange reactions of R_2Be with Et_3SnH have not been particularly useful for the preparation of RBeH and their complexes. Exchange does occur with aluminium hydrides and organoberyllium compounds. For example $[BeH_2 \cdot NMe_3]_2$ has been obtained from reaction of the Et_2Be/Et_2AlH adducts with NMe_3 [10]. Likewise $Be(OBu^t)_2$, Et_2Be and EtBeH all undergo exchange with $NaAlEt_3H$ producing sodium beryllium hydrides of varying composition [11]. Exchange between $NaBEt_3H$ and organomagnesium compounds produces RMgH at low temperature; disproportionation occurs at room temperature [12]. We have therefore studied the use of hydriodotrialkylboronates as reagents for the preparation of beryllium hydrides.

Diethylberyllium readily undergoes exchange with an equimolar quantity of $NaBEt_3H$ in ether at room temperature to form a solution containing EtBeH which was not isolated, as separation from $NaBEt_4$ could not be achieved. When the ratio of reactants was increased to 1/2 and also to 1/4, even after ~18 h, exchange had gone little beyond the EtBeH stage.

Reaction of $NaBEt_3H$ with organoberyllium halides has been used for the preparation of $RBeH \cdot NMe_3$ ($R = Ph$ [13], Me_3CCH_2 [14]). The reaction of EtBeCl and $NaBEt_3H$ in equimolar proportions produces an immediate precipitate of salt and on evaporation of solvent up to 70 °C, 92% of the total Et_3B present was collected. The remaining triethylborane was removed by the addition of trimethylamine which allowed isolation of the ethylberyllium hydride as its amine complex $(EtBeH \cdot NMe_3)_2$, obtained earlier by tin–hydride–Be–alkyl exchange and which has an enthalpy of coordination of the amine of about 40 kJ mol^{-1}.

The reaction of $NaBEt_3H$ with $BeCl_2$ in equimolar proportions was investigated as a route to HBeCl and its coordination complexes. Although an immediate precipitate of salt was formed, the addition of THF to the filtrate in an attempt to isolate HBeCl as a coordination complex resulted in the immediate precipitation of $BeCl_2 \cdot 2THF$ [8]. When the reagents were mixed in a 2/1 ratio, after removal of the salt precipitate, evaporation of the filtrate and subsequent heating in a vacuum up to 100 °C for 12 h resulted in the evolution of ca. 68% of the total triethylborane present, leaving a residue having the approximate composition $H_{1.49}Be(Et_3BH)_{0.51}$. In a further experiment the residue was heated up to 180 °C under vacuum and the final insoluble residue had a Be/B mole ratio of 12/1. Attempts to remove more triethylborane from the beryllium hydride by complexing with trimethylamine and removal in vacuum were not successful. A claim has been made that the reaction of $NaBEt_3H$ with $BeCl_2$ in a little ether followed by refluxing in xylene at 120 °C yields 94.4 mole% BeH_2 contaminated with triethylborane [15]. Using the methyl analogue instead of $NaBEt_3H$, evaporation of the filtrate yielded a compound of approximate composition $HBe(BMe_3H)(OEt_2)_{1.16}$: the removal of Me_3B was not significantly better than Et_3B to warrant further investigation.

When $NaBEt_3H$ and $BeCl_2$ were allowed to react in a 4/1 ratio, after removal of salt, the residue after evaporation of solvent was heated up to 180 °C. Although the residue had a H/Be/B ratio of 3.68/1/0.03 its X-ray powder pattern was very similar to that of NaH rather than Na_2BeH_4.

References

1 J.B. Honeycutt and J.M. Riddle, J. Am. Chem. Soc., 83 (1961) 369.
2 N.A. Bell, H.M.M. Shearer and C.B. Spencer, Acta Crystallogr. C, 39 (1983) 694.
3 J.A. Heslop, PhD Thesis, Durham, 1967.
4 P. Binger, G. Benedikt, G.W. Rotermund and R. Koster, Liebigs Ann. Chem., 717 (1968) 21.
5 H.C. Brown, A. Khuri and S.C. Kim, Inorg. Chem., 16 (1977) 2229.
6 E.R.H. Walker, Chem. Soc. Rev., 5 (1976), 23 and ref. therein.
7 N.A. Bell and G.E. Coates, J. Chem. Soc., (1965) 692.
8 N.Y. Turova, A.V. Novoselova and K.N. Semenenko, Russ. J. Inorg. Chem., 4 (1959) 1104.
9 N.A. Bell, Comprehensive Organometallic Chemistry, p. 142, 1982, Pergamon, Oxford.
10 L.H. Shepherd, G.L. Ter Haar and E.M. Marlett, Inorg. Chem., 8 (1969) 976.
11 N.A. Bell and G.E. Coates, J. Chem. Soc. A, (1968) 628.
12 G.E. Coates and J.A. Heslop, J. Chem. Soc. A, (1968) 514.
13 G.E. Coates and M. Tranah, J. Chem. Soc. A, (1967) 615.
14 G.E. Coates and B.R. Francis, J. Chem. Soc. A, (1971) 1305.
15 L.H. Shepherd, U.S. Pat. 3,845,199.