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Hindered Organoboron Groups in Organic Synthesis. 17 [1]. Synthesis of 2,4,6-Triisopropylphenylborane $(TripBH_2)_2$, a Useful Alternative to Thexylborane.

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ABSTRACT

2,4,6-Triisopropylphenylborane (tripylborane, $TripBH_2$) resembles thexylborane in having a single, bulky organic group attached to boron, but the group is aromatic rather than aliphatic. The compound has been synthesized by two alternative routes, one involving direct reduction of dimethoxytripylborane and the other involving redistribution between ditripylborane and borane. It is a solid which is considerably more stable than thexylborane.

INTRODUCTION

Thexylborane is well known as a useful hydroborating agent [2]. It is capable of hydroborating two molar equivalents of relatively unhindered alkenes to give the corresponding thexyldialkylboranes [3]. In some cases the reaction can be used to produce unsymmetrical trialkylboranes by sequential reactions with two different alkenes [2], whilst dienes can often be hydroborated in a cyclic manner to produce β-thexylboracyclanes [4]. Furthermore, the thexyl group exhibits a low migratory aptitude in some important synthetic reactions of the thexyldialkylboranes so produced, such as the ketone syntheses involving their carbonylation [5] or cyanidation [6]. For these reasons thexylborane is one of the most important and widely used hydroborating agents [7].

However, it is not without its disadvantages. Firstly, the reagent slowly isomerizes at room temperature from a tertiary to a primary alkylborane [2] and therefore has to be prepared freshly and used at low temperature. Secondly, its reactions with simple terminal alkenes cannot be controlled to allow stepwise introduction of two different primary alkyl groups and are not much more regioselective than those of borane itself [2, 7]. On the other hand, its reactions with relatively hindered alkenes are accompanied by substantial displacement of 2,3-dimethyl-2-butene (80% with 1-methylcyclohexene, for example) [2], again preventing the clean formation of the corresponding mixed organoboranes. Thus, the range of thexyldialkylboranes which are easily available is quite restricted.

Isomerization and displacement should not be serious problems with arylboranes, and by choice of a suitably hindered aryl group it might be possible to produce a reagent which could successfully hydroborate alkenes in both a highly regioselective and sequential fashion. We surmised that the 2,4,6-triisopropylphenyl (tripyl, Trip) group might provide about the right degree of hindrance and therefore undertook to synthesise tripylborane [8]. We now describe the successful synthesis of this monoarylborane by two different methods and report upon its stability. Its hydroborating properties and migrating aptitude are currently under investigation and will be reported in due course.

RESULTS AND DISCUSSION

Scheme 1 shows the most direct route to tripylborane. Formation of the Grignard reagent (**1**) was

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This paper is dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

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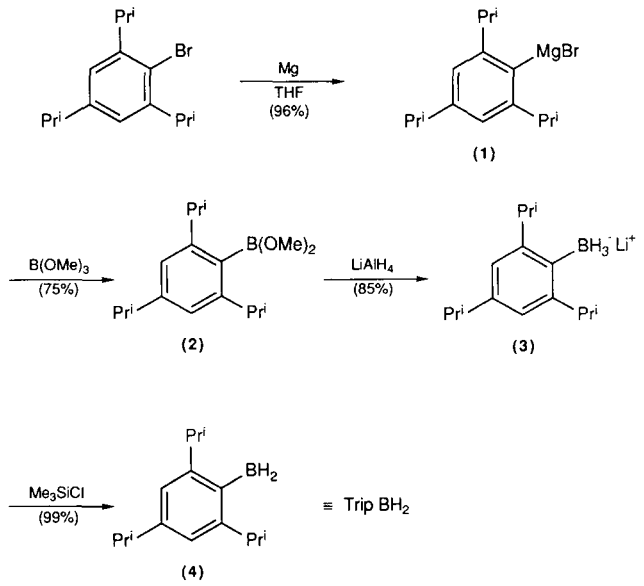
straightforward and went in at least 96% yield, according to analysis by titration against standard acid. Its reaction with trimethoxyborane gave pure, redistilled tripyldimethoxyborane (**2**) in 75% yield (72% overall from tripyl bromide). This material is therefore a readily available, stable precursor for tripylborane.



SCHEME 1

A solution of the stoichiometric amount of lithium aluminum hydride in diethyl ether was used to convert the dimethoxy compound (**2**) (also in ether) into the corresponding trihydroborate (**3**). The advantage of this approach was that the by-product, dimethoxyalane, is essentially insoluble in diethyl ether and can be removed by centrifugation-decantation [9]. The sequence was then completed by addition of chlorotrimethylsilane in diethyl ether-pentane [10]. This allowed precipitation and removal of lithium chloride to leave a solution of tripylborane (4). The solid could be obtained by simple evaporation of the solution.

An alternative approach to tripylborane would involve redistribution between ditripylborane and borane-THF [11] (eq. 1). In practice, this process was extremely simple; merely mixing stoichiometric proportions of the components in THF and allowing the mixture to stand at 20°C for 4 hours resulted in quantitative conversion into tripylborane.

$$Trip_2BH + BH_3 \longrightarrow (TripBH_2)_2 \qquad (1)$$

The ease and selectivity of this process may reflect the monomeric nature of ditripylborane [8] and the driving force for removing interactions between different tripyl groups attached to the same boron atom. Whatever the precise explanation, the process provides an alternative approach to tripylborane. However, because it involves the previous synthesis of ditripylborane, the first approach will generally be preferable.

In order to test the stability of tripylborane, samples of the solid and of its THF and diethyl ether solutions were allowed to stand at ambient temperature under nitrogen and monitored periodically by hydrolysis-gas titration and methanolysis-gas chromatography. Over a period of 23 days, the solid showed no evidence for redistribution or isomerisation and only 4% decomposition. The solutions in THF and EE showed no evidence for redistribution or isomerisation after 180 hours. The THF solution showed 20% decomposition after 36 hours and no further decomposition up to 180 hours. The solution in ethyl ether behaved similarly. The initial decomposition may have been due to small quantities of air introduced through the frequent initial samplings. It is clear that the solid may be stored satisfactorily and that the solution can be kept for appreciable periods. The only decomposition product seen was 1,3,5-triisopropylbenzene which does not interfere with subsequent reactions.

The next stage in this study, already underway, is the investigation of the hydroborating properties of this interesting monoarylborane. The results will be presented in due course.

EXPERIMENTAL

All solvents were appropriately dried under argon in a still. All apparatus was dried in an oven at 120°C, assembled and cooled under nitrogen. Trimethoxyborane was dried over and distilled from CaH_2 [12].

Preparation of Dimethoxytripylborane (2)

A dry, three-necked 100 mL round bottomed flask equipped with a pressure equalising funnel, reflux condenser, magnetic stirrer and a rubber septum was charged with magnesium turnings (2.8 g, 119 mmol) and a crystal of iodine, flushed with dry nitrogen and kept under a positive pressure of nitrogen. A solution of dry, redistilled bromo-2,4,6-triisopropylbenzene (25.92 g, 91.6 mmol) in dry THF (70 mL) was transferred by double-ended needle into the dropping funnel and then added dropwise to the stirred preheated (hair dryer) magnesium turnings. After addition, the reaction mixture was heated under reflux for 2 hours and then cooled to room temperature (96% yield by titration).

A dry, three-necked 500 mL round bottomed flask was equipped with a condenser, mechanical stirrer and a rubber septum, flushed with nitrogen and maintained under a positive nitrogen pressure.

Trimethoxyborane (35 mL, 303 mmol, freshly distilled from CaH_2), was added by syringe followed

by diethyl ether (80 mL). The solution was cooled to −15°C, well stirred, and the solution of previously prepared Grignard reagent (**1**) was transferred dropwise by nitrogen pressure through a double-ended needle. The temperature was kept at −15°C during the transfer. Good stirring was required at this stage due to the appearance of a dense white precipitate.

The reaction mixture was allowed to warm to room temperature, stirred for 20 hours and filtered and the precipitated salts were then washed with dry pentane (2 × 150 mL). The combined filtrates were concentrated (70°C, 760 mm Hg) and distilled to give dimethoxytripylborane (18.2g, 72%, b.p. 106–108°C/1 mm Hg). ^{1}H n.m.r. (ppm) 1.22–1.26(18H, $(C\underline{H}_3)_2CH$-), 2.64(2H, 2 × $C\underline{H}(CH_3)_2$), 2.87(1H,$C\underline{H}(CH_3)_2$), 3.56(6H,s,$OC\underline{H}_3$), 6.95(2H,s, Ar-H). ^{13}C n.m.r. 24.08($(\underline{C}H_3)_2CH$), 24.58(2 × $\underline{C}H_3)_2CH$), 35.09($\underline{C}H(CH_3)_2$), 35.23(2 × $\underline{C}H(CH_3)_2$), 52.46($O\underline{C}H_3$), 120.13(C-3), 122.6(C-1), 149.3(C-4), 150.27(C-2). Mass spec. m/e 276(100), 245(80), 261(40). M^+ 276.2260, calculated for $C_{15}H_{29}BO_2$ 276.2261; λ_{max} = 231.9nm (log ϵ 2.845), 264.9(2.451).

*Preparation of Tripylborane (**4**) via Lithium Trihydrotripylborate (**3**)*

Dimethoxytripylborane (2.02g, 7.32 mmol), diethyl ether (60 mL) and pentane (15 mL) were placed, under nitrogen, in a 250 mL round bottomed flask equipped with a septum capped tap adapter and magnetic stirrer and the solution stirred at 0°C. A solution of lithium aluminum hydride in ether 8.5 mL of 0.87 M, 7.4 mmol) was added through a syringe, on which a white precipitate immediately resulted [9]. The ice-bath was removed and the reaction mixture stirred for a further 3 hours, after which it was transferred to a centrifuge tube, under nitrogen, and the precipitate spun down. The clear supernatent was transferred by double-ended needle into a dry flask and the precipitate washed with a mixture of ethyl ether (60 mL) and pentane (15 mL). Centrifugation was again followed by decantation. The combined supernatents were concentrated (0.2 mm Hg) to give $LiTripBH_3$ (**3**) as a white solid (1.42 g, 6.34 mmol, 87%); ν_{max} 2200 cm^{-1} (B-H) [9]. Hydrogen analysis gave 6.62 mmol. Methanolysis gave $TripB(OMe)_2$ in quantitative yield with no trace of $Trip_2BOMe$, by g.c. analysis.

$LiTripBH_3$ (1.26 g, 5.63 mmol) was dissolved in diethyl ether (20 mL) and pentane (5 mL) and stirred under nitrogen. Trimethylsilyl chloride (0.55 mL, 5.8 mmol, distilled from CaH_2, under N_2) was added dropwise, and the mixture stirred for 3 hours at room temperature. The precipitate that separated out was removed by centrifugation. The solution (hydrogen analysis 5.7 mmol) may be used directly, or the solvent removed at 0.2 mm Hg to give tripylborane (1.14 g, 5.28 mmol, 94%) as a white stable solid ν_{max} 2503 cm^{-1} (B-H), 1580 cm^{-1} (B···H···B) [13]; M^+ 216.205, calculated for $C_{15}H_{25}B$ is 216.205. G.C. analysis of the methanolysis product of (4) showed the quantitative formation of $TripB(OMe)_2$, with no trace of $Trip_2BOMe$.

REFERENCES

[1] Part 16: K. Smith, A. Pelter, and A. Norbury, *Tetrahedron Lett., 32*, 1991, 6243.

[2] E. Negishi and H. C. Brown, *Synthesis*, 1974, 77.

[3] G. Zweifel and H. C. Brown, *J. Am. Chem. Soc., 85*, 1963, 2066.

[4] H. C. Brown and C. D. Pfaffenberger, *J. Am. Chem. Soc., 89*, 1967, 5475; H. C. Brown and E. Negishi, *ibid., 94*, 1972, 3567.

[5] H. C. Brown and E. Negishi, *J. Am. Chem. Soc., 89*, 1967, 5285, 5477; *Synthesis*, 1972, 196.

[6] A. Pelter, M. G. Hutchings, and K. Smith *J. C. S. Chem. Commun.*, 1971, 1048; A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J. C. S. Perkin Trans. 1*, 1975, 129.

[7] A. Peter, K. Smith, and H. C. Brown: *Borane Reagents*, Academic Press, London, 1988.

[8] We have previously reported the preparation and properties of ditripylborane: A. Pelter, K. Smith, D. Buss, and A. Norbury, *Tetrahedron Lett., 32*, 1991, 6239.

[9] B. Singaram, T. E. Cole, and H. C. Brown, *Organometallics, 3*, 1984, 774.

[10] H. C. Brown, T. E. Cole, M. Srebnik, and K.-W. Kim, *J. Org. Chem., 51*, 1986, 4925.

[11] See B. M. Mikhailov and V. A. Dorokhov, *Zh. Obshch. Khim., 31*, 1961, 4020 for an example of a redistribution reaction leading to an arylborane; ref. 7, pp 208–210 provides a brief discussion and literature background for redistribution reactions in general.

[12] For a discussion of procedures for handling and estimating organoboranes, see: H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, *Organic Syntheses via Boranes*, John Wiley and Sons, New York, 1975.

[13] E. Negishi, J. J. Katz, and H. C. Brown, *J. Am. Chem. Soc., 94*, 1972, 4025.