

The Chemistry of Organoborates. Part III.¹ Protonation of Trialkylcyanoborates

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Protonation of trialkylcyanoborates in bis-(2-methoxyethyl) ether (diglyme) leads to migration of two alkyl groups from boron to carbon and the production of derivatives of 1,4-diaza-2,5-diboracyclohexane. On oxidation, these compounds yield ketones.

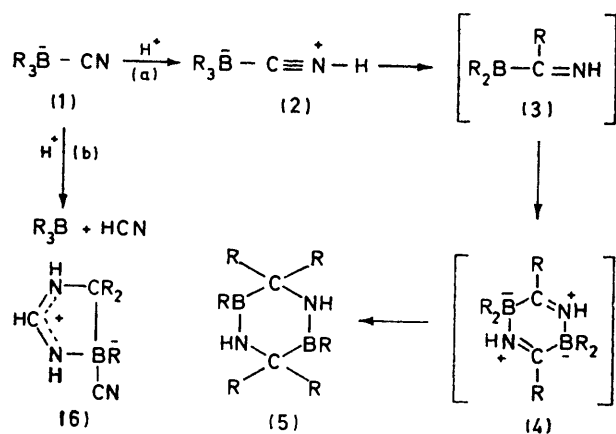
As part of a general examination of the reactions of electrophiles with certain organoborate salts² we have previously reported studies of the acylation of trialkylcyanoborates.^{1,2} The simplest electrophile is the proton and this paper is concerned with the reaction of

¹ Part II, A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, preceding paper.

protic acids with such salts. Protonation of a trialkylcyanoborate (1) could yield the ylide (2) [Scheme 1, path (a)], a process formally equivalent to the addition of hydrogen isocyanide to a trialkylborane. The reaction of neat hydrogen cyanide with trialkylboranes

² Part I, A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J.C.S. Perkin I*, 1974, 129.

has been investigated³ and small yields of (5) (5–14%) and also (6) (2–10%), produced by the reaction of hydrogen cyanide with (3),⁴ have been reported. The



SCHEME 1

pathway leading to (5) is similar to pathways proposed for the reactions of isonitriles with trialkylboranes.⁵⁻⁸

It was hoped that protonation of (1) would give intermediate (2) by path (a) in a manner analogous to the protonation of cyanopentacarbonylmetalates.⁹ Such an intermediate would not be expected in any quantity in the hydrogen cyanide reaction owing to the known instability of hydrogen isocyanide with respect to hydrogen cyanide.¹⁰ From (2) the products (4) or (5) would be anticipated.

RESULTS AND DISCUSSION

Treatment of sodium cyanotriethylborate in aqueous bis-(2-methoxyethyl) ether (diglyme) with hydrochloric acid followed by oxidation gave only octan-1-ol. However, when the same salt was prepared in diglyme and treated with dry hydrogen chloride at 25° some migrations did occur as evidenced by the isolation of a little diethyl ketone (*ca.* 2%) on oxidation. Repetition of the reaction in more forcing conditions (5 h at 110°) gave the ketone in *ca.* 45% yield but no improvement was effected by further heating. The use of other acids (toluene-*p*-sulphonic acid or its hydrate, methanesulphonic acid, or β -naphthylsulphonic acid hydrate) gave identical results, although trichloroacetic acid did not induce migration. Other trialkylboranes also gave yields of ketones consistently in the range 40–50%. Although this was considerably better than that obtained by the reaction of hydrogen cyanide with a trialkylborane (7% in the one case given)⁴ it fell short of the yield required for a useful synthetic reaction.

Since the production of the organoborate salt is essentially a quantitative process^{1,2} and since variations

³ W. Haussleiter, Dissertation, University of Erlangen, Nurnberg, 1967.

⁴ G. Hesse, H. Witte, and H. Haussleiter, *Angew. Chem. Internat. Edn.*, 1966, **5**, 723.

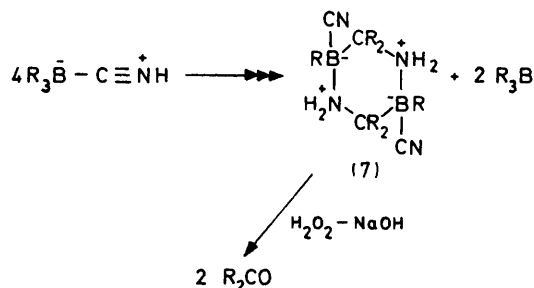
⁵ G. Hesse, H. Witte, and G. Bittner, *Annalen*, 1963, **687**, 9.

⁶ J. Casanova, jun., and R. E. Schuster, *Tetrahedron Letters*, 1964, 405.

⁷ H. Witte, *Tetrahedron Letters*, 1965, 1127.

in the borane, type of acid, proportions of reactants (*e.g.* excess of acid), temperature, and order of addition of the reagents, did not increase the yield, it appeared that a limiting yield of *ca.* 50% for the product of a double migration might be an intrinsic part of the reaction. If four molecules of (2) were ultimately giving rise to one molecule of (7), the hydrogen cyanide adduct of (5), and leaving two molecules of trialkylborane unchanged (Scheme 2), then the yield of ketone would be limited to a 50% maximum. The validity of this hypothesis was tested by isolation of an intermediate.

Isolation and Characterisation of an Intermediate.—For isolation purposes, cyanotriethylborate was used as starting material. When the protonation was carried out in diglyme it was possible to distill tricyclopentylborane from the filtered reaction mixture in accord with the pathway in Scheme 2. The residue from the distillation was not easily purified so attention was turned to the use of tetrahydrofuran (THF) as solvent. In this solvent, process (b) (Scheme 1) predominated, in strong contrast to the reaction occurring in diglyme,¹¹ the reactions being monitored by their i.r. spectra. However, control reactions using a large excess of hydrogen cyanide with the trialkylborane under the same conditions showed that very little migration occurred. Thus the presence of some trialkylborane



SCHEME 2

and hydrogen cyanide produced by path (b) does not interfere seriously with the reaction under investigation and indeed the purified product from the reaction in THF had the same i.r. characteristics as the crude product from the diglyme reaction. Filtration of the reaction mixture (the supernatant liquid contained tricyclopentylborane) and removal of THF at the pump gave a colourless crystalline product which was recrystallised from cyclohexane. It was stable under nitrogen but hygroscopic in air. The i.r. spectrum showed peaks at 3280–3000 ($\text{>}\dot{N}H_2$ stretch), 2200 ($C \equiv N$ stretch), 1625, 1570 ($\text{>}\dot{N}H_2$ bend), and 1500 cm^{-1} ($\text{>}\dot{B}-\dot{N}<$) in accord with structure (7). In addition bands at 1055 and 890 cm^{-1} suggested solvation by

⁸ J. Casanova, jun., and H. R. Kiefer, *J. Org. Chem.*, 1969, **34**, 2579, and references therein.

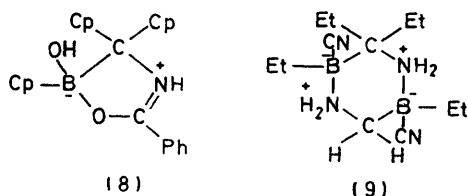
⁹ R. B. King, *Inorg. Chem.*, 1967, **6**, 25.

¹⁰ N. V. Sidgwick, 'The Chemical Elements and their Compounds,' Oxford, University Press, London, 1950, p. 669.

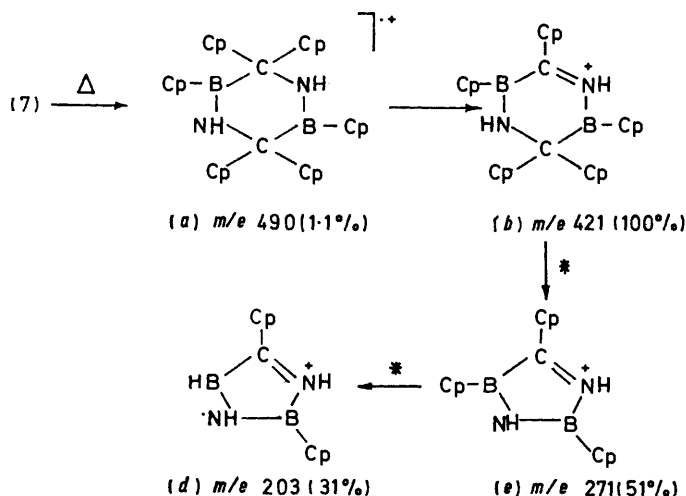
¹¹ C. R. Harrison, University College of Swansea, unpublished observations.

THF, a proposal confirmed by the ^1H n.m.r. spectrum which gave a ratio of THF to (7) of *ca.* 1.5:1.0. The n.m.r. spectrum showed little else of significance except broad signals at low field which disappeared on addition of deuterium oxide.

The mass spectrum corresponded to structure (5), the compound having presumably lost two molecules of hydrogen cyanide prior to volatilisation. This is not unexpected as compound (8) loses water in the same way,² but is a contrast to the recorded spectrum of (9) where the highest ion observed was $M^+ - \text{C}_2\text{H}_5$ (*m/e* 275).³ A possible breakdown pattern of (7; R = Cp)



(Cp = cyclopentyl) is given in Scheme 3, the composition of all peaks having been determined by accurate mass measurements.



SCHEME 3 An asterisk indicates the observation of a metastable peak for the transformation

The evidence in hand points to the structure (7) for the intermediate in the reaction. The only point of doubt remaining is whether the intermediate is (7), the di-adduct of hydrogen cyanide with (5) or a possible mono-adduct. Unfortunately, (7) was both air-sensitive and hygroscopic and therefore accurate analyses were not possible. However, Haussleiter³ has shown that (5; R = Et) picks up 2 mol. equiv. of hydrogen cyanide to give (9), the i.r. spectrum of which is very similar to that of our intermediate. The stoichiometry of the protonation reaction also favours (7) as the intermediate. The stage at which abstraction of the elements of hydrogen cyanide from (2) occurs is not known.

¹² H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, 1967, **89**, 2738.

Synthetic Applications of the Protonation Reaction.—In order that the reaction studied be synthetically attractive the yields had to be raised above 45%. This was achieved by maintaining an excess of hydrogen cyanide in the reaction mixture during reaction, through continuous slow addition of a diglyme solution of hydrogen cyanide. The role of the hydrogen cyanide was to satisfy the requirements of compound (5), leaving (2) intact and available for further migration. The yields of ketone based on starting olefin were di-*n*-octyl ketone, 68%; di-*n*-butyl ketone, 65%; dicyclopentyl ketone, 69%; dicyclohexyl ketone, 50%; and dinorbornyl ketone, 62%, all yields being of isolated purified product.

CONCLUSION

Protonation of trialkylcyanoborates in diglyme with strong acids, followed by a period of heating at *ca.* 100°, leads to compounds of structure (7). Oxidation with alkaline hydrogen peroxide produces ketones, but the yield based on starting olefin is low (40–45%). The yields can be boosted to synthetically viable levels by addition of an excess of hydrogen cyanide to the reaction mixture, but remain lower than those obtained on acylation of trialkylcyanoborates.

EXPERIMENTAL

Synthesis of Ketones by Protonation of Trialkylcyanoborates.—The apparatus was a three-necked flask fitted with a magnetic stirrer, two stopcocks (one bearing a serum cap above it), and a pressure-equalising dropping funnel which was also topped by a serum capped stopcock. The uncapped stopcock was connected to a three-way tap, which led to a dry, oxygen-free nitrogen supply and to a vacuum pump. Sodium cyanide (0.54 g, 11 mmol) was placed in the flask and the apparatus was deoxygenated by repeated evacuation-refilling with nitrogen. Trialkylboranes were prepared in the dropping funnel from alkene (30 mmol) and $\text{BH}_3\text{-THF}$ (6.7 ml; 1.5M solution in THF) in diglyme (15 ml). The solution was run onto the cyanide and the funnel washed with more diglyme (2×5 ml). THF was then removed at the pump and the mixture stirred for 1 h at 20°. Methanesulphonic acid (1.15 g, 12 mmol) was added by syringe to the stirred solution at 25°. A solution of hydrogen cyanide in diglyme (1.5M; 7 ml) was added and the temperature of the reaction mixture was raised to 110°, a small (*ca.* 4 cmHg) positive pressure of nitrogen being maintained throughout. A further 20 ml of the 1.5M-hydrogen cyanide was slowly added over 7 h from the dropping funnel.

The mixture was cooled to 0° and oxidised in the usual way.² Normal work-up² gave the ketones, which were identical with samples prepared by acylation of cyanoborates:² di-*n*-octyl ketone, yield 1.73 g (68%), m.p. 48.5–49° (lit.,¹² 49.5–50.5°); di-*n*-butyl ketone, yield 0.92 g (65%), b.p. 185° at 760 mmHg (lit.,¹³ b.p. 188.4°), n_D^{19} 1.4283 (lit.,¹² n_D^{20} 1.4201); dicyclopentyl ketone, yield 1.14 g (69%), b.p. 92–93° at 5 mmHg, n_D^{22} 1.4785 (lit.,¹² n_D^{20} 1.4976); dinitrophenylhydrazones, m.p. 94.0–94.5°; dicyclohexyl ketone, yield 0.97 g (50%), b.p. 145° at 15 mmHg, n_D^{19} 1.4849 (lit.,¹² n_D^{20} 1.4847); di-*exo*-2-nor-

¹³ 'Handbook of Chemistry and Physics,' 53rd edn., The Chemical Rubber Company, Cleveland, 1973.

bornyl ketone, yield 1.35 g (62%), m.p. 52–54° (from methanol) (lit.,¹² 53–54°).

Preparation of 2,5-Dicyano-2,3,3,5,6,6-hexacyclopentyl-1,4-diazonia-2,5-diboratacyclohexane (7; R = cyclopentyl).—The standard cyanoborate apparatus² was used and cyanotricyclopentylborate (15 mmol) was prepared as usual, in THF. A solution of dry hydrogen chloride in THF (1.5M; 10 ml) was added and the mixture warmed at 60° for 40 h whilst maintaining a small positive pressure of nitrogen. The reaction mixture was filtered in a closed system and THF was pumped off to give a glass which partly crystallised. The material was crystallised from cyclohexane (all operations carried out in a dry-box under nitrogen) and the cyclohexane (containing tricyclopentylborane) removed with a syringe. The solid was washed with pentane and finally all solvent was removed

at the pump. The material was hygroscopic and definitive analyses could not be obtained, ν_{\max} . (Nujol) 3280–3000 (NH_2), 2200 ($\text{C}\equiv\text{N}$), 1625, 1570 ($\text{>N}^+\text{H}_2$), 1500 (B–N), 1055, and 890 cm^{-1} (THF), m/e 490, 421, 271, and 203 (all these peaks had isotope ratios of 16:8:1 as expected for a B_2 compound). Found for the ions in Scheme 3; (a), m/e 490.4612 ($\text{C}_{32}\text{H}_{56}\text{N}_2^{11}\text{B}_2$ requires 490.4629); (b), m/e 421.3931 ($\text{C}_{27}\text{H}_{47}\text{N}_2^{11}\text{B}_2$ requires 421.3925); (c), m/e 271.2518 ($\text{C}_{16}\text{H}_{29}\text{N}_2^{11}\text{B}_2$ requires 271.2517); and (d), m/e 203.1904 ($\text{C}_{11}\text{H}_{21}\text{N}_2^{11}\text{B}_2$ requires 203.1891). The n.m.r. spectrum showed that the molecule was solvated by *ca.* 1.5 equiv. of THF.

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