New Uses for Old Complexes. Hydroborations involving Nitrogen and Phosphorus Complexes of Borane

By Andrew Pelter,*[a] Richard Rosser,[a] and Stuart Mills[b]

[[a] *Department of Chemistry, University College of Swansea, Swansea* SA2 8PP, *West Glamorgan* and
[b] *I.C.I. (Pharmaceuticals) Ltd., Alderley Park, Macclesfield* SK10 4TG, *Cheshire*]

Summary Two novel methods are presented for utilising stable and readily available borane complexes for hydroboration in mild conditions; crystalline triphenyl phosphite–borane may be used without activation.

Alkenes are normally hydroborated by use of either Me_2S–BH_3(BMS) or tetrahydrofuran (THF)–BH_3 complexes.[1,2] However these weak complexes are sensitive to oxygen and moisture and their use involves special storage and handling techniques.[2] The very stable phosphine complexes of borane up till now have found no use as hydroborating agents and the trialkylamine–borane complexes only very limited use for high temperature hydroboration in a limited number of cases.[1] We therefore set ourselves to see whether, by conversion of the Lewis base ligand into a neutral molecule under mild conditions, it would be possible to use stable borane complexes as hydroborating agents.

We first examined the commercially available triethylamine–borane complex. This substance hydroborates oct-1-ene to the extent of 29%† after 2 h reflux in THF. This was raised to 70% by the inclusion of 1 equiv. of methyl iodide and to 93% (g.c.) by reflux for 6 h in THF containing 3 equiv. of methyl iodide. The reaction is solvent-sensitive (*e.g.* with the same excess of methyl iodide, reflux in CH_2Cl_2 for 24 h gave only a trace of hydroboration) and methyl iodide was the best of the alkylating agents tried.

Pyridine–borane hydroborates oct-1-ene to the extent of 38% in 2 h in refluxing THF but, unlike the triethylamine complex, hydroboration is not significantly increased by the presence of methyl iodide.

---

† The degree of hydroboration was estimated by oxidation and g.c. estimation or isolation of the resulting alcohols. For all hydroborations reported in this paper, the ratio of 1- and 2-alcohols was the same as for hydroboration with THF–BH_3, showing *that no isomerisation of the intermediate alkylboranes had occurred.*

Triphenylphosphine–borane (TPPB) is a crystalline solid, m.p. 189 °C, which was unchanged after six months on the open bench and was recovered from attempted oxidation with alkaline hydrogen peroxide. It has been reported to resist 3 M-HCl at 150 °C for 3 h, but will exchange the hydrogen atoms attached to boron for deuterium or halogen.[3]

We find that TPPB alone *can* hydroborate oct-1-ene but the reaction is incomplete (75%) even after 16 h reflux in 1,2-dimethoxyethane (DME) at 85 °C. However addition of methyl iodide (3 mol. equiv.) led to efficient hydroboration, the optimal conditions being 6 h reflux in THF (88%, g.c.) or 2 h reflux in DME (95%, g.c.). It is particularly noteworthy that the production of tricyclohexylborane (95%, g.c.) requires no modification of the reaction conditions. Oxidation of the reaction mixture leads to alcohols which are readily separable by flash chromatography from the byproducts.

In order to check that the phosphonium iodide produced was not detrimental to further reactions, particularly carbon–carbon bond formation, hex-1-ene was carried through the three-migration cyanoborate reaction[4] to yield trihexylmethanol in 76% (g.c.) yield while cyclohexene was subjected to the two-migration process[5] to yield dicyclohexyl ketone in 74% (isolated) yield.

Another method for activating triphenylphosphine–borane to hydroboration would be to oxidise the triphenylphosphine to the inert, neutral triphenylphosphine oxide. However oxidising conditions are incompatible with the survival of borane and instead we chose to study the production of triphenylphosphine sulphide. It is known[6] that trialkyl- and triaryl-phosphines react exothermically with elemental sulphur, at different rates depending on the allotrope of sulphur used.[7] We therefore added sulphur (S_8) in the ratio of one atom of sulphur : one molecule of TPPB to the reaction mixture and found that this was an even more efficient process than alkylation for the induction of hydroboration. Oct-1-ene was hydroborated (92%, g.c.) after only 2 h reflux in THF and to the extent of 97% (g.c., 93% isolated) after 1 h reflux in DME, whilst cyclohexene was 97% (g.c.) hydroborated also after 2 h reflux in THF.

Both the alkylation and sulphurisation reactions are solvent sensitive and use of dichloromethane or benzene dramatically lowers the yields. The reactions are summarised in equations (1) and (2), and represent completely new methods for the activation of borane complexes. It should be noted that neither reaction is of use for the activation of trialkylphosphine–borane complexes.

$$\mathrm{Ph_3P.BH_3 + 3C_8H_{16} + MeI \rightarrow (C_8H_{17})_3B + Ph_3\overset{+}{P}Me\ I^-} \tag{1}$$

$$\mathrm{Ph_3P.BH_3 + 3C_8H_{16} + S \rightarrow (C_8H_{17})_3B + Ph_3P{=}S} \tag{2}$$

Triphenyl phosphite–borane [$(PhO)_3P.BH_3$] is a white, crystalline solid m.p. 48—49 °C[8] readily prepared by mixing equimolar proportions of triphenyl phosphite and borane—THF. It proved a ready hydroborating agent and completely hydroborated oct-1-ene after 2 h in refluxing DME (96% g.c.; 85% isolated) or 6 h in refluxing THF (92%, g.c.). After storing for 30 weeks with no special protection from moisture the complex still hydroborated oct-1-ene to the extent of 84% (g.c.) in 2 h in refluxing DME. Nor does the presence of triphenyl phosphite inhibit the formation of carbon–carbon bonds as cyclohexene was converted into dicyclohexyl ketone[5] in excellent yields (84% g.c., 80% isolated) using $(PhO)_3P.BH_3$ for the hydroboration step. Trialkyl phosphite complexes could not be similarly utilised.

As a result of these studies, borane for hydroboration is for the first time available in a readily manipulated, stable form that can be kept in the laboratory and activated under mild conditions.

We shall report separately on our studies of the phosphine and phosphite complexes of 1,1,2-trimethylpropylborane and related alkylboranes.[9]‡

One of us, R. R., thanks the S.R.C. and I.C.I. (Pharmaceuticals) Ltd. for financial support.

(*Received*, 10*th July* 1981; *Com.* 807.)

---

‡ We thank Professor H. J. Bestmann (Erlangen) for informing us of his latest results on the formation and alkylation of alkylborane–triphenylphosphine complexes.

[1] A. Pelter and K. Smith, 'Comprehensive Organic Chemistry,' Vol. III, ed. D. N. Jones, Pergamon Press, Oxford, 1980, pp. 695—790.

[2] H. C. Brown, 'Organic Synthesis *via* Boranes,' Wiley Interscience, New York, 1975.

[3] M. A. Frisch, H. G. Heal, H. Mackle, and I. O. Madden, *J. Chem. Soc.*, 1965, 899.

[4] A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, *J. Chem. Soc., Perkin Trans.* 1, 1975, 138.

[5] A. Pelter, K. Smith, M. G. Hutchings, and K. Rowe, *J. Chem. Soc., Perkin Trans.* 1, 1975, 129.

[6] W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 1944, 276; J. R. von Wazer, 'Phosphorus and its Compounds,' Interscience, New York, 1958, p. 307.

[7] P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, 1956, **78**, 3710.

[8] P. A. Chopard and R. F. Hudson, *J. Inorg. Nucl. Chem.*, 1963, **25**, 801.

[9] J. H. Bestmann, R.S.C. Symposium on Metallo-organic Chemistry, 'Book of Slides,' 1980; Am. Chem. Soc. Meeting Report, International Conference on Phosphorus Chemistry, 1981.