The Reactions of Electrophilic Reagents with Trialkylcyanoborates: Some New Efficient Ketone Syntheses

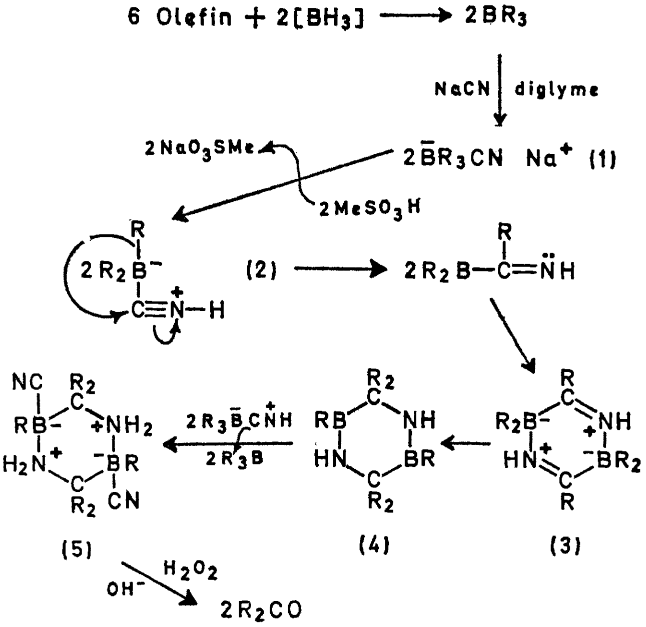
By ANDREW PELTER,* M. G. HUTCHINGS, and K. SMITH
(*Chemistry Department, The University, Manchester* M13 9PL)

Summary Trialkylcyanoborates can be used in the preparation, in high yield, of the corresponding dialkyl ketones, by treatment with an electrophilic reagent followed by alkaline hydrogen peroxide.

TRIALKYLCYANOBORATES (1) offer attractive possibilities as synthetic intermediates since attack by electrophiles can convert them from stable salts[1] into ylides and so promote alkyl migrations from boron to carbon. In addition, new reactions in which the nitrogen of the cyanide group has been retained in the products may be expected. A recent report[2] on the acetylation of potassium triethylcyanoborate to yield, after oxidation, diethyl ketone in *ca.* 40% yield prompts a brief report of our own studies.[3]

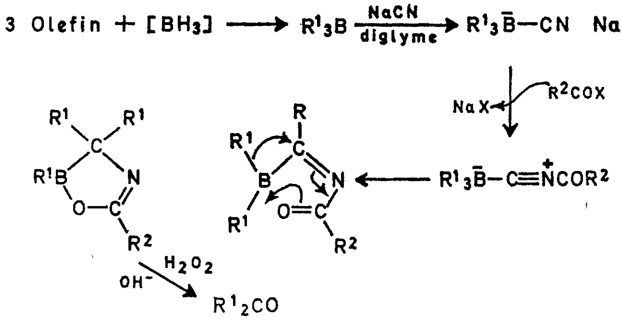
For the purposes of organic synthesis no intermediates need be isolated. The salts (1) are prepared *in situ* by adding the trialkylborane to a stirred suspension of sodium cyanide in diglyme. After dissolution of the solid, the electrophilic reagent is added and after a suitable time the reaction mixture is treated with alkaline hydrogen peroxide. The ketone is isolated and purified by chromatography on a silica column. All the yields given in the Table refer to isolated, pure products, and are calculated from the initially added olefin.

The action of proton acids (methanesulphonic acid being the most convenient) was first studied. The pathway shown in Scheme 1 is suggested. The processes as far as (4) are entirely analogous to those occurring in the isonitrile addition to trialkylboranes.[4] However in the present case (4) is converted into the stable adducts (5) by abstraction of hydrogen cyanide from the ylide (2), thus limiting the potential yield of ketone to 50%, those realised being of the order of 40—45%. Slow addition of a solution of hydrogen cyanide in diglyme raised the yields to acceptable levels (see Table). Direct addition of hydrogen cyanide to trialkylboranes gives ketone in only *ca.* 10% yield after oxidation.[5] Presumably in these circumstances the production of ylide (2) is not favoured, or else it reacts further before migration.



SCHEME 1

In agreement with Hesse[2] it was found that acetylation of (1) gave only *ca.* 45% of ketone, on account of diketen formation. However when trifluoracetic anhydride or benzoyl chloride were used as electrophiles reaction proceeded according to Scheme 2 in a highly efficient fashion (see Table).



SCHEME 2

The reactions are rapid, are carried out in one flask, and proceed under mild conditions [room temperature for $(CF_3CO)_2O$ and 45° for PhCOCl]. No specific manipulative techniques are required and the overall result, particularly using the aliphatic anhydride compares very favourably with carbon monoxide insertion.[6]

In our hands, alkylation using triethyloxonium borofluoride or dimethyl sulphate gave ketone, but unexpectedly in *ca.* 50% yield only.

% *Yields of ketones from olefins*

	Electrophilic reagent		
R	H^+/HCN	$(CF_3CO)_2O$	PhCOCl
n-Octyl ..	68	95	89
n-Butyl ..	65	94	74
Cyclopentyl ..	69	84	87
Cyclohexyl ..	50	100	65
Norbornyl ..	62	99	85

A typical experiment is outlined below (all manipulations except oxidation are carried out under dry nitrogen). Trinorbornylborane (10 mmoles) in diglyme (8 ml) was prepared in the usual way in a dropping funnel from norbornene (30 mmoles), and added to a suspension of powdered NaCN (12 mmoles) in diglyme (4 ml). The mixture was stirred at room temp. for 45 min., cooled to −78°, and trifluoroacetic anhydride (15 mmoles) was added. The reaction was allowed to reach room temperature, then stirred for 1 h. Oxidation was carried out with NaOH (3N, 12 ml) and H_2O_2 (50%, 8 ml) for 3 h. at room temp. then 10 min. at 50°. The product was taken up into pentane and the crude neutral fraction washed on to a dry silica column with a little pentane. Elution with pentane was followed by elution with benzene to yield di-*exo*-norbornyl ketone (2·17 g, 99%).

(*Received, September 28th,* 1970; *Com.* 1668.)

---

[1] H. Witte, E. Brehm, and G. Hesse, *Z. Naturforsch.*, 1967, **22b**, 1083.
[2] E. Brehm, A. Haag, G. Hesse, and H. Witte, *Annalen*, 1970, **737**, 70.
[3] K. Smith, M.Sc. Thesis, Manchester University, 1969.
[4] J. Casanova and H. R. Kiefer, *J. Org. Chem.*, 1969, **34**, 2579; G. Hesse and H. Witte, *Annalen*, 1965, **687**, 1.
[5] G. Hesse, H. Witte, and H. Haussleiter, *Angew. Chem.*, 1966, **78**, 748.
[6] H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, 1967, **89**, 2738.