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New Method for the Synthesis of Organoboranes

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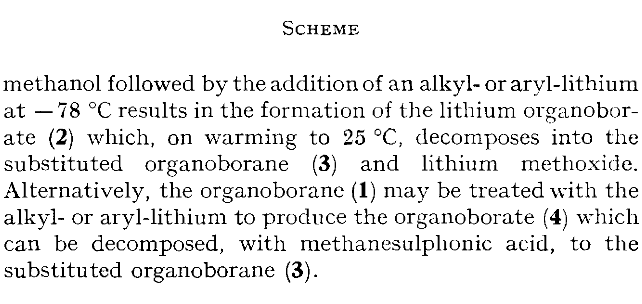
Summary Mixed organoboranes can be conveniently prepared in a single stage by treatment of a dialkylborane with various lithium dialkyl- or diaryl-cuprates.

MIXED organoboranes may be prepared by the hydroboration of unsaturated systems [equation (1)].[1,2]

$$R^1R^2C{=}CR^3R^4 + HBR^5R^6 \rightarrow R^1R^2CH\text{-}CR^3R^4\text{-}BR^5R^6 \quad (1)$$

For the preparation of *B*-methyl and *B*-aryl organoboranes where hydroboration is not possible, alternative methods are available (Scheme).[3,4] The treatment of a borane (**1**) with methanol followed by the addition of an alkyl- or aryl-lithium at −78 °C results in the formation of the lithium organoborate (**2**) which, on warming to 25 °C, decomposes into the substituted organoborane (**3**) and lithium methoxide. Alternatively, the organoborane (**1**) may be treated with the alkyl- or aryl-lithium to produce the organoborate (**4**) which can be decomposed, with methanesulphonic acid, to the substituted organoborane (**3**).



SCHEME

Recently, we had reason to synthesise, *in situ*, various *B*-alkyl-9-borabicyclo[3·3·1]nonane (9-BBN) derivatives. The methods already described appeared inconvenient because there was excess of alcohol in the system and two stages were required to produce the desired product.

We report here a convenient synthesis of *B*-alkyl-9-BBN derivatives that not only circumvents the problems of introducing protic elements, but also allows a completely new, single-stage approach to their preparation.

Our synthesis involves the alkylation of the electron-deficient boron atom of 9-BBN (**5**) [equation (2)] with readily available lithium dialkylcuprates.[5] The reaction is extremely clean and the product organoboranes (**6**) are either isolated from the reaction mixture (Table) or used in further synthetic reactions. They were identified by g.l.c. comparison with authentic compounds prepared using published procedures.[3,4]

$$\underset{(\mathbf{5})}{\text{B-H-9-BBN}} + R_2CuLi \xrightarrow{-78 \rightarrow 20\ ^\circ C} \underset{(\mathbf{6})}{\text{B-R-9-BBN}} + Cu^0 + Li^0 + RH \quad (2)$$

TABLE. Reactions of the organoborane B-H-9-BBN (**5**) with lithium dialkylcuprates R$_2$CuLi to give the derivatives B-R-9-BBN [reaction (2)].

	Product B-R-9-BBN		
	B.p./°C	% Yield	
R$_2$CuLi	(mmHg)	G.l.c.	Isolated
Me$_2$CuLi	38—40 (1)	98	93
Bu$^n_2$CuLi	79—82 (1)	96	90
Ph$_2$CuLi [a]	110 (0·5)	90	80

[a] Tetrahydrofuran–ether as solvent.

The mechanism probably involves an alkylation of the boron atom to produce lithium *B*-alkyl-9-BBN-hydride followed by a hydride reduction of the released alkyl copper to Cu^0, Li^0, and the corresponding alkane. This argument is supported by the action of the readily available lithium triethylborohydride on methylcopper in ether at 0 °C [equation (3)]. Colloidal copper was precipitated and triethylborane was formed. Our results are listed in the Table.

$$Li^+ Et_3BH^- + MeCu \rightarrow Et_3B + Cu^0 + Li^0 + CH_4 \qquad (3)$$

We are presently exploiting the reaction of other functionalised dialkyl cuprates with 9-BBN and subsequently with other borane derivatives.[6]

The following experimental procedure is representative. A mixture of copper(I) iodide (5·0 mmol) and dry ether (30 mls) was cooled to 0 °C, and methyl-lithium (10·0 mmol) added slowly *via* a syringe. The solution was stirred at this temperature (10 min), cooled to −78 °C, 9-BBN (Aldrich; 5·0 mmol) added, and the whole allowed to reach room temperature. At −35 °C a black colloidal suspension of copper began to form with a concomitant evolution of gas (methane.) The clear, colourless solution was stirred at room temperature for 1 h and then carefully decanted off, the solvent removed under reduced pressure, and the residue carefully distilled to afford an oil [632 mg, 93%, b.p. 38—40 °C (1 mmHg)], identified as *B*-methyl-9-borabicyclo-[3·3·1]nonane.†

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† Analogous by g.l.c. with an authentic sample.

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