encountered in many reactions of organoboranes in which only one of the three groups on boron is utilized.[2] Indeed, we have observed that the B-R-9-BBN derivatives may be advantageously utilized in the alkylation of esters,[6] the alkylation of ketones,[7] and the synthesis of cyclopropanes.[8]

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(6) H. C. Brown and M. M. Rogic, *J. Am. Chem. Soc.*, **91**, 2146 (1969).
(7) H. C. Brown, M. M. Rogic, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).
(8) H. C. Brown and S. P. Rhodes, *ibid.*, **91**, 2149 (1969).
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Reaction of B-Alkyl-9-borabicyclo[3.3.1]nonanes with Ethyl Mono- and Dihaloacetates under the Influence of Potassium *t*-Butoxide. A Convenient Procedure for the Conversion of Olefins into Esters or α-Halo Esters *via* Hydroboration

Sir:

We recently reported that trialkylboranes undergo facile reaction with ethyl bromoacetate under the influence of potassium *t*-butoxide,[1] providing a remarkably simple synthesis of esters with the addition of a two-carbon moiety to the structure (carbethoxymethylation) (1). This reaction can be extended to ethyl di-

$$R_3B + BrCH_2CO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} RCH_2CO_2C_2H_5 \quad (1)$$

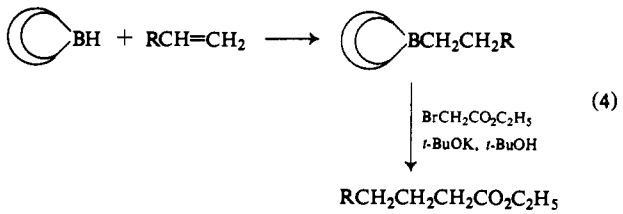
bromoacetate or ethyl dichloroacetate, providing an equally simple synthesis of the corresponding α-halocarboxylic acid esters[2] (2, 3).

$$R_3B + Br_2CHCO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} \underset{\displaystyle Br}{RCHCO_2C_2H_5} \quad (2)$$

$$R_3B + Cl_2CHCO_2C_2H_5 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} \underset{\displaystyle Cl}{RCHCO_2C_2H_5} \quad (3)$$

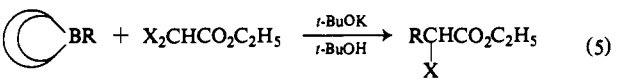
Unfortunately, in these carbethoxymethylation reactions, as in the related one-carbon-atom homologation (carbonylation)[3] and three-carbon-atom homologation (γ-propanalation)[4] reactions, only 33% of the olefin used to form the organoborane, or one of the three alkyl groups on the organoborane, R_3B, is utilized. This limitation could constitute a major difficulty in cases where it is desired to apply these homologation reactions to valuable intermediates.

We previously reported that the use of the B-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN)[5] solved this difficulty for the aldehyde synthesis.[6] We now wish to report that the use of these intermediates likewise solves this difficulty for the ester synthesis (4).



(4)

The yields observed were in the range of 50–80%, indicating some competition between migration of the B-alkyl group and the boron–cyclooctyl bond. However, preferential migration of the B-alkyl groups was greatly enhanced in the corresponding reactions with ethyl dibromoacetate and ethyl dichloroacetate, providing the corresponding α-halocarboxylic acid esters in yields of 70–90% (5).



(5)

The results are summarized in Table I.

The following procedure is illustrative. A dry flask equipped with the usual accessories[6] and maintained under nitrogen was charged with 170 ml of tetrahydrofuran and 28.6 ml of a solution of borane (100 mmol) in the same solvent. To the stirred solution at room temperature 12.3 ml (100 mmol) of *cis*-1,5-cyclooctadiene was added over a period of 15 min. At the end of the addition, the temperature had risen to 55–60°. The reaction mixture was refluxed for 1.5 hr and then cooled to 45°. Cyclohexene, 10.1 ml (100 mmol), was introduced and the reaction mixture stirred at 45–50° for 2 hr and then cooled in an ice bath. (The hydroboration of cyclohexene is relatively slow). In most other cases the hydroboration with 9-BBN[5] is complete in a few minutes at 25°.) *t*-Butyl alcohol, 50 ml, and 12.2 ml (100 mmol) of ethyl dichloroacetate was introduced followed by the dropwise addition of 100 ml of 1.00 *M* potassium *t*-butoxide in *t*-butyl alcohol over a period of 30 min. Glpc analysis of the reaction mixture indicated an 81% yield of ethyl α-chlorocyclohexylacetate. To the reaction mixture was added 33 ml of 3 *M* sodium acetate, followed by dropwise addition of 22 ml of 30% of hydrogen peroxide. The reaction mixture was stirred at room temperature for 30 min and then saturated with sodium chloride. The organic layer was separated, dried over magnesium sulfate, and distilled. There was obtained

(1) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *J. Am. Chem. Soc.*, **90**, 818 (1968).
(2) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 1811 (1968).
(3) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968).
(4) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, **89**, 5709 (1967); H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogić, *ibid.*, **90**, 4165 (1968); H. C. Brown, M. W. Rathke, G. W. Kabalka, and M. M. Rogić, *ibid.*, **90**, 4166 (1968).
(5) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280, 5281, 5283 (1968).
(6) H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969).

Table I. Conversion of Olefins into Ethyl Alkanoates and 2-Haloalkanoates by the Reaction of the Corresponding B-Alkyl-9-borabicyclo[3.3.1]nonanes with Ethyl α-Haloacetates under the Influence of Potassium *t*-Butoxide[a]

Olefin	Ethyl α-haloacetate	Product	Yield, %[c]
Ethene	Br	Ethyl *n*-butyrate[b]	51
1-Butene	Br	Ethyl hexanoate	59
2-Butene	Br	Ethyl 3-methylpentanoate	68
Isobutylene	Br	Ethyl 4-methylpentanoate	53
1-Hexene	Br	Ethyl octanoate	74
1-Hexene	Cl	Ethyl octanoate	74
Cyclopentene	Br	Ethyl cyclopentylacetate	63
1-Methylcyclopentene	Br	Ethyl (*trans*-2-methylcyclopentyl)acetate[d]	57
Cyclohexene	Br	Ethyl cyclohexylacetate	62
Cyclohexene	Br_2	Ethyl α-bromocyclohexylacetate	68
Cyclohexene	Cl_2	Ethyl α-chlorocyclohexylacetate	88
Cyclopentene	Cl_2	Ethyl α-chlorocyclopentylacetate	90

[a] In each experiment, 10 mmol of potassium *t*-butoxide in *t*-butyl alcohol was added to 10 mmol of B-R-9-BBN and 10 mmol of the ethyl α-haloacetate at 0°. [b] 25°. [c] Analysis by glpc. [d] For discussion of stereochemistry, see H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *J. Am. Chem. Soc.*, **91**, 2150 (1969).

13.7 g (67% yield) of ethyl α-chlorocyclohexylacetate, bp 119.5° (12 mm), $n^{20}D$ 1.4654.

Hydroboration of 1-hexene with borane produces 94% 1-hexyl and 6% 2-hexyl groups. Since the reaction of trialkylboranes with the ethyl haloacetates exhibits little selectivity between primary and secondary alkyl groups, the products thus obtained are contaminated with small amounts of the isomeric esters. This difficulty is avoided by the use of 9-BBN.

Another major advantage is the apparently much smaller steric difficulties offered by the reagent. Thus, in the reaction of the ethyl dihaloacetates with trialkylboranes we previously experienced difficulties in utilizing relatively hindered organoboranes.[2] For example, tricyclopentylborane gave a product containing 54% ethyl α-chlorocyclopentylacetate and 30% of the corresponding α-*t*-butoxy derivative.[2] Use of B-cyclopentyl-9-BBN gave 90% of the desired ester, essentially free of the α-*t*-butoxy derivative (Table I). Similarly, our initial attempts to achieve the carbethoxymethylation of 1-methylcyclopentene by allowing the organoborane from this hindered olefin to react with ethyl bromoacetate failed. However, B-*trans*-2-methylcyclopentyl-9-BBN reacted readily, yielding the desired ester (Table I).

Recently, Hooz and Linke have reported that diazoacetone, diazoacetonitrile, and ethyl diazoacetate react with trialkylboranes to yield the corresponding ketones, nitriles, and esters.[7] This reaction also utilizes only one of the three alkyl groups on boron. We examined the reaction of B-*n*-butyl-9-BBN with ethyl diazoacetate. A rapid evolution of nitrogen was observed, but the reaction product corresponded to migration of one of the cyclooctylboron bonds, rather than to migration of the *n*-butyl group. Oxidation produced an 80% yield of a product tentatively identified as ethyl (*cis*-5-hydroxycyclooctyl)acetate.

It therefore appears that certain reactions of B-R-9-BBN involve preferential migration of the R-B bond, whereas other reactions take place with preferential migration of the B-cyclooctyl bond.[8] We have developed a tentative explanation, but prefer to defer discussion until it has been subjected to more extended testing.

(7) J. Hooz and S. Linke, *J. Am. Chem. Soc.*, **90**, 5936, 6891 (1968).

(8) A further puzzle is the observation that acrolein, which reacts with remarkable speed even with hindered trialkylboranes,[4] fails to react with B-R-9-BBN. See H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **91**, 2150 (1969).

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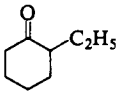
Reaction of B-Alkyl-9-borabicyclo[3.3.1]nonanes with α-Bromo Ketones under the Influence of Potassium *t*-Butoxide. A Convenient Procedure for the α Alkylation of Ketones

Sir:

Recently we reported that α-bromo ketones, such as phenacyl bromide and α-bromocyclohexanone, react readily with triethylborane under the influence of potassium *t*-butoxide in tetahydrofuran to produce the corresponding α-ethyl derivatives[1] (1, 2).

$$C_6H_5COCH_2Br + (C_2H_5)_3B + t\text{-BuOK} \xrightarrow{0^\circ} C_6H_5COCH_2CH_2CH_3 + t\text{-BuOB}(C_2H_5)_2 + KBr \quad (1)$$

$$+ (C_2H_5)_3B + t\text{-BuOK} \xrightarrow{0^\circ}$$



$$+ t\text{-BuOB}(C_2H_5)_2 + KBr \quad (2)$$

Attempts to use organoboranes in which the alkyl groups are highly substituted close to the reaction center, organoboranes such as tri-*sec*-butylborane and triisobutylborane, failed. Evidently the α-bromocarbanions from such α-bromo ketones are far more sensitive to the steric environment of the borane acceptor than are the corresponding α-halocarbanions from esters.[2] This represents a serious difficulty, apparently limiting this new alkylation procedure to relatively unhindered alkyl groups. The fact that only one of the three alkyl groups

(1) H. C. Brown, M. M. Rogic, and M. W. Rathke, *J. Am. Chem. Soc.*, **90**, 6218 (1968).

(2) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968).