temperature was added 24.6 ml (200 mmol) of *cis*-1,5-cyclooctadiene over a period of 15 min. At the end of the addition the temperature of the reaction mixture was 60–65°. The reaction mixture was refluxed for 1.5 hr and then cooled to 0°. *cis*-2-Butene, 11.2 g (200 mmol), was introduced from a cylinder and the reaction mixture stirred for 30 min to complete the hydroboration stage. One of the dropping funnels was charged with 39.8 g of phenacyl bromide in 200 ml of THF and the other with 200 ml of a 1.00 *M* solution of potassium *t*-butoxide in the same solvent. The two solutions were added simultaneously to the solution of B-*sec*-butyl-9-BBN maintained at 0°. Glpc examination of the solution indicated a 65% yield of β-methylvalerophenone. To the reaction mixture was then added 66 ml of 3 *M* sodium acetate, followed by dropwise addition of 45 ml of 30% hydrogen peroxide. The reaction mixture was stirred at room temperature for 1 hr and then diluted with the same volume of pentane. The pentane layer was then washed with 100-ml portions of water and dried, and the solvents were removed. Distillation, 88° at 1 mm, gave 17.6 g, a 50% yield, of β-methylvalerophenone, semicarbazone mp 179–180°.[4]

We have a caution to make. In condensation reactions experience indicates that the reaction conditions must be carefully adjusted to the characteristics of the reagents in order to achieve maximum yield.[5] The present synthesis has many of the characteristics of a condensation reaction. The results indicate that once conditions have been established for satisfactory reaction for a particular α-bromo ketone, such as phenacyl bromide or α-bromopinacolone, these same conditions are applicable to a large variety of alkyl groups in the form of the B-R-9-BBN derivative. However, each α-bromo ketone doubtless has its own characteristic, and it will probably be necessary to vary the reaction conditions (base, solvent, temperature) to achieve maximum yield.[6]

In spite of these difficulties, it is evident that this new alkylation procedure has many promising possibilities. Thus it has proven possible to alkylate with *sec*-butyl, isobutyl, cyclopentyl, and cyclohexyl groups, groups that are difficult to introduce by the usual reaction of alkyl halides with carbanions. We are currently exploring the introduction of aryl groups with the aid of B-aryl-9-BBN. Consequently, this new alkylation procedure is not merely an alternative to the procedures presently available for the alkylation of ketones, but it promises to make possible the introduction of groups which cannot be handled by the other processes currently available.

(5) See H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 7, for a discussion of the alkylation of active methylene compounds.

(6) For example, in one experiment with α-bromocyclohexanone and B-ethyl-9-BBN (Table I) no yield of α-ethylcyclohexanone was realized although we had previously realized a yield of 68% using triethylborane[1] for the alkylation. Yet with phenacyl bromide and α-bromopinacalone our yields with B-R-9-BBN were invariably higher than with the corresponding R_3B.

(7) Visiting scholar on funds provided by the Mitsui Petrochemical Co., Tokyo, Japan.

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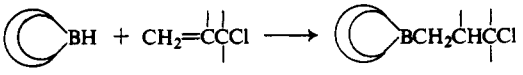
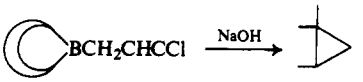
Facile Cyclization of B-(γ-Chloropropyl)-9-borabicyclo[3.3.1]nonanes. An Improved Synthesis of Cyclopropane Derivatives *via* Hydroboration

Sir:

We wish to report that B-(γ-chloropropyl)-9-borabicyclo[3.3.1]nonanes, readily available by the reaction of the parent borane, 9-BBN,[1] with appropriate allylic chlorides (1), undergo cyclization with aqueous sodium hydroxide, to form the corresponding cyclopropane derivatives (2).

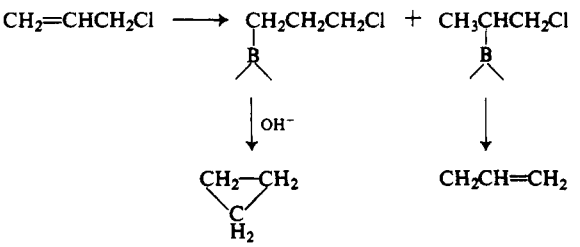


(1)



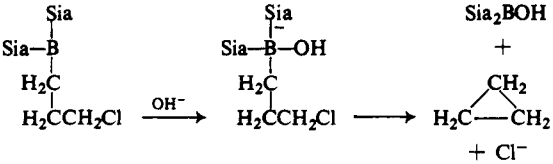
(2)

The cyclization of hydroborated allylic chlorides to form the corresponding cyclopropanes was discovered by Hawthorne and Dupont[2] and subsequently applied to the synthesis of a variety of cyclopropanes.[3] A major difficulty with this procedure is revealed by the parent compound, allyl chloride. The powerful directive effect of the substituent directs hydroboration with diborane to give roughly 50:50 of the two isomeric boron derivatives (3). Consequently, in such cases the maximum yield of cyclopropane derivative cannot be greater than approximately 50%.



(3)

This difficulty was circumvented by the use of the more selective hydroborating agent, disiamylborane.[4] It was subsequently observed that the use of this highly hindered borane introduced difficulty, especially when the chlorine substituent is relatively reactive.[5] The cyclization reaction apparently requires prior coordination of the base with the boron atom to produce a quaternary derivative which then undergoes cyclization (4). In the



(4)

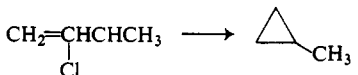
case of highly reactive chlorides, loss of the substituent is competitive with the slow coordination and cyclization.

(1) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5280, 5283 (1968).
(2) M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).
(3) M. F. Hawthorne, *ibid.*, **82**, 1886 (1960).
(4) H. C. Brown and K. A. Keblys, *ibid.*, **86**, 1791 (1964).
(5) Research in progress.

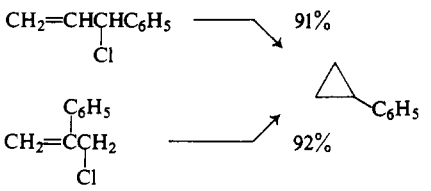
This difficulty can often be circumvented by utilizing more reactive bases, such as sodium triethylborohydride[6] or methyllithium,[5] in nonaqueous systems.

We have recently observed that 9-BBN exhibits the selectivity of disiamylborane in its hydroborations.[1] At the same time, the boron atom in the resulting derivatives, B-R-9-BBN, appears to be unusually open and susceptible to attack by nucleophiles.[7,8] This suggested an exploration of the applicability of 9-BBN for this cyclopropane synthesis. Indeed, we discovered that 9-BBN is ideal for the purpose, giving us considerably improved yields in many cases with a greatly simplified procedure.

In this way 1-methylallyl chloride was converted into methylcyclopropane in a yield of 85% (5). Similarly, both 1-phenylallyl chloride and 2-phenylallyl chloride are converted into phenylcyclopropane in yields of 91 and 92%, respectively (6).

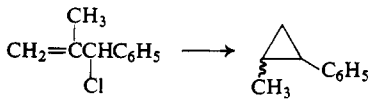


(5)

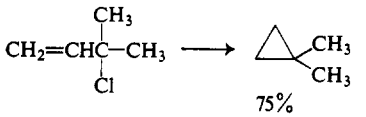


(6)

Even the relatively hindered 1-phenyl-2-methylallylic chloride (7) and the reactive tertiary chloride, 1,1-dimethylallyl chloride (8), are converted into the corresponding cyclopropanes without difficulty.

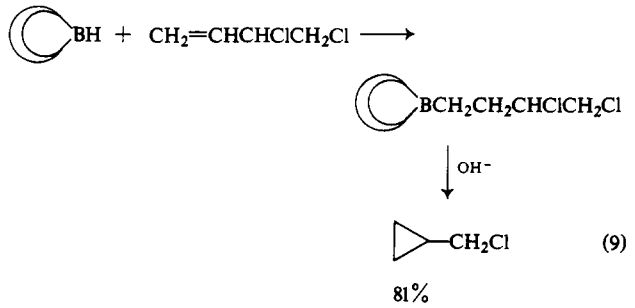


92% (*cis* + trans)
(7)



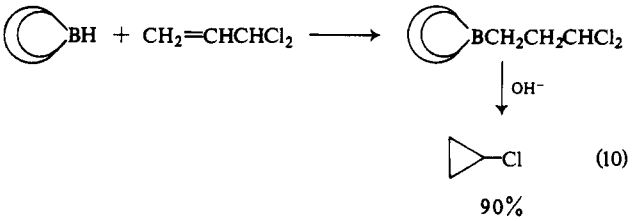
75%
(8)

To illustrate the utility of this new procedure we converted the commercially available 3,4-dichloro-1-butene into the highly reactive cyclopropylcarbinyl chloride in a yield of 81% (9).



81%
(9)

Finally, we transformed 1,1-dichloropropene, readily available from acrolein, into cyclopropyl chloride in a yield of 90% (10).



90%
(10)

The following procedure for the synthesis of cyclopropylcarbinyl chloride is illustrative. A dry flask, equipped with a septum inlet, a pressure-equalizing dropping funnel, and magnetic stirrer, was flushed with nitrogen and maintained under a static pressure of the gas. In the flask was placed 143 ml of 0.70 *M* 9-BBN (100 mmol) in THF. Then 12.5 g of 3,4-dichloro-1-butene[8] (100 mmol) was added neat, at 25°, through the dropping funnel over 10 min. The reaction mixture was stirred at 25° for 1 hr, and then 40 ml of 3 *M* aqueous sodium hydroxide (120 mmol) was added dropwise. After 2 hr, anhydrous potassium carbonate was added and the upper THF layer was separated, dried, and distilled. Glpc analysis indicated a yield of 81%. Distillation through a spinning-band column gave 6.3 g of cyclopropylcarbinyl chloride, bp 83–90° (742 mm), identical in pmr spectra with that reported.[9]

In the case of certain allylic chlorides which are highly unstable, we synthesized them utilizing a procedure similar to that previously described[10] and utilized them without isolation for hydroboration with 9-BBN.

It is evident that this new cyclopropane synthesis possesses a number of interesting possibilities, and we are continuing to explore these possibilities.

(6) P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).
(7) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Am. Chem. Soc.*, **91**, 2144 (1969); H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146 (1969); H. C. Brown, M. M. Rogic, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).
(8) Provided by the Petro-Tex Chemical Corp., Houston, Texas.
(9) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).
(10) W. G. Young, F. F. Caserio, Jr., and D. D. Brandon, Jr., *J. Am. Chem. Soc.*, **82**, 6163 (1960).
(11) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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Stereochemistry of the Carbonylation, Carbethoxymethylation, and γ-Propanalation Reactions of Organoboranes. Substitution Reactions at Carbon That Proceed with Retention of Configuration

Sir:

Protonolysis of organoboranes with carboxylic acids,[1] oxidation with alkaline hydrogen peroxide,[2] and amination with O-hydroxylaminesulfonic acid[3] all proceed

(1) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).
(2) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).
(3) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, **88**, 2970 (1966).