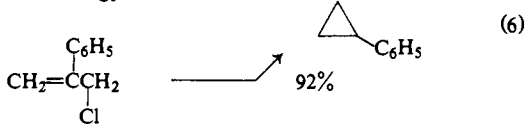
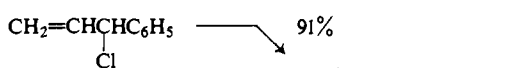
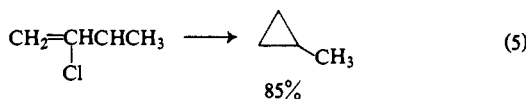


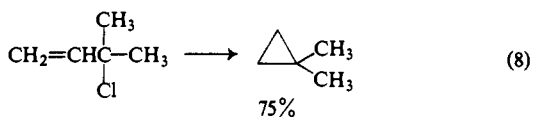
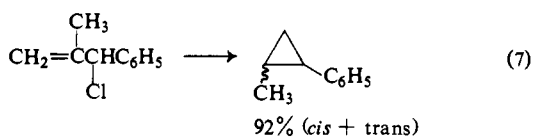
This difficulty can often be circumvented by utilizing more reactive bases, such as sodium triethylborohydride⁶ or methyllithium,⁵ in nonaqueous systems.

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.

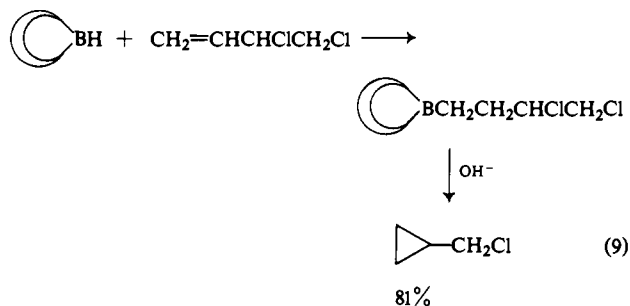
In this way 1-methylallyl chloride was converted into methylcyclopropane in a yield of 85% (5). Similarly, both 1-phenylallyl chloride and 2-phenylallyl chloride are converted into phenylcyclopropane in yields of 91 and 92%, respectively (6).



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.



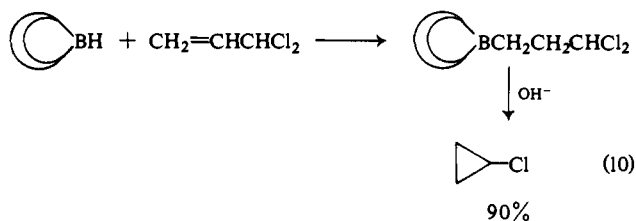
To illustrate the utility of this new procedure we converted the commercially available 3,4-dichloro-1-butene



- (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. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969).
 (8) Provided by the Petro-Tex Chemical Corp., Houston, Texas.

into the highly reactive cyclopropylcarbonyl chloride in a yield of 81% (9).

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



The following procedure for the synthesis of cyclopropylcarbonyl 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-butene⁸ (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 cyclopropylcarbonyl 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 described¹⁰ 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.

(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, Carboethoxymethylation, and γ -Propanalation Reactions of Organoboranes. Substitution Reactions at Carbon That Proceed with Retention of Configuration

Sir:

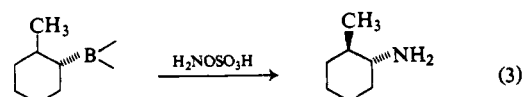
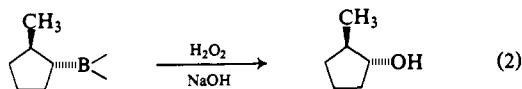
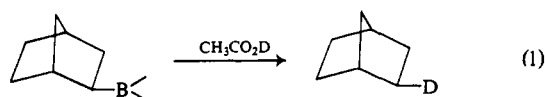
Protonolysis of organoboranes with carboxylic acids,¹ oxidation with alkaline hydrogen peroxide,² and amination with O-hydroxylaminesulfonic acid³ all proceed

(1) H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961).

(2) H. C. Brown and G. Zwiefel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(3) M. W. Rathke, N. Inoue, K. R. Varma, and H. C. Brown, *ibid.*, **88**, 2970 (1966).

with retention of configuration at the carbon atom undergoing reaction. That is to say, in these reactions the replacement of the boron atom by hydrogen,¹ oxygen,² and nitrogen³ proceeds with the new function taking the identical place on carbon previously occupied by boron (1-3).



We now wish to report that the one-carbon-atom homologation of organoboranes with carbon monoxide (carbonylation),⁴ the two-carbon-atom homologation with ethyl bromoacetate (carbethoxymethylation),⁵ and the three-carbon-atom homologation with acrolein (γ -propanalation)⁶ are also highly stereospecific reactions in which the original boron-carbon bond is replaced by a carbon-carbon bond with retention of the original stereochemistry.

Hydroboration of 1-methylcyclopentene proceeds rapidly to bis(*trans*-2-methylcyclopentyl)borane and more slowly to tris(*trans*-2-methylcyclopentyl)borane. Oxidation of either derivative with alkaline hydrogen peroxide gives essentially pure *trans*-2-methylcyclopentanol.^{2,7} This is in agreement with the conclusion that the hydroboration stage involves an anti-Markovnikov *cis* addition of the boron-hydrogen bond to the double bond.²

Unfortunately, tris(*trans*-2-methylcyclopentyl)borane failed to react with carbon monoxide and lithium trimethoxyaluminumhydride under the standard reaction conditions.⁴ However, B-(*trans*-2-methylcyclopentyl)-9-borabicyclo[3.3.1]nonane (B-R-9-BBN), obtained in the hydroboration of 1-methylcyclopentene with the new reagent, 9-BBN,⁸ undergoes rapid carbonylation under these conditions. Since it was simpler to characterize the product as the methylol derivative, rather than as the more labile aldehyde, the reaction intermediate was hydrolyzed with sodium hydroxide in ethanol. Distillation gave a 50% yield of *trans*-2-methylcyclopentylmethanol, bp 54° (5 mm), n_D^{20} 1.4359, 3,5-dinitrobenzoate, mp 55-56°.⁹

(4) H. C. Brown, R. A. Coleman, and M. W. Rathke, *J. Am. Chem. Soc.*, **90**, 499 (1968); H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969).

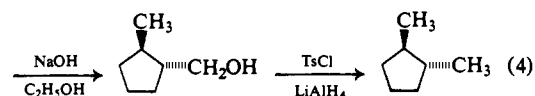
(5) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818, 1911 (1968); H. C. Brown and M. M. Rogic, *ibid.*, **91**, 2146 (1969).

(6) H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogic, *ibid.*, **90**, 4165 (1968).

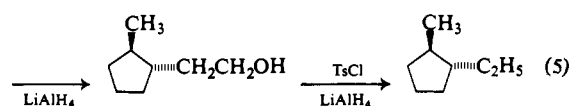
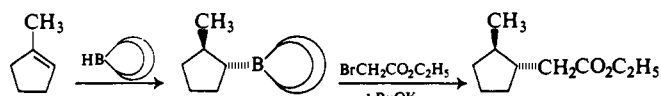
(7) The product contains about 1.5% of the tertiary alcohol, 1-methylcyclopentanol, but the presence of the *cis* isomer in more than traces could not be established.

(8) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280, 5281, 5283 (1968).

The alcohol was converted to the tosylate and the latter reduced to the hydrocarbon with lithium aluminum hydride in ether. Glpc analysis revealed that the product, obtained in a yield of 80%, was essentially pure *trans*-1,2-dimethylcyclopentane, as indicated by comparison with an authentic sample of the *cis* and *trans* isomers¹⁰ (4).



Tris(*trans*-2-methylcyclopentyl)borane also failed to react with ethyl bromoacetate and potassium *t*-butoxide under the usual conditions.⁵ Again 9-BBN solved the difficulty. The alkylated ester was obtained in 60% yield, and glpc analysis of the isolated product (54% yield) indicated it to be at least 98% pure ethyl (*trans*-2-methylcyclopentyl)acetate,¹¹ bp 80° (10 mm). There was 1.5-2% of an isomeric material which could be the *cis* isomer.¹² The alcohol was converted to the tosylate and the tosylate reduced to *trans*-1-methyl-2-ethylcyclopentane, identified by comparison with an authentic sample¹⁰ (5).



In contrast to the previous two cases, the B-R-9-BBN derivative failed to react with acrolein. However, the highly hindered tris(*trans*-2-methylcyclopentyl)borane reacted rapidly with acrolein under the standard reaction conditions.⁶ Glpc analysis of the reaction mixture, after the usual oxidation with sodium acetate-hydrogen peroxide, indicated the presence of two components in a 96:4 ratio. The aldehyde fraction was treated with sodium borohydride to reduce the aldehyde. Distillation gave a 91% yield of *trans*-2-methylcyclopentyl-3-propanol, bp 92° (7 mm), n_D^{20} 1.4565.¹³ The alcohol was converted to the tosylate and reduced with lithium aluminum hydride in ether. The major product was identified as *trans*-1-methyl-2-*n*-propylcyclopentane by comparison with an authentic sample¹⁰ (6).

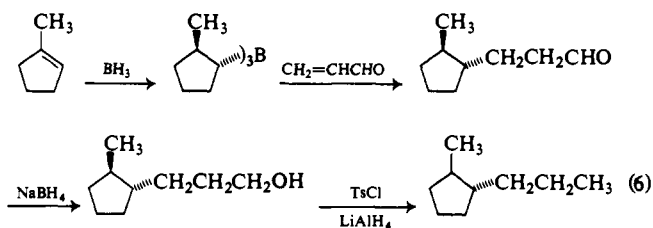
(9) L. N. Owen and A. G. Peto, *J. Chem. Soc.*, 2383 (1955), report mp 56°.

(10) We are indebted to Dr. K. S. Greenlee, Chemical Samples Co., Columbus, Ohio, for samples of the isomeric hydrocarbons.

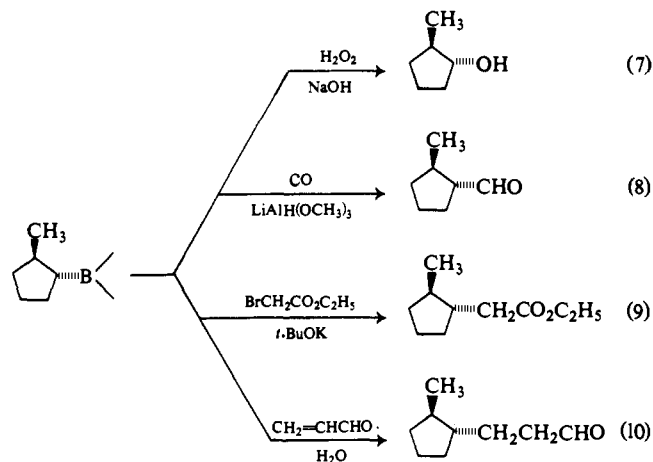
(11) Analytical and spectral data for these products are consistent with these structures.

(12) Oxidation of the B-R-9-BBN derivative also indicated the presence of 1.5-2.0% of a material with longer retention time, which might be the *cis* isomer.

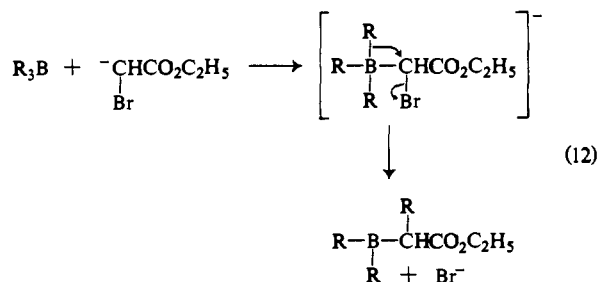
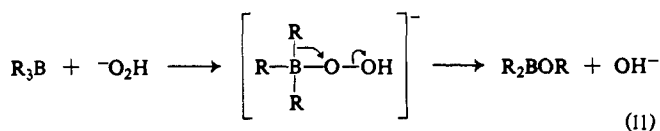
(13) W. Herz, *J. Org. Chem.*, **20**, 1062 (1955), reports bp 96-92° (7 mm), n_D^{20} 1.4561.



Consequently, the conversion of the *trans*-2-methylcyclopentylboron moiety into the alcohol (7), the aldehyde (8), the ester (9), and the γ -propanol derivative (10) all proceed with retention at the carbon atom undergoing substitution.



In these reactions the alkyl group is believed to migrate with its bonding pair from boron to another electron-deficient atom, as illustrated for oxidation² and the carboxymethylation⁵ reactions (11, 12).



This mechanism suggests that the migration of the group R from boron to carbon should involve an inversion at the receiving center. Indeed, Pasto and Hickman have demonstrated such an inversion in the rearrangement of α -haloorganoboranes obtained in the hydroboration of appropriate vinyl halides.¹⁴

It is evident that it is now becoming possible to control

(14) D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967).

substitution processes to achieve either substitution with inversion or substitution with retention merely by controlling the reagents and reactions utilized. These developments greatly add to the versatility of the available procedures for organic synthesis.

(15) Graduate research assistant on Grant GM 10937 from the National Institutes of Health.

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Some Consequences of the Conservation of Angular Momentum in Chemical Kinetics

Sir:

Unimolecular fission reactions in which two radicals are formed have a "loose" transition state in which the two largest moments of inertia of the reactant molecule are appreciably larger than they are in the "ground" state.^{1,2} One consequence of this, which has been discussed recently,^{2,3} is that the rate constants for such reactions tend to be faster, both at the high- and low-pressure limits, than those for tight transition states.

A further consequence which has not been discussed explicitly is that the average reacting molecule undergoing fission is rotationally "hot." This effect has been demonstrated in the photolysis of NO_2 ⁴ by showing that NO_2 could be photodissociated into $NO + O$ by 4047 Å, which was about 1.3 kcal lower in energy than the bond dissociation energy. The energy deficit was provided by rotational energy.

The converse of this behavior should be exhibited by association reactions. Methyl radical recombination provides an excellent example. The measured rate of CH_3 recombination is about $10^{10.5}$ l./mole sec.⁵ If we count only singlet collisions as effective (*i.e.*, $1/4$), this rate constant at 400°K corresponds to a "hard-sphere" collision diameter of 3.5 Å. If we compare this to the ground-state C-C bond length of 1.54 Å, and treat the collision as a hypothetical diatomic pair, this corresponds to $r^*/r = 2.27$ and $I^*/I = 5.2$.⁶ Now the average relative translational energy of an approaching $CH_3 \cdots CH_3$ pair will be RT , so that the newly formed $C_2H_6^*$ molecule will be rotationally hot by $5.2RT$. At 400°K this corresponds to 4.2 kcal and at 1000°K, with the same recombination diameter, to 10.4 kcal.⁷ Similar values apply to C_2H_5 recombination.

(1) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(2) R. A. Marcus, *J. Chem. Phys.*, **43**, 2658 (1965); **20**, 364 (1952); R. A. Marcus and O. K. Rice, *J. Phys. Colloid. Chem.*, **55**, 894 (1951).

(3) W. Forst, *J. Chem. Phys.*, **48**, 3665 (1968).

(4) J. N. Pitts, Jr., J. H. Sharp, and S. I. Chan, *ibid.*, **42**, 3655 (1964). The authors estimated that about 85% of the total rotational energy was available for bond breaking. This would suggest an increase in moment of inertia of about a factor of 6.

(5) G. B. Kistiakowsky and E. K. Roberts, *ibid.*, **21**, 1637 (1953). We are ignoring here the small corrections suggested by A. Shepp, *ibid.*, **24**, 939 (1956), since they yield an unreasonably higher value for CD_3 recombination than for CH_3 .

(6) r^* and I^* correspond to internuclear distance and moment of inertia in the transition state.