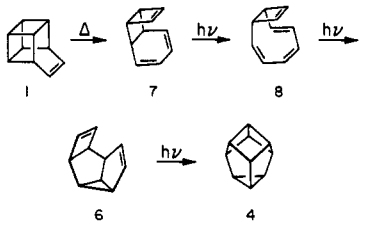
into **3**.[16] We have demonstrated that **7** is formed and present under our reaction conditions by trapping it as a 1:1 adduct with maleic anhydride.[17] A search for other $(CH)_{10}$ intermediates made with glpc using capillary columns revealed that **6** was present (*ca.* 0.2%) after short irradiation times (5 hr).[18] The amount of **6** observed decreased with time, and it was not detectable after extended irradiation.

A reaction pathway which relates **6** to **7** and also accounts for the conversion of **1** into **4** is outlined in Scheme I. The photoinduced conrotatory opening

Scheme I



of **7** to the *cis,cis,trans*-cyclooctatriene derivative **8** is a well-known phenomenon.[19-21] There is abundant precedent for photorearrangement of **8** into **6**.[19,21-24] As shown above, **6** undergoes direct photochemical closure to **4**. This (2 + 2) cyclization is a widely observed event.[20,25]

Additional interrelations of the isomers in this area of $(CH)_{10}$ chemistry will be reported in a subsequent paper. We also are investigating the chemistry of the new systems **4** and **6**.

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant GP-30743X. We thank Professor D. M. Grant and Dr. R. J. Pugmire for the carbon-13 nmr work which was done by the Regional Nuclear Magnetic Resonance Biomedical Facility supported by the Division of Research Resources, National Institutes of Health, Grant No. RR-574-01.

(16) H. H. Westburg, E. N. Cain, and S. Masamune, *J. Amer. Chem. Soc.*, **91**, 7512 (1969); E. Vedejs, *Chem. Commun.*, 536 (1971).

(17) E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969).

(18) Compound **6** was identified by comparison of retention times and by enrichment of the photolysis mixtures with authentic **6** on two different 500 ft × 0.03 in. open tubular capillary columns (95% OV-101, 5% Igepal, and Carbowax 20M). A regular 15 ft × 1/8 in. 20% SE-30 on Chromosorb W column also gave similar results.

(19) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *J. Amer. Chem. Soc.*, **94**, 4285 (1972).

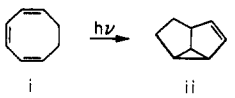
(20) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(21) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **89**, 1755 (1967); **88**, 2850 (1966).

(22) See A. Padwa, L. Brodsky, and S. Clough, *ibid.*, **94**, 6767 (1972), for a list of pertinent references.

(23) J. Zirner and S. Winstein, *Proc. Chem. Soc., London*, 235 (1964); O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964); W. R. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **92**, 969 (1970).

(24) In this regard, it is interesting that irradiation of *cis,cis,cis*-cyclooctatriene (i) under conditions similar to ours produces ii as one



of the products.[23] The formation of ii is not predicted on the basis of orbital symmetry considerations. This suggests that the reaction either involves an undetected cis-trans isomerization or proceeds in a stepwise fashion *via* radical intermediates. In the case of **8**, the stereochemistry is proper for an allowed closure.

(25) R. N. Warrener and J. B. Bremmer, *Rev. Pure Appl. Chem.*, **16**, 117 (1966).

(26) National Science Foundation Trainee, 1969-1973.

Evan L. Allred,* Boyd R. Beck[26]
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112
Received August 18, 1972

Facile Reaction of Alkyl- and Aryldichloroboranes with Organic Azides. A General Stereospecific Synthesis of Secondary Amines

Sir:

Alkyldichloroboranes,[1,2] $RBCl_2$, as well as aryldichloroboranes,[3] react readily with organic azides, $R'N_3$, in benzene solution, producing an intermediate, $RR'NBCl_2$, readily converted by alkaline hydrolysis to the corresponding secondary amines, RR'NH, in yields of 84 to 100% (eq 1). The reaction possesses wide

$$RBCl_2 + R'N_3 \xrightarrow{-N_2} RR'NBCl_2 \xrightarrow[H_2O]{NaOH} RR'NH \qquad (1)$$

generality and proceeds with retention of stereochemistry of the alkyl group in the alkyldichloroborane. Consequently, this development provides a new, simple route to secondary amines far more general than any method now available.

Trialkylboranes react with a variety of organic azides in refluxing xylene.[4] Basic hydrolysis produces the secondary amine. Unfortunately, this reaction is relatively slow and very sensitive to steric requirements. Recently, we discovered that the dialkylchloroboranes circumvent these problems.[5,6] However, this procedure suffers from a further significant disadvantage—only one of the two alkyl groups on boron is utilized in the synthesis.

This development suggested that alkyldichloroboranes might not only give a fast reaction with organic azides, but also provide for complete utilization of the alkyl groups. Indeed, when *n*-butyldichloroborane (5 mmol) was placed in 5 ml of benzene and *n*-butyl azide (5 mmol) was added dropwise at room temperature, gas (presumably nitrogen) was vigorously evolved. The solution was heated briefly to reflux to ensure completion of the reaction, cooled to room temperature, and hydrolyzed with base. Analysis by glpc indicated an 84% yield of di-*n*-butylamine. These results were encouraging. Consequently, a representative series of alkyldichloroboranes was synthesized, and the reactions with representative organic azides were investigated. These results are summarized in Table I.

The following procedure for the preparation of *N*-cyclohexylaniline is representative. A dry 250-ml flask equipped with a septum inlet, reflux condenser, and

(1) H. C. Brown and A. B. Levy, *J. Organometal. Chem.*, **44**, 233 (1972).

(2) H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 2396 (1973).

(3) Phenyldichloroborane is available from Ventron Corp. Others may be prepared by the method of Hooz: J. Hooz and J. G. Calgada, *Org. Prep. Proced.*, submitted for publication.

(4) A. Suzuki, S. Sono, M. Itoh, H. C. Brown, and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 4329 (1971).

(5) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **94**, 2114 (1972).

(6) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **94**, 3662 (1972).

Table I. The Reaction of Alkyl- and Aryldichloroboranes with Organic Azides for the Synthesis of Secondary Amines

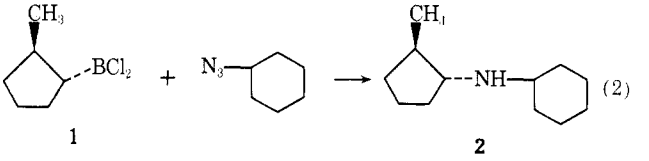
Alkyl- and aryldichloroborane[a] $RBCl_2$ R =	Organic azide[b] $R'N_3$ R′ =	Secondary amine product RR′NH	Yield,[c] %
n-Butyl	*n*-Butyl	Di-*n*-butylamine	84
	Cyclohexyl	*N*-*n*-Butylcyclohexylamine	92
	Phenyl	*N*-*n*-Butylaniline	89
2-Methyl-1-pentyl	Cyclohexyl	*N*-(2-Methyl-1-pentyl)-cyclohexylamine	92
3-Hexyl	Cyclohexyl	*N*-3-Hexylcyclohexylamine	85
Cyclopentyl	*n*-Butyl	*N*-*n*-Butylcyclopentylamine	96
	Cyclohexyl	*N*-Cyclohexylcyclopentyl-amine	88
	Phenyl	*N*-Cyclopentylaniline	84
Cyclohexyl	*n*-Butyl	*N*-*n*-Butylcyclohexylamine	95
	Cyclohexyl	Dicyclohexylamine	92
	Phenyl	*N*-Cyclohexylaniline	94 (91)
trans-2-Methyl-cyclopentyl	Cyclohexyl	*N*-(*trans*-2-Methylcyclo-pentyl)cyclohexylamine	90[d]
exo-Norbornyl	*n*-Butyl	*N*-*n*-Butyl-*exo*-norbornyl-amine	86
	Phenyl	*N*-*exo*-Norbornylaniline	92[e]
Phenyl[f]	*n*-Butyl	*N*-*n*-Butylaniline	100
	Cyclohexyl	*N*-Cyclohexylaniline	96

[a] 5 mmol in 5 ml of benzene. [b] 5 mmol added dropwise. [c] Analysis by glpc (isolated yield in parentheses). All compounds exhibited analytical and spectral data in accordance with the assigned structures. [d] The product was pure trans amine by glpc. [e] The product was pure exo amine by nmr. [f] Reference 3.

magnetic stirring bar was flushed with nitrogen. The flask was charged with 100 ml of benzene and 15.9 g (100 mmol) of phenyldichloroborane.[3] Cyclohexyl azide,[7] 12.5 g (100 mmol), was added dropwise over 30 min at 20° (water bath). The solution was stirred an additional 15 min, then slowly heated to 80° over a 45-min period. Gas evolution had ceased at this point. The solution was cooled to 0° and very carefully hydrolyzed by slowly adding 10 ml of water (*exothermic!*). An additional 90 ml of water was added and the precipitate removed by filtration. The organic phase was separated and washed with 100 ml of 3 *N* hydrochloric acid. The combined aqueous layers and precipitate were made strongly basic with 40% potassium hydroxide. The amine was extracted with ether. The ether solution was dried (K_2CO_3) and the ether removed under vacuum. Upon distillation there was collected 15.9 g (91%) of *N*-cyclohexylaniline, bp 82–84° (0.1 mm), $n^{20}D$ 1.5600 (lit.[8] bp 87–89° (0.21 mm); $n^{20}D$ 1.5614).

With less hindered boranes or azides, such as *n*-butyl, the reaction is rapid, evolving gas, at room temperature. In the more hindered cases, such as cyclohexyl, the reaction is slower, requiring 3–4 hr for completion. Gradually raising the temperature of the benzene solution to gentle reflux brings the reaction to completion in approximately 30–40 min (*too rapid heating of large-scale reactions may cause a violent exothermic reaction*). Nearly quantitative yields of amines were obtained in all cases examined.

The stereochemistry of *N*-*exo*-norbornylaniline prepared by the present procedure was established by comparison with a mixture of exo and endo amines obtained in the reduction of phenylnorbornylimine with lithium aluminum hydride (LAH).[9] Only the exo amine was observed by nmr analysis, corresponding to retention in the reaction of the *exo*-norbornylboron moiety produced in the hydroboration.[2] Similarly, *trans*-2-methylcyclopentyldichloroborane (**1**) reacted stereospecifically with cyclohexyl azide (eq 2) to give

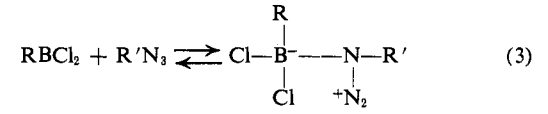


(2)

1 2

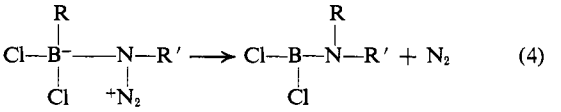
(glpc analysis) pure *N*-(*trans*-2-methylcyclopentyl) cyclohexylamine (**2**). In contrast, reduction of *N*-cyclohexyl-2-methylcyclopentylimine with LAH gives a mixture of 78% trans (**2**) and 22% cis amine by glpc analysis.

The reaction is much faster and proceeds under considerably milder conditions than the corresponding reaction with dialkylchloroboranes. However, the use of a complexing solvent, such as ethyl ether or tetrahydrofuran, stops the reaction, suggesting that the increase in reactivity may be due to an increase in the Lewis acidity of boron in the organodichloroboranes, which facilitates the initial coordination of the azide with the boron derivative (eq 3). This may be followed



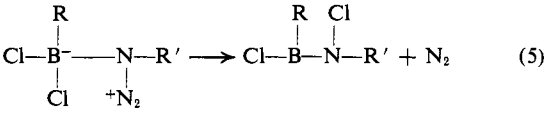
(3)

by transfer of an alkyl group (eq 4) or a chloride moiety



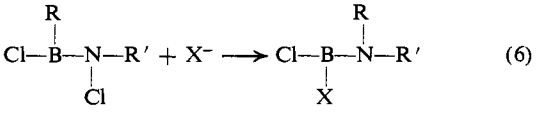
(4)

(eq 5) from boron to nitrogen with loss of nitrogen gas.



(5)

Chloride migration leads to an intermediate which, upon attack by a nucleophile, X^-, can undergo alkyl group migration (eq 6), as may occur in the reaction of trialkylboranes with chloramine.[10]



(6)

In an attempt to determine which pathway is followed (*e.g.*, eq 3 or 4), *n*-butyl- and phenyldichloroborane were allowed to react with phenyl and butyl azide, respectively. The proton nmr spectra of the intermediates were identical. Furthermore, both products gave a single ^{11}B nmr absorption at −31 ppm from boron trifluoride etherate, characteristic of *N*,*N*-dialkylaminodichloroboranes.[11] Therefore, the two intermediates

(7) Cyclohexyl azide was prepared from cyclohexyl bromide and excess sodium azide in dimethylformamide, in analogy with the procedure of A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

(8) Universal Oil Products Co., Netherlands Application for Patent, 6,410,986 (1966); *Chem. Abstr.*, **65**, 3766*d* (1966).

(9) R. S. McDaniel and A. C. Oehlschlager, *Tetrahedron*, **25**, 1381 (1969).

(10) H. C. Brown, W. R. Heydkemp, E. Breuer, and W. S. Murphy, *J. Amer. Chem. Soc.*, **86**, 3565 (1964).

(11) H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

are presumably identical, so that the reaction must follow the pathway indicated in eq 4. Alternatively, alkyl displacement of the chloride must be rapid, possibly catalyzed by the aminoborane itself.

The use of alkyldichloroboranes provides for the first time a highly useful stereospecific synthesis of secondary amines. The reaction is rapid and gives excellent yields for a wide variety of alkyl and aryl groups. However, for this reaction to be synthetically useful, we required a simple general preparation of the alkyldichloroboranes. The successful development of such a synthesis is reported in the accompanying communication.[2] Aryldichloroboranes may be readily prepared by the method of Hooz and Calgada.[3]

(12) (a) National Science Foundation Predoctoral Fellow, 1970–1972; (b) Postdoctorate Research Associate on Grant No. GM 10937 from the National Institutes of Health.

H. C. Brown,* M. Mark Midland,[12a] Alan B. Levy[12b]
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907
Received December 22, 1972

Reaction of Representative Olefins with Dichloroborane Ethyl Etherate Induced by Boron Trichloride. An Exceptionally Simple, General Synthesis of Alkyldichloroboranes and Alkylboronic Acid Derivatives *via* Hydroboration

Sir:

Representative olefins fail to react in pentane with dichloroborane diethyl etherate, $BHCl_2:OEt_2$, at any significant rate. However, the addition of 1 mol equiv of boron trichloride induces a rapid reaction. This procedure provides a simple, general synthesis of alkyldichloroboranes, $RBCl_2$, and their derivatives. The alkyldichloroboranes are easily isolated by distillation after separating the solution from the precipitated solid. Alternatively, they can be converted to the corresponding boronic acid esters by adding the alcohol to the reaction mixture and the esters recovered. Consequently, this procedure provides a simple and straightforward synthesis of monoalkyl boron derivatives.

Monochloroborane diethyl etherate, $BH_2Cl:OEt_2$, in diethyl ether solution readily reacts with a variety of olefins, providing an exceptionally simple synthesis of dialkylchloroboranes.[1] The need for representative monoalkyldichloroboranes in our studies[2] led us to explore the possible reaction of dichloroborane, $BHCl_2$, with olefins as a route to these compounds. The reaction of olefins with $BHCl_2$ is extremely slow in THF.[3,4] We discovered that the reaction is also slow in diethyl ether, in contrast to the fast reaction of BH_2Cl in this solvent. In benzene solution, or neat, dichloroborane diethyl etherate, $BHCl_2:OEt_2$, reacted with terminal olefins almost completely in several hours at 25°. However, the product was mainly dialkylchloroborane, R_2BCl, and not the desired $RBCl_2$.

Presumably, the reason for the low reactivity of $BHCl_2:OEt_2$ toward olefins is the strong complexation between the strongly acidic $BHCl_2$ and the basic Et_2O components, considerably larger than that involved in the case of BH_2Cl. It was thought that the complexed ether molecule could be removed by using a stronger Lewis acid. If so, the synthesis of undisproportionated $RBCl_2$ might be achieved. Indeed, the presence of boron trichloride in a mixture of the olefin and reagent in inert solvents resulted in a rapid reaction (eq 1).

$$BHCl_2:OEt_2 + \text{olefin} + BCl_3 \longrightarrow RBCl_2 + BCl_3:OEt_2 \quad (1)$$

For example, addition of $BHCl_2:OEt_2$ to a benzene solution of equivalent amounts of 1-octene and BCl_3 at 0° resulted in the uptake of 99% of the olefin in 5 min. When 1-butene was used in place of 1-octene, the quantitative formation of *n*-$BuBCl_2$ was observed (*n*-$BuBCl_2$ was analyzed by glpc as *n*-$BuB(OCH_3)_2$ after methanolysis). However, the solubility of $BCl_3:OEt_2$ introduced difficulties in the isolation of $RBCl_2$ in pure form from the benzene solution. The use of pentane as the reaction medium circumvented these difficulties.

Addition of $BHCl_2:OEt_2$ to a mixture of olefin and BCl_3 in pentane at 0° resulted in the precipitation of a white, thick solid, $BCl_3:OEt_2$, on the sides of the flask. Within 5 min after the addition of $BHCl_2:OEt_2$, 90% of the olefin had undergone the reaction at 0°. On warming to room temperature, the remaining olefin was converted within 15 min. Simple distillation of the pentane solution, after separation from the solid $BCl_3:OEt_2$, provides the monoalkyldichloroborane in yields of 80–90%. Alternatively, the alkylboronic acid esters can be obtained by simply adding excess alcohol at 0°. The reaction is quite general, as shown by the fact that olefins of such a wide range of structure as 1-octene, *cis*-2-octene, 2-methyl-1-pentene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclohexene, and styrene all were readily converted into the corresponding alkyldichloroboranes or the esters. The results are summarized in Table I.

Table I. Synthesis of Alkyldichloroboranes and Dimethyl Alkylboronates by the Hydroboration of Olefins with Dichloroborane Ethyl Etherate Induced by Boron Trichloride

Alkyldichloroborane or Dimethyl Alkylboronate	Yield, %	Bp, °C (mm Hg)
$RB(OCH_3)_2$, R =		
1-Butyl	90[a]	
2-Butyl	88[a]	
2-Methyl-1-propyl	97[a]	
Cyclopentyl	76[b]	76–78 (40)
$RBCl_2$, R =		
2-Methyl-1-butyl	87[b]	110–112 (746)
1-Hexyl	81[b]	102–104 (100)
3-Hexyl	77[b]	88–90 (102)
Cyclopentyl	79[b]	136–138 (751)
trans-2-Methylcyclopentyl	80[b]	94–96 (110)
exo-Norbornyl	83[b]	95–98 (50)

[a] Glpc yield. [b] Isolated yield. The $RBCl_2$ was identified by methanolysis and characterizing the $RB(OCH_3)_2$ by pmr. The regiospecificity and the stereospecificity of the products were established by glpc analysis of the isomeric alcohols produced in the usual oxidation of the $RBCl_2$ with alkaline hydrogen peroxide.

The $BHCl_2:OEt_2$ was prepared by slowly adding with stirring a 1.3–1.5 *M* solution of lithium borohydride in diethyl ether to a 1.3–1.4 *M* solution of BCl_3 in diethyl ether at 0°,[5] in accordance with the reaction shown in

(1) H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **94**, 2112 (1972).
(2) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **95**, 2394 (1973).
(3) G. Zweifel, *J. Organometal. Chem.*, **9**, 215 (1967).
(4) D. J. Pasto and P. Balasubramaniyan, *J. Amer. Chem. Soc.*, **89**, 295 (1967).
(5) H. C. Brown and P. A. Tierney, *J. Inorg. Nucl. Chem.*, **9**, 51 (1959).