CHCl; (b) $CH_3F < CH_3Cl \sim CH_3Br$; (c) $C_2H_5Cl < CHF_3$; (d) $CH_3Cl < CH_3CF_3$; (e) $C_2H_5Cl < CH_3NO_2 \sim CH_3CN \sim CH_3OH$. The cluster $Cl^-(CF_4)$ is the least stable of these series.

A direct quantitative comparison with the results of Kebarle[4,5] shows that our trends are at least compatible with those established by high-pressure mass spectroscopy, where ions are presumably thermalized. Following the procedure outlined by Bowers,[9] equilibrium constants determined for reaction 4 were found

$$Cl^-(CH_3CN) + CH_3OH \rightleftharpoons CH_3CN + Cl^-(CH_3OH) \quad (4)$$
$$\Delta G^\circ = -0.2 \pm 0.3 \text{ kcal/mol}$$

to be independent of pressure in the range of 6×10^{-5} to 4×10^{-4} Torr. The resulting ΔG° compares very favorably with the calculated value of -0.5 kcal/mol.[4,5] Thus, the above trends can be regarded as truly representative of the relative clustering ability of the neutrals.

The fact that CH_3CF_3, CH_3NO_2, and CH_3CN form very stable cluster ions can be accounted for by their relatively large dipole moments[13] resulting in a favorable ion–permanent dipole interaction. For compounds with similar dipole moments as in (a) and (b), the increasing stability follows the increase in polarizability of these compounds.[14] This polarizability trend is thus similar to that previously observed in our work with "solvated" alkoxide ions.[15] Such an observation points out again the relevant role of ion-induced dipole interactions in determining the behavior of ions in the gas phase.[6,8] The high relative stability of $Cl^-(CHF_3)$ suggests a hydrogen bonding type of interaction in this case, similar to that in CH_3OH and $CHCl_3$.[4]

A preliminary investigation on the structural aspects of an ion like $Cl^-(CH_3Cl)$ indicates that the chlorines in this moiety are not equivalent. Such a conclusion is based on a triple resonance experiment performed by observing the behavior of reactions 5 while ejecting one of the precursor ions obtained from phosgene.

$$(CH_3{}^{35}Cl{}^{37}Cl)^- + CH_3CF_3 \rightarrow {}^{35}Cl^-(CH_3CF_3) + CH_3{}^{37}Cl \quad (5a)$$
$$(CH_3{}^{35}Cl{}^{37}Cl)^- + CH_3CF_3 \rightarrow {}^{37}Cl^-(CH_3CF_3) + CH_3{}^{35}Cl \quad (5b)$$

Conventional pulsed double resonance shows that reaction 5a and 5b are equally probable. Ejecting $CO^{37}Cl^-$ continuously, reaction 5b is affected, but no appreciable effects take place in reaction 5a. The opposite behavior is observed when $CO^{35}Cl^-$ is ejected continuously. Thus, the chlorine originally present in the precursor ion is transferred preferably in the secondary reaction.

The method introduced in this communication can be used to produce other cluster ions of interest. Thus, esters, ketones, benzene, acetylene, and phosgene itself have been found to yield cluster ions by reaction 1. Studies on these species are presently in progress. It is interesting to note that reaction 1, with CO acting as a convenient energy sink for the bimolecular clustering reaction at low pressures, is very reminiscent of the alkoxide–alkyl formate reaction used in the study of alkoxide ion clusters.[15]

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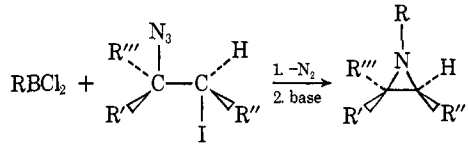
Facile Reaction of Alkyl- and Aryldichloroboranes with 2-Iodoalkyl Azides. A Stereospecific Synthesis of *N*-Alkyl- and *N*-Arylaziridines

Sir:

2-Iodoalkyl azides, now readily available,[1] undergo a facile reaction with aryl-[2] and alkyldichloroboranes[3,4] to produce β-iodo secondary amines. These amines, without isolation, undergo ring closure with base to provide the corresponding *N*-aryl- and *N*-alkylaziridines in good yields (73–94%). Significantly, the stereochemistry of the original 2-iodoalkyl azide is maintained, providing for the first time a synthesis of *N*-aryl- and *N*-alkylaziridines with known stereochemistry (eq 1).



(1)

Recently, we established that aryl- and alkyldichloroboranes react readily with organic azides[5] to provide a convenient synthesis of the corresponding secondary amines in high yield (eq 2). These results suggested

$$RBCl_2 + R'N_3 \xrightarrow{-N_2} \underset{\displaystyle BCl_2}{RNR'} \xrightarrow[OH^-]{H_2O} RR'NH \quad (2)$$

the possibility that 2-iodoalkyl azides might react with organodichloroboranes to give the corresponding β-iodo-*sec*-amines. If so, these amines should undergo ring closure with base to give the corresponding N-substituted aziridines. Dropwise addition of 1-azido-2-iodoethane to phenyldichloroborane in benzene results in vigorous evolution of nitrogen, complete within

(1) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).
(2) Phenyldichloroborane is commercially available from Ventron Corp. Other aryldichloroboranes may be prepared by the method of J. Hooz and J. G. Calgada, *Org. Prep. Proced.*, 4, 219 (1972).
(3) H. C. Brown and A. B. Levy, *J. Organometal. Chem.*, **44**, 233 (1972).
(4) H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 2396 (1973).
(5) H. C. Brown, M. M. Midland, and A. B. Levy, *ibid.*, **95**, 2394 (1973).

(13) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.
(14) J. Applequist, J. R. Carl, and K. K. Fung, *J. Amer. Chem. Soc.*, **94**, 2952 (1972).
(15) L. K. Blair, P. C. Isolani, and J. M. Riveros, *ibid.*, **95**, 1057 (1973).

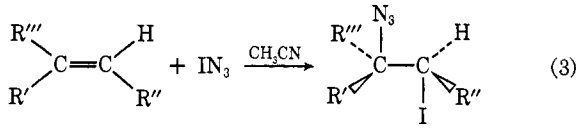
Table I. The Reaction of Organodichloroboranes with 2-Iodoalkyl Azides for the Synthesis of *N*-Alkyl- or *N*-Phenylaziridines

$RBCl_2$,[a] R =	$R'N_3$[b]	Product	Yield,[c,d] %
n-Hexyl	*erythro*-2-Azido-3-iodobutane	*N*-*n*-Hexyl-*trans*-2,3-dimethylaziridine	92
	trans-1-Azido-2-iodocyclohexane	*N*-*n*-Hexyl-7-azabicyclo[4.1.0]heptane	92, 86,[e] 94[f]
	1-Azido-2-iodohexane	*N*-*n*-Hexyl-2-*n*-butylaziridine	91 (83)
2-Methyl-1-pentyl	*trans*-1-Azido-2-iodocyclohexane	*N*-(2-Methyl-1-pentyl)-7-azabicyclo[4.1.0]heptane	87
3-Hexyl	*trans*-1-Azido-2-iodocyclohexane	*N*-3-Hexyl-7-azabicyclo[4.1.0]heptane	86
Cyclopentyl	*trans*-1-Azido-2-iodocyclohexane	*N*-Cyclopentyl-7-azabicyclo[4.1.0]heptane	94
Cyclohexyl	*trans*-1-Azido-2-iodocyclohexane	*N*-Cyclohexyl-7-azabicyclo[4.1.0]heptane	86 (81)
Phenyl	2-Iodoethyl azide	*N*-Phenylaziridine	73[e,g]
	trans-1-Azido-2-iodocyclohexane	*N*-Phenyl-7-azabicyclo[4.1.0]heptane	73[e]
	threo-2-Azido-3-iodobutane	*N*-Phenyl-*cis*-2,3-dimethylaziridine	83[e]
	erythro-2-Azido-3-iodobutane	*N*-Phenyl-*trans*-2,3-dimethylaziridine	76 (72)[e]

[a] 5 mmol in 5 ml of benzene. [b] 5 mmol added dropwise. [c] Analysis by glpc (isolated yields in parentheses were run on a 10 mmol scale). All compounds exhibited analytical and spectral data in accordance with the assigned structure. [d] Ring closure unless otherwise noted by heating with 5 ml of 40% potassium hydroxide for 1–3 hr. [e] Ring closure with 5 mmol of *n*-butyllithium at room temperature for 15 min in benzene. [f] Ring closure by heating with 25 mmol of potassium carbonate in refluxing benzene for 1–3 hr. [g] Yield by nmr.

30 min. Hydrolysis of the intermediate with aqueous base gives the secondary amine. The organic phase can be separated, dried, and treated with *n*-butyllithium to provide *N*-phenylaziridine in a yield of 73%.

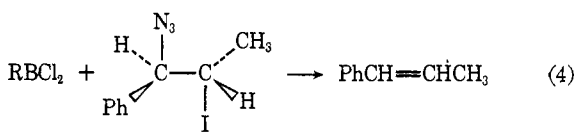
The main value of this new approach rests upon the ready availability of the requisite 2-iodoalkyl azides with defined stereochemistry, resulting from the recent investigations of Hassner and his coworkers (eq 3).[1]



(3)

If these derivatives react with the organodichloroboranes with maintenance of the stereochemistry of the 2-iodoalkyl azide, we would have available a stereospecific synthesis of substituted aziridines. Consequently, a number of these azides were prepared by the Hassner method and treated with a representative series of organodichloroboranes. These results are summarized in Table I.

We encountered one failure. No nitrogen was evolved on treatment of *erythro*-1-azido-2-iodo-1-phenylpropane[1] with an organodichloroborane. Instead, the solution became purple in color. Glc analysis of the organic phase, after work-up, showed the presence of β-methylstyrene, and the absence of aziridine (eq 4). Reductive elimination[6] of the elements



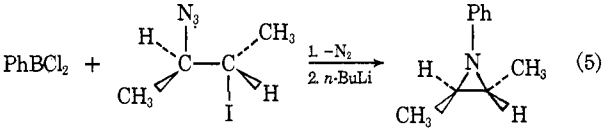
(4)

of iodine azide by lithium aluminum hydride has previously been noted. Such eliminations appear to be favored by electrophilic reducing agents, by phenyl groups vicinal to the azide, and by compounds in which the anti conformation of azide and iodine are preferred.

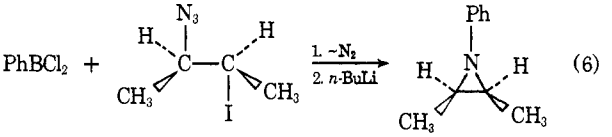
The following procedure for the preparation of *N*-cyclohexyl-7-azabicyclo[4.1.0]heptane is representative. A dry 50-ml flask equipped with a septum inlet, reflux condenser and magnetic stirring bar was flushed with nitrogen. The flask was charged with 10 ml of benzene and 1.67 g (10 mmol) of cyclohexyldichloroborane.[3] *trans*-1-Azido-2-iodocyclohexane,[1] 2.50 g (10 mmol), was added dropwise. After the addition was complete, the reaction mixture was brought to 80° over a 1-hr period. Gas evolution had ceased at this point. The solution was cooled to 0° and carefully hydrolyzed with 10 ml of 10% hydrochloric acid (exothermic!). To ensure complete precipitation of the salt, 15 ml of hexane was added. The precipitate was removed by filtration. The organic phase was separated and washed with 30 ml of 10% hydrochloric acid. The combined aqueous layers and precipitate were made strongly basic with 40% potassium hydroxide. The amine was extracted with 30 ml of benzene and the resulting solution heated under reflux with 30 ml of 40% potassium hydroxide for 1 hr. The organic phase was separated and dried ($CaSO_4$) and benzene was removed under vacuum. Distillation in a kugelrohr oven gave 1.46 g (81%) of *N*-cyclohexyl-7-azabicyclo[4.1.0]heptane, bp 80–82° (41 mm), $n^{20}D$ 1.4835. *Anal.* Calcd for $C_{12}H_{21}N$: C, 80.44; H, 11.72; N, 7.82. Found: C, 80.46; H, 11.65; N, 8.00.

The ring closure of the intermediate β-iodoalkylamine can be effected by treating the amine in benzene with one of several convenient bases. Aqueous potassium hydroxide is suitable. Excess anhydrous potassium carbonate is especially useful for cases where substituents are sensitive to aqueous base. Another alternative is treatment of the intermediate with 1 equiv of *n*-butyllithium at room temperature. Because of the instability of *N*-phenylaziridines to aqueous base[7] and/or heat, this is the preferred procedure for the synthesis of these derivatives.

The stereochemistry of *N*-phenyl-*cis*- and *N*-phenyl-*trans*-2,3-dimethylaziridine (eq 5 and 6) is suggested



(5)



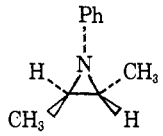
(6)

by their 100-MHz nmr spectra in carbon disulfide at

(6) A. Hassner, G. J. Mathews, and F. W. Fowler, *J. Amer. Chem. Soc.*, **91**, 5046 (1969).

(7) S. J. Brois, *J. Org. Chem.*, 27, 3532 (1962).

−80°. At this temperature, the phenyl group is frozen into one conformer rather than rapidly equilibrating. Thus the trans isomer shows two absorptions (2 m, δ 1.79 and 2.09) for the ring protons, and two broadened doublets (δ 0.85 and 1.26) for the methyl groups. This strongly suggests that hydrogen and methyl exist both syn and anti to the phenyl (conformer **1**). In accordance with expectations, the cis



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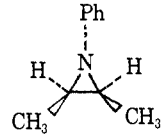

2

isomer showed only one absorption (multiplet, δ 2.07) for the ring protons and one absorption (d, δ 1.24) for the methyl group (conformer **2**) at −80°. This stereochemical assignment is in accordance with prediction and with similar reactions of this type.[6,8]

This procedure provides for the first time a convenient synthesis of ring substituted *N*-phenyl- and *N*-alkylaziridines in which the stereochemistry of the ring substituents may be easily defined. Furthermore, based on previous work, the N-alkyl groups must retain the original stereochemistry of the group attached to boron.[5] Consequently, the present procedure is exceptionally promising for providing a relatively simple, direct route to aziridines with well defined stereochemistry.

(8) A. Hassner and J. E. Galle, *J. Amer. Chem. Soc.*, **92**, 3733 (1970).
(9) Postdoctorate Research Associate on Grant No. 10937 from the National Institutes of Health.

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Controlled Reaction of Oxygen with Alkyldichloroborane Etherates. A Convenient Synthesis of Alkyl Hydroperoxides in High Yield

Sir:

Alkyldichloroboranes in inert solvents react remarkably rapidly with 0.5 molar equiv of oxygen, either at 0 or −78°. The reaction is strongly inhibited by iodine and must involve a free-radical chain process, yet the product contains little peroxide. In diethyl ether the reaction proceeds readily with the uptake of 1 molar equiv of oxygen. The product is readily hydrolyzed to the corresponding alkyl hydroperoxide. This procedure provides a convenient new route to the alkyl hydroperoxide in excellent yield.

Trialkylboranes undergo a facile free-radical chain autoxidation[1] which may be stoichiometrically controlled to give essentially quantitative conversions into alcohols.[2] At low temperature the initially formed peroxide (eq 1) reacts with a second mole of oxygen to

$$R_3B + O_2 \longrightarrow RO_2BR_2 \quad (1)$$

produce a diperoxide (eq 2). The hydroperoxide can

$$RO_2BR_2 + O_2 \longrightarrow (RO_2)_2BR \quad (2)$$

be liberated by the addition of 30% hydrogen peroxide (eq 3).[3] This process provides a valuable route to

$$(RO_2)_2BR + H_2O_2 + 2H_2O \longrightarrow ROH + 2RO_2H + B(OH)_3 \quad (3)$$

alkyl hydroperoxides. It is limited in that only two of the alkyl groups on boron are converted to the desired peroxide. It would be highly desirable to have a borane in which the alkyl group is converted entirely to the hydroperoxide.

Accordingly, the autoxidation of a number of *B*-alkylborane derivatives was examined in the automatic gasimeter[4] adapted for oxidation as previously described.[2,3] *B*-Alkyl-9-borabicyclo[3.3.1]nonane[5] undergoes rapid oxidation. Unfortunately, the cyclooctyl–boron bonds are preferentially oxidized. *B*-Alkyl-3,5-dimethylborinanes have been used successfully to transform the *B*-alkyl group selectively in free-radical reactions.[6] However, selective oxidation of the *B*-alkyl group failed. Dimethyl alkylboronic esters failed to oxidize. The *B*-alkyl catecholborane esters[7] reacted only sluggishly with oxygen.

However, the uptake of oxygen by *n*-butyldichloroborane[8,9] in toluene or hexane was exceptionally fast, the reaction being complete in less than 2 min at 0° or even at −78°. This reaction was strongly inhibited by iodine,[10] the presence of 5 mol % causing no oxygen to be absorbed in over 96 hr.[11] Consequently, the reaction must involve a free-radical chain process. Yet the product contained only traces of peroxide.

It appears, therefore, that the reaction must proceed through the formation of the alkylperoxydichloroborane (eq 4–6) but the latter must be lost in a rapid

$$RBCl_2 + O_2 \longrightarrow R\cdot + \cdot O_2BCl_2 \quad (4)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (5)$$

$$RO_2\cdot + RBCl_2 \longrightarrow RO_2BCl_2 + R\cdot \quad (6)$$

subsequent reaction (eq 7). This proposed mechanism

$$RO_2BCl_2 + RBCl_2 \longrightarrow 2ROBCl_2 \quad (7)$$

also accounts for the stoichiometry observed, an uptake of 0.5 mol of oxygen/mol of borane.

We discovered that the presence of ether greatly decreased the rate of the intermolecular oxidation (eq 7) without seriously affecting the rate of autoxidation at 0°. This is evidently a consequence of the coordination of alkyldichloroboranes with ethyl ether (eq 8).[8,12]

(1) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969).
(2) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).
(3) H. C. Brown and M. M. Midland, *ibid.*, **93**, 4078 (1971).
(4) C. A. Brown and H. C. Brown, *ibid.*, **84**, 2829 (1962); *J. Org. Chem.*, **31**, 3989 (1966).
(5) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *J. Amer. Chem. Soc.*, **91**, 2147 (1969).
(6) H. C. Brown and M. M. Midland, *ibid.*, **93**, 3291 (1971); H. C. Brown and E. Negishi, *ibid.*, **93**, 3777 (1971).
(7) H. C. Brown and S. K. Gupta, *ibid.*, **93**, 1816 (1971).
(8) The alkyldichloroboranes are reported to be spontaneously flammable in air: P. A. McCusker, E. C. Ashby, and H. S. Makowski, *ibid.*, **79**, 5182 (1957).
(9) H. C. Brown and A. B. Levy, *J. Organometal. Chem.*, **44**, 233 (1972); H. C. Brown and N. Ravindran, *J. Amer. Chem. Soc.*, **95**, 2396 (1973).
(10) M. M. Midland and H. C. Brown, *ibid.*, **93**, 1506 (1971).
(11) This extremely long induction period (tri-*n*-butylborane oxidation is inhibited for 12.5 min by 5 mol % of iodine) suggests a very inefficient initiation step. This is evidently due to the electronic effect of the two chlorines on the boron.
(12) At −78° the rate of autoxidation becomes negligible, presumably because dissociation of the complex is too small to permit the chain reaction to proceed. The presence of 1.2 mol of tetrahydrofuran, a stronger complexing agent, greatly reduces the rate of oxidation and leads to lower yields of peroxide.