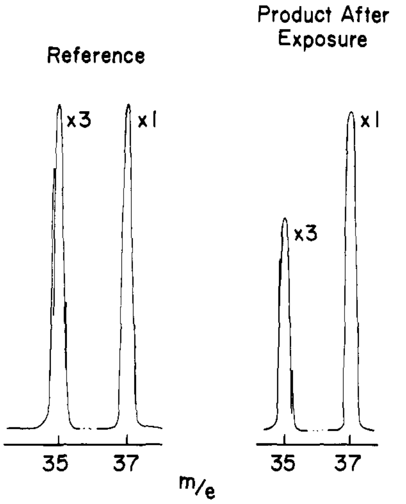

Figure 3. Mass spectrum of the *m/e* 35 and 37 peaks for (a) naturally occurring *trans*-ClHC=CHCl and (b) *trans*-ClHC=CHCl separated from the exposed reaction mixture. The ×3 peak is recorded on a scale three times smaller than the ×1 peak.

posed starting material is observed, demonstrating laser-controlled isotope interchange. Further confirmation of enrichment is provided by examining the ratio of other mass peaks. For example, $P_{48}:P_{50} = 4.26$ for reference *trans*-ClHC=CHCl while $P_{48}:P_{50} = 3.68$ for exposed *trans*-ClHC=CHCl. Here P_{48} is mainly due to $^{12}CH^{35}Cl$ and P_{50} to $^{12}CH^{37}Cl$.

The *cis*-ClHC=CHCl photoproduct also shows isotope enrichment, e.g., $P_{35}:P_{37} = 2.89$. In addition to the gaseous products, a pink nonvolatile liquid is formed during irradiation which has been identified as the photoaddition product $C_2H_2ICl_3$.

So far, our most impressive isotope separation has been achieved using 1,2-dibromoethylene as a scavenger under the same condition as *trans*-dichloroethylene. Several photoproducts are formed, viz., C_2H_2BrCl and *cis*- and *trans*-ClHC=CHCl, presumably resulting from the subsequent reaction of C_2H_2BrCl with ICl*. For the *trans*-ClHC=CHCl product, the $P_{35}:P_{37}$ ratio changes from 3.01 to 2.03, as shown in Figure 3. Moreover, the ICl in the exposed mixture is found to be enriched in ^{35}Cl, since its ^{37}Cl has been depleted by reaction.

Various laser isotope separation schemes have been proposed, and in some cases demonstrated.[2-11] In particular, photochemical enrichment of chlorine isotopes has been previously reported by Lamotte, Dewey, Keller, and Ritter[11] who used the photoaddition reaction between electronically excited thiophosgene and diethoxyethylene. By exciting the individual rotational lines of isotopically selected $CSCl_2$, they obtained an enrichment in the unreacted $CSCl_2$ comparable to ours. We anticipate, however, that our degree of isotopic enrichment will increase markedly when our laser line width is narrowed so as to excite individual rotational lines of $I^{35}Cl$ or $I^{37}Cl$. Moreover, it should be stressed here that we now have a convenient system for the study of the dynamics of organic gas-phase photochemical reactions in which mechanisms for isotopic scrambling and retention—a central problem in isotope separation schemes—can be well understood.

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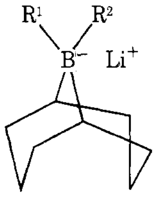
9-BBN Ate Complexes as a New Type of Reducing Agent for the Selective Reduction of Tertiary Alkyl, Benzyl, and Allyl Halides to Hydrocarbons

Sir:

We wish to report on the interesting reducing character of 9-borabicyclo[3.3.1] nonane (9-BBN) ate complexes (**1**). The reagents enable the selective removal of tertiary alkyl, benzyl, and allyl halides to afford the corresponding hydrocarbons in excellent yields without concomitant attack on secondary, primary, and aryl derivatives (eq 1).



$$+ \quad R^3X \xrightarrow{\text{room temp}}$$

$X = Cl, Br$

1a, $R^1 = R^2 = n$-Bu

b, $R^1 = CH_3$; $R^2 = n$-Bu

$R^3 =$ tertiary alkyl, benzyl, or allyl

$$R^3H + LiX + \text{borane} \qquad (1)$$

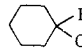
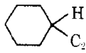
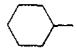
Although hydride character in the tetraalkylboron compounds was originally proposed by Wittig,[1] only sparse reports of their reducing ability have appeared.[2] In the course of studies on borate complexes, certain observations suggested that the bridgehead hydrogens of **1** must be exceptionally labile as hydride sources. Accordingly, we examined the reaction of benzyl chloride with the *n*-butyl ate complexes[3] of tri-*n*-butylborane, tri-*sec*-butylborane, and B-*n*-Bu-9-BBN. As is apparent from Table I, the secondary

Table I. Reactions of Benzyl Chloride with Ate Complexes[a]

Ate complex	Toluene (%)[b]	Benzyl chloride (%)[b]
Li (n-Bu)$_4$B	0	100
Li (n-Bu)(sec-Bu)$_3$B	75	18
1a	100	0

[a] Benzyl chloride (10 mmol) was added to the mixture of ate complex (10 mmol) and *n*-hexane at 0°. The resultant mixture was stirred at 20° for 3 hr, and then oxidized with NaOH–H_2O_2. [b] By GLPC analysis.

Table II. Reduction with 1 in Hexane at 20°[a]

Entry	Substrate	Agent	Time (hr)	Product	Yield (%)
1	$n\text{-}C_4H_9CBr(CH_3)(C_2H_5)$	1a	3	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	98 (83)
2	$n\text{-}C_4H_9CBr(CH_3)(C_2H_5)$	1b	18	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	92
3	$n\text{-}C_4H_9CCl(CH_3)(C_2H_5)$	1a	3	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	94 (85)
4	$n\text{-}C_4H_9CCl(CH_3)(C_2H_5)$	1b	18	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	96
5		1a	3		90 (81)
6	1-Bromoadamantane	1a	4	Adamantane	100 (89)
7	1-Bromooctane	1a	18	Octane	0[b]
8	2-Bromooctane	1a	18	Octane	Trace[b]
9	 —X (X = Cl, Br, I)	1a	18	Cyclohexane	0[b]
10	Chlorobenzene	1a	18	Benzene	0[b]
11	Benzyl chloride	1a	0.5	Toluene	100 (81)
12	Benzyl chloride	1b	18	Toluene	92
13	1-Bromo-1-phenylethane	1a	18	Ethylbenzene	81
14	Diphenylchloromethane	1a	18	Diphenylmethane	60
15	Cinnamyl bromide	1a	18	β-Methylstyrene	90[c] (72)
16	1,2-dibromo-1-phenylethane	1a	16	1-Bromo-2-phenylethane	60[d]

[a] All runs were performed on a 5-mmol scale with the same method as in Table I. The yields are based on GLPC analysis, and not necessarily optimum. The isolated yields are indicated in the parentheses. [b] The halides were recovered. [c] Allylbenzene (10%) was produced. [d] Trace amounts of styrene were detected.

alkylborates possess enhanced reducing ability over the primary example. However, the 9-BBN derivative is the most effective among the ate complexes examined.

Table II summarizes the results obtained in the reaction of **1** with various halides. As evident, tertiary (entries 1-6), benzylic, and allylic (entries 11-15) halides are smoothly reduced, while primary, secondary, and aryl halides are inert (entries 7-10). Therefore, this reagent may be valuable for the selective reduction of such halides without simultaneous attack on secondary and primary halogens present in the system. The *vic*-dihalide undergoes removal of the benzylic halogen with high selectivity (entry 16), in contrast to other agents which cause either elimination[4] to the olefin or complete dehalogenation[5] leading to the hydrocarbon.

Recently developed dehalogenation methods[6] and the well-known methods via $LiAlH_4$,[4a,7] AlH_3,[7] $NaBH_4$,[5,8] or dissolving metals[7] seem to be unsuitable for such selective removal, since the ease of reduction with other metal hydrides decreases along the series primary > secondary > tertiary.[4a,6c,7] Tertiary and secondary halides are reduced by $NaBH_4$ under solvolytic conditions,[9] organotin hydrides,[4b] diborane in liquid SO_2 or nitromethane,[10] and $NaBH_4$ in sulfolane.[11] However, the superior selectivity, mildness, and high yields obtainable recommend the present procedure for synthetic applications and compliment the utility of other hydride reduction methods.

In the present case, the α-hydrogen acts as the reducing species. This is supported by the structure of the borane isolated from the reaction mixture.[12] Retardation by hydroquinone was not observed, suggesting that a radical mechanism is not responsible for the reduction. Although the mechanism is not clear at present, the results indicate an obvious difference between **1** and the presently known hydride reagents, where the hydrides directly attached to metals act as the reducing species. Consequently, the reducing character of **1** toward other functional groups offers promising possibilities and is now under investigation.

The following procedure for the reduction of 1-bromoadamantane is representative. In a 100-ml flask, equipped with a magnetic stirrer and maintained under N_2, was placed 25 ml of dry *n*-hexane and 4.1 ml (20 mmol) of B-*n*-Bu-9-BBN.[13] *n*-Butyllithium in hexane (14.4 ml, 20 mmol) was added at 0°, and the resultant mixture (white gel) was stirred at 20° for 1 hr. 1-Bromoadamantane (4.30 g, 20 mmol) was then added at 0°, and the mixture was stirred overnight at 20°. Oxidation was accomplished in the normal fashion and the organic layer was separated and filtered through the column of alumina (40 g). Consecutive elution with hexane (60 ml), followed by evaporation of the solvent, gave 2.43 g (17.8 mmol) of adamantane (89% yield), mp (sublimes) 212-215° (lit.[14] 205-210°).

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