sine.[10] Cyclization of **4** to a tetrahydrobenzazepine **5** could be followed by oxidative fission of one aromatic ring in a manner analogous to the degradation of aromatic rings observed in a variety of living systems.[11] Two successive cyclizations transform **5** into a tetracyclic compound, **6**. Rearrangement of **6** could then give desmethylcephalotaxinone (**7**), which has been isolated from *Cephalotaxus* plants.[12] This hypothesis predicts that cephalotaxine should be labeled as shown in **7**. Experiments are in progress to determine if this prediction is correct.

Acknowledgment. We wish to thank Dr. R. G. Powell for gifts of alkaloids and Dr. Robert F. Perdue for dried plant material. Financial support from the National Institutes of Health (GM-19220) is gratefully acknowledged as is support from the National Science Foundation (GU 3852, GP 37156) which allowed purchase of a Bruker WH-90 NMR spectrometer used in this work.

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Received December 14, 1974

Laser Separation of Chlorine Isotopes. The Photochemical Reaction of Electronically Excited Iodine Monochloride with Halogenated Olefins

Sir:

We report here the photochemical separation of ^{35}Cl and ^{37}Cl when a mixture of ICl and the scavengers *trans*-ClHC=CHCl and 1,2-dibromoethylene (cis, trans mixture) is irradiated by a CW tunable dye laser that selectively excites I^{37}Cl. The scavenger has the property that it does not react with ground state ICl but does react with ICl in the excited A $^3\Pi_1$ state. Thus, from *trans*-ClHC=CHCl, both the photoproduct *cis*-ClHC=CHCl and the starting material *trans*-ClHC=CHCl show ^{37}Cl-^{35}Cl exchange. The latter demonstrates for the first time laser-controlled isotope interchange. In the case of BrHC=CHBr, all photoproducts are ^{37}Cl enriched; in particular, the *trans*-ClHC=CHCl photoproduct has a ^{35}Cl:^{37}Cl ratio of 2:1 compared to 3:1 for naturally occurring *trans*-ClHC=CHCl. This technique of selective laser excitation and subsequent isotope labeling provides us with a new means of following organic gas-phase photochemical reactions with state selection of the reactants.

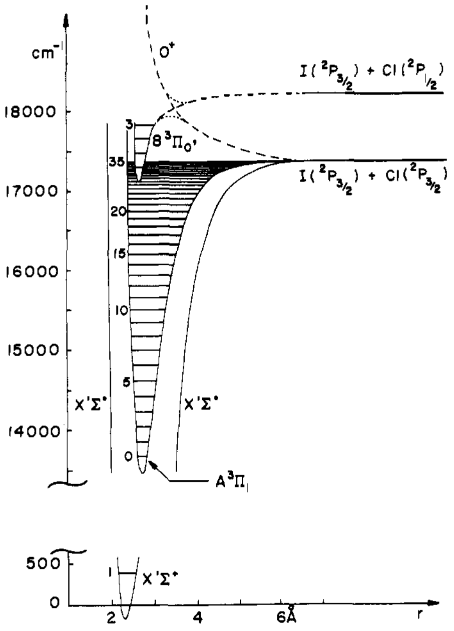

Figure 1. Potential energy curves for the X, A, and B states of ICl, taken from ref 1b with minor modification.

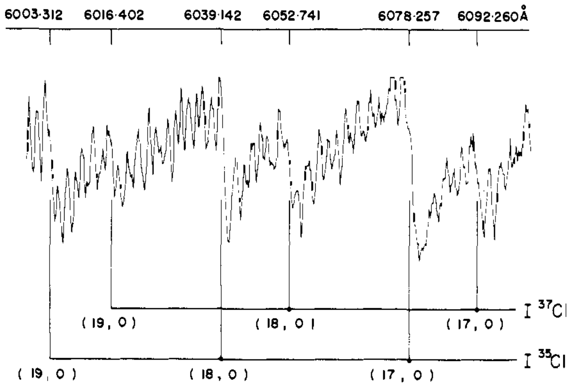

Figure 2. Low-resolution visible absorption spectrum of ICl taken from 6000 to 6100 Å. Note that the separation between the I^{35}Cl and I^{37}Cl bandheads are about 15 Å in this spectral region.

The visible absorption spectrum of I^{35}Cl and I^{37}Cl has been extensively studied,[1] and the relevant potential energy curves are shown in Figure 1. By tuning the CW dye laser to the (18, 0) bandhead of the I^{37}Cl A-X system at 6053 Å (see Figure 2), we can be assured that no photodissociation or photopredissociation occurs because the $v' = 18$ level of the A state lies ~784 cm^{-1} below the X state dissociation limit. Our laser has an average power of 10 mW and a relatively wide band width (3 Å); this permits preferential excitation of the I^{37}Cl molecule, although some I^{35}Cl is also excited.

A 1:1 mixture of ICl and *trans*-ClHC=CHCl (10 Torr each) is placed inside a Pyrex tube 1 m long and 5 cm diameter, and exposed for 3 hr. In the single-pass reaction cell about one-third of the laser beam (5-mm spot size) is absorbed. Then excess C_2H_4 is added to trap unreacted ICl. The products are separated by gas-liquid phase chromatography (GC). The presence of an extra peak in the GC spectrum is analyzed to be the photoproduct *cis*-ClHC=CHCl.

Isotope analysis of the products is accomplished using a Nier-type mass spectrometer having an accuracy in the ratio of the mass peaks, *P*, of four parts per thousand. For starting material, *trans*-ClHC=CHCl, the ratio $P_{35}:P_{37} = 3.01$, while for exposed *trans*-ClHC=CHCl $P_{35}:P_{37} = 2.73$. A small but significant enrichment of ^{37}Cl in the ex-

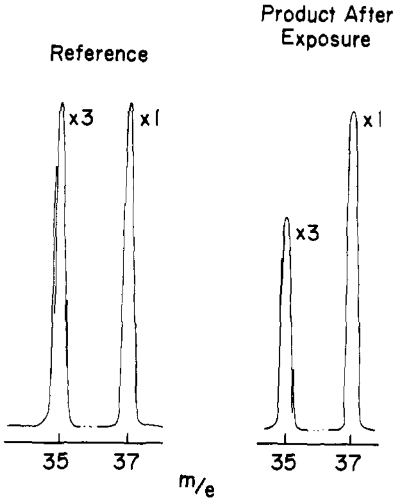

Figure 3. Mass spectrum of the m/e 35 and 37 peaks for (a) naturally occurring *trans*-ClHC=CHCl and (b) *trans*-ClHC=CHCl separated from the exposed reaction mixture. The ×3 peak is recorded on a scale three times smaller than the ×1 peak.

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.

Acknowledgment. This work is dedicated to the memory of the late Professor T. I. Taylor (Department of Chemistry, Columbia University). In this work, we used the mass spectrometer which he constructed. Financial support was provided by the National Science Foundation.

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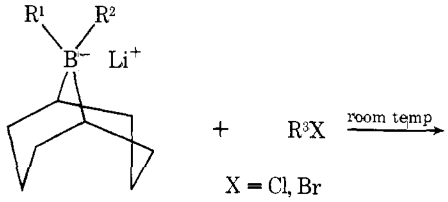
Received January 27, 1975

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).



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

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

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 $(n\text{-Bu})_4$B	0	100
Li $(n\text{-Bu})(sec\text{-Bu})_3$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.