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Date June 8, 1987

THE ADDITION OF HI TO UNSATURATED HYDROCARBONS USING I_2 and Al_2O_3

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Lyman Jay Stewart

August 1987

DEDICATION

This is dedicated to my parents, Lyman and Barbara, because without their loving guidance, dedication, support, and faith, none of this would have been possible.

This is also dedicated to the memory of Hubert Ray Belk, who never got to see any of this happen.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. George W. Kabalka and Dr. Richard M. Pagni for their guidance, patience, and insight during the course of this study. The author further wishes to acknowledge the financial support of The University of Tennessee and especially that of Dr. Kabalka.

Thanks are also extended to Donna L. Gray for her assistance on this project.

ABSTRACT

Previous investigators demonstrated that it is possible to iodinate arenes with iodine on dehydrated gamma alumina. This work focused on the hydroiodination of cyclic and acyclic alkenes using iodine and dehydrated gamma alumina. The mechanism of this addition of HI was also studied.

The results of this investigation show that cyclic alkenes such as cyclopentene, cyclohexene, cycloheptene, and cyclooctene react with I_2 on alumina to give the corresponding alkyl iodide. Acyclic such as 1-octene and alkynes such as 1-hexyne also react with I_2 on alumina to give iodinated products. The reaction involves the addition of HI to a carbon-to-carbon multiple bond and the addition takes place on the surface of the alumina. The reaction appears to proceed via a classical carbocation mechanism.

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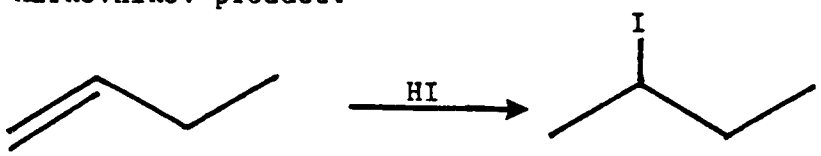
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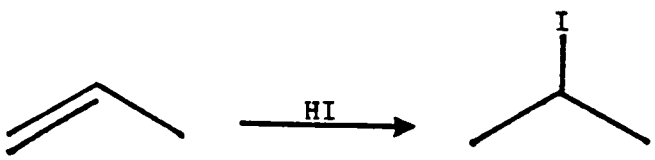
CHAPTER I

INTRODUCTION

Interest in the incorporation of iodine into organic compounds has become more pronounced in recent years due to the utility of radioactive iodine-123 in radiopharmaceuticals used in medicinal imaging.[1] This new application for organic iodides has resulted in an increased effort to develop new, milder methods for incorporating iodine into molecules containing important functional groups. This brief overview will not attempt to cover all the methods for iodinations but will highlight the most common iodination methods.

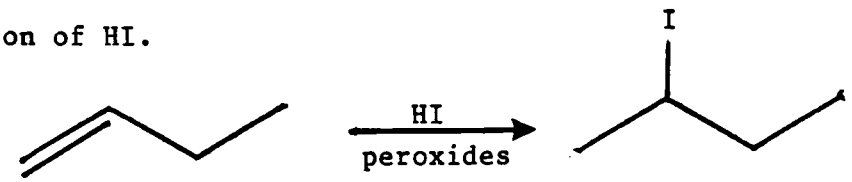
The classical method for synthesizing alkyl iodides involves the reaction between alkenes and HI. The first reported syntheses of alkyl iodides by this method were developed by Erlenmeyer[2], Buterlow[3], and Wurtz.[4] They showed that HI added to alkenes to give only the Markovnikov product.

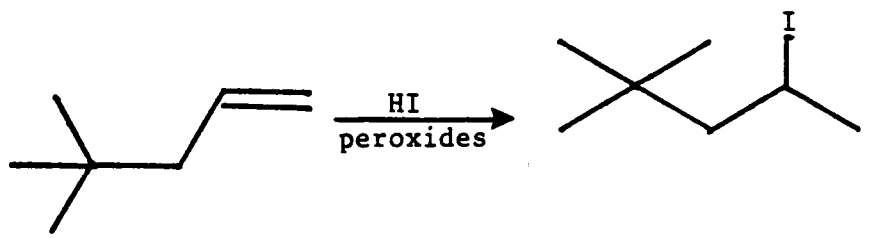




After it had been shown that the Markovnikov product is easily obtained, Kharasch and Hannum[5] attempted to make the anti-Markovnikov product by adding peroxides to the reaction mixture. The reaction of HI with alkenes is suprisingly unaffected by the presence of peroxides.

The addition of peroxides did increase the velocity of the reaction, but did not yield the desired anti-Markovnikov product.[6] It is likely that the reducing action of HI towards peroxides is responsible for this result, with the liberated I_2 acting as a catalyst for the addition of HI.





In the early 1940's, Hartman, Byers, and Dickey published an iodination method involving the reaction of an alcohol with PI_3. This method has its drawbacks because it does not allow other oxygen containing functionalities to be present in the starting material since PI_3 reacts quickly with any oxygen atom, whether or not it is in the desired alcohol. The resulting phosphorous acid is also extremely corrosive.[7]

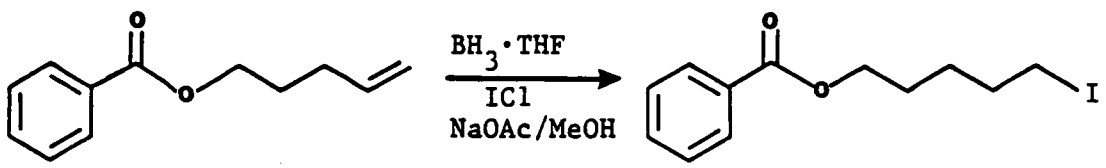
$$3\ C_{16}H_{33}OH + PI_3 \longrightarrow 3\ C_{16}H_{33}I + H_3PO_3$$

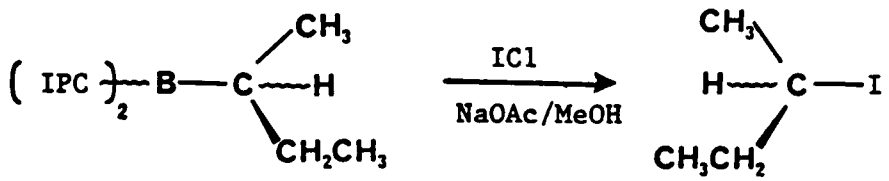
The first general synthesis of the anti-Markovnikov alkyl iodide was developed by Brown and associates who found that the reaction of R_3B with I_2 in methanolic NaOH gave primary alkyl iodides. Unfortunately, the extremely basic reaction conditions limited the synthetic utility of the organoborane iodination sequence.[8]

$$3\ CH_3CH_2CH{=}CH_2 \xrightarrow{BH_3\cdot THF} (CH_3CH_2CH_2CH_2-)_3B$$

$$R_3B \xrightarrow{3\ I_2} \xrightarrow{3\ NaOH/MeOH} 3\ CH_3CH_2CH_2CH_2I$$

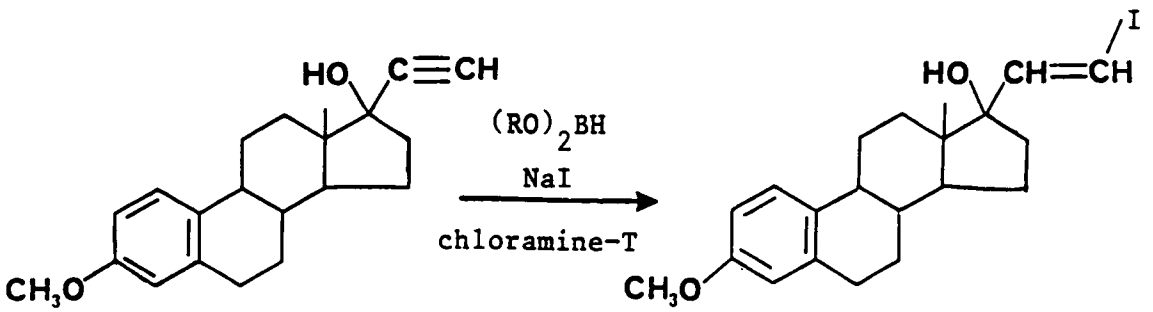
The first procedure that allowed for the presence of functional groups in the target molecule was developed by Kabalka and Gooch.[9] Their method involved the reaction of R_3B with ICl to give the corresponding alkyl iodide. This method also produced excellent yields. It became possible, by this method, to control the stereochemistry of the reaction products. If the borane is optically active, then the resulting alkyl iodide is optically active.[10]





(IPC = Isopinocamphyl)

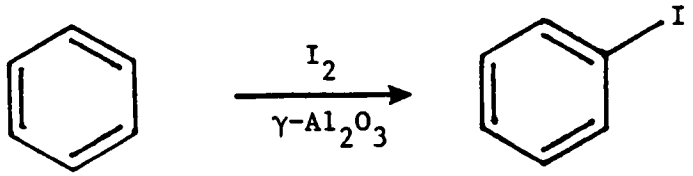
In order to provide an even milder conversion of the organoborane to the alkyl iodide, Kabalka and Gooch used NaI and chloramine-T.[11] This is a very convenient method for converting the organoborane to the alkyl iodide, and has led to the synthesis of several useful iodinated radiopharmaceuticals.[12-14]

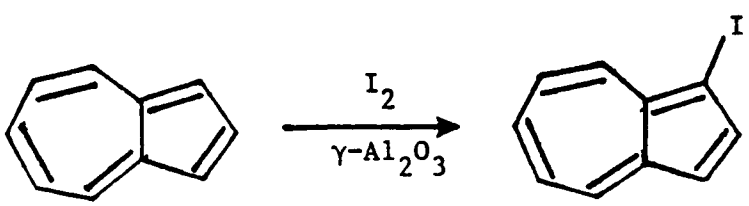


One of the newest and most interesting methods for incorporating iodine into organic substrates involves using metals. Tsipis and coworkers, for example, have been able to isolate the di-iodinated product of the reaction between an alkene and iodobis(N,N-dimethyl-dithiocarbamato)iron(III) complexes.[15]

$$CH_2{=}CH_2 \xrightarrow{2\,[Fe(S_2CNMe_2)_2I]\;I_2} CH_2ICH_2I$$

Metal oxides, such as alumina, also catalyze iodination reactions. It has been demonstrated that these reactions take place on the surface of dehydrated gamma alumina. Boothe et al. have shown that it is possible to iodinate benzene, toluene, and even azulene by adsorbing the substrate onto the activated alumina along with I_2.[16]





During his research, Boothe found that cyclohexene is easily converted into cyclohexyl iodide when reacted with I_2 on gamma alumina. This discovery led to the research that is the subject of this thesis.

The goal of this research was to utilize the catalytic ability of dehydrated gamma alumina to achieve the iodinations of cyclic alkenes in a straightforward manner, with few side reactions which would permit the easy recovery of product. The method that is described in this thesis meets these criteria; in addition, the method can be used to iodinate acyclic alkenes and alkynes regio-specifically.

CHAPTER II

RESULTS AND DISCUSSION

The iodination of cyclic and acyclic alkenes was performed using a procedure called the slurry method. This involved the following: a small amount of alkene and excess I_2 were added to distilled, low-boiling petroleum ether. Dehydrated activity grade 1 neutral alumina was then added, and the reaction run at the reflux temperature of the ether, 35°C, for an appropriate time. The dehydrated alumina was prepared at 400°C under vacuum using the procedure of Pagni and co-workers.[17]

The yields of the iodinated products were determined, in most cases, by injecting a known ammount of an alkane standard into the reaction mixture and then analyzing the mixture by gas chromatography. The amount of standard used corresponded to a 50% yield of the product.

For all the reactions outlined below, the reaction times indicated were those that gave the maximum yield of product.

A. Cyclohexene

Cyclohexene was treated with I_2 using the method described above, and only one iodinated product was obtained. The ^1H and ^{13}C NMR spectra of this compound were obtained and compared to the spectra of standard cyclohexyl iodide purchased from the Aldrich Chemical Corporation. This comparison showed the two compounds to be identical. See figures 1 and 2.

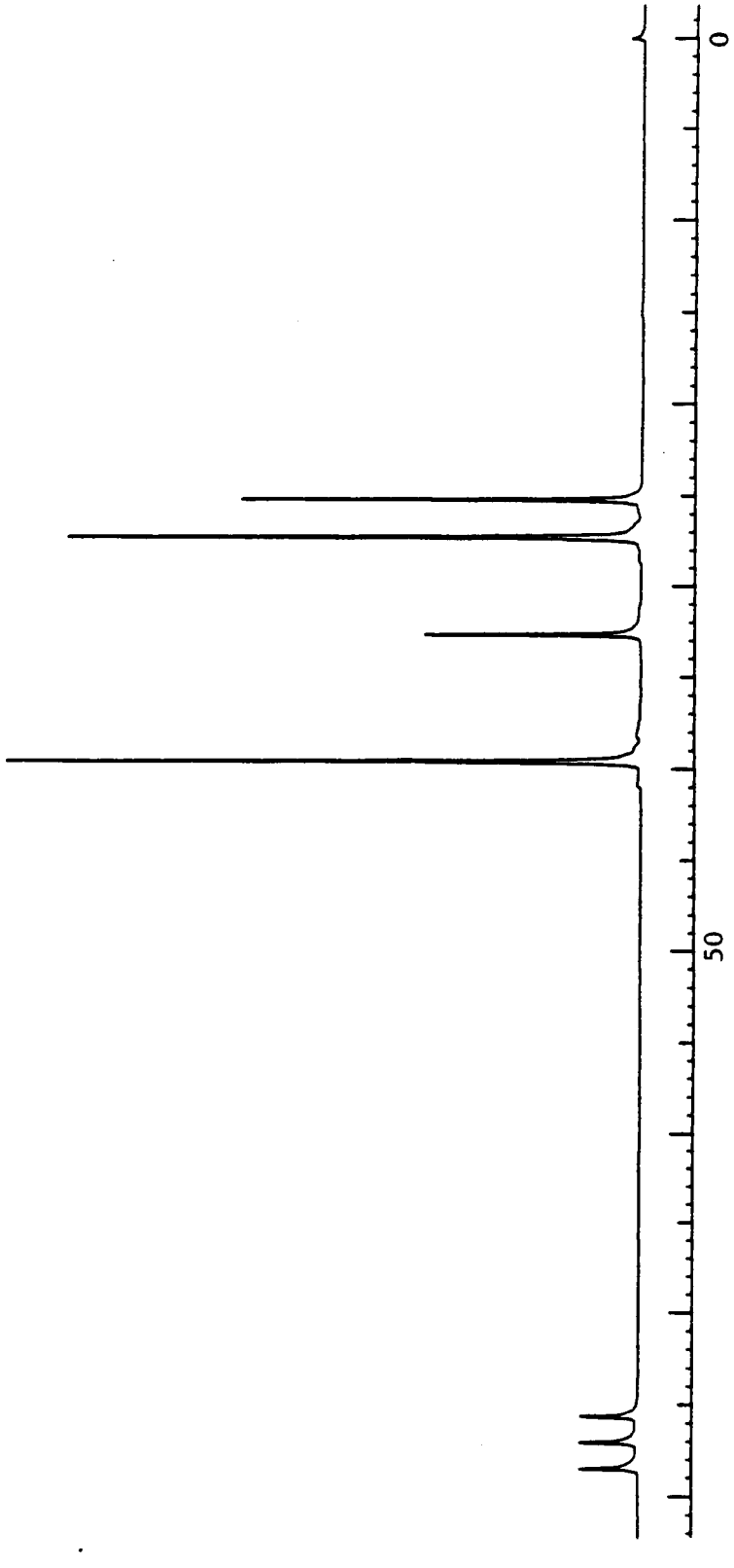


Figure 1. ^{13}C NMR spectrum of standard cyclohexyl iodide.

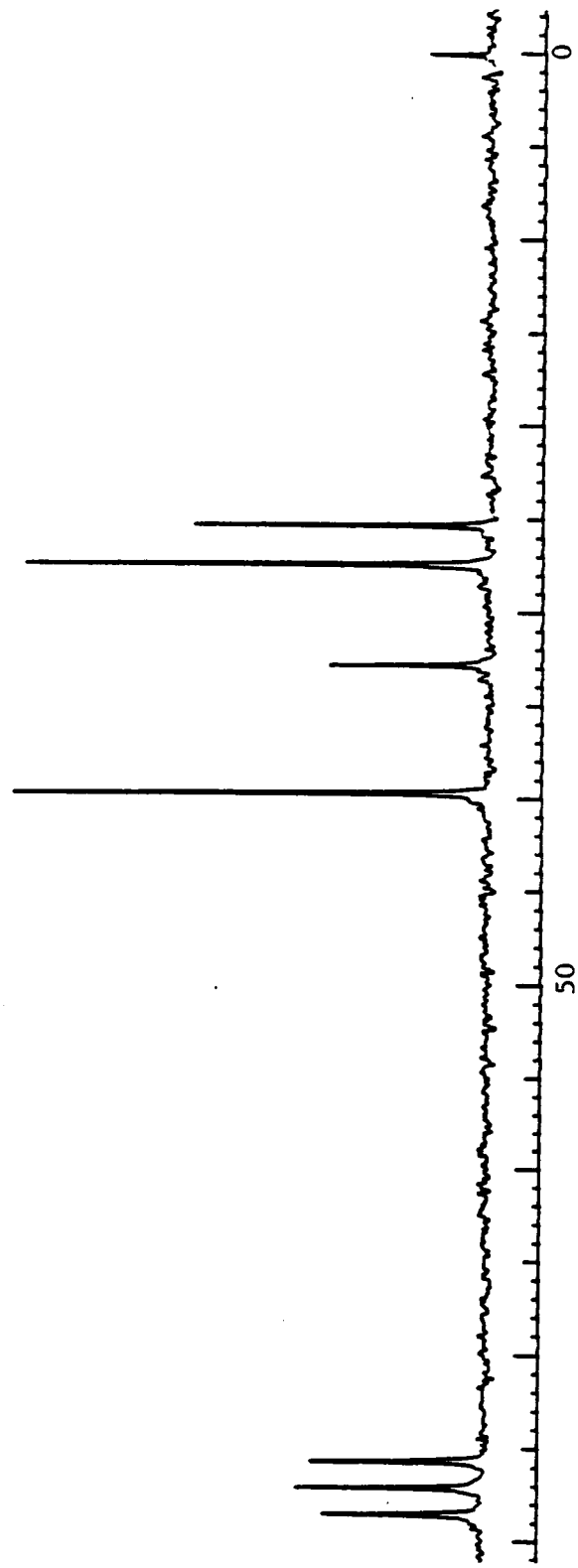
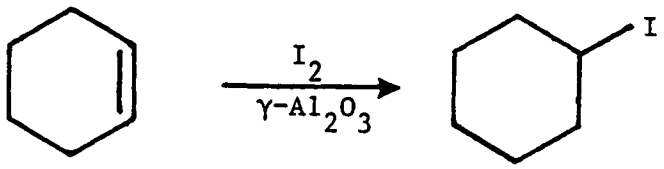


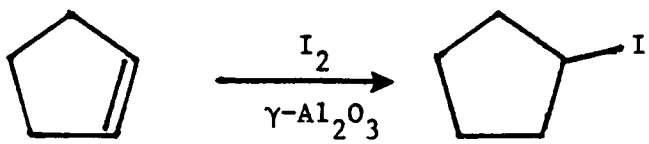
Figure 2. ^{13}C NMR spectrum of cyclohexyl iodide from the alumina reaction.



The reaction of cyclohexene and iodine at reflux for 2 hours gave an 85.1% yield of the iodinated product as determined by the gas chromatographic method.

B. Cyclopentene

Cyclopentene was treated with I_2 using the procedure described above, and only one iodinated product was obtained. Because standard spectra of cyclopentyl iodide were not available and the product was not commercially available, the compound was prepared by the reaction of cyclopentanol and PI_3[7]. The standard's ^1H and ^{13}C NMR spectra were identical to those of the alumina reaction product. The ^{13}C NMR spectra are presented in figures 3 and 4.



A 1.75 hour reflux of cyclopentene, iodine, and alumina gave a 42% yield of the iodinated product.

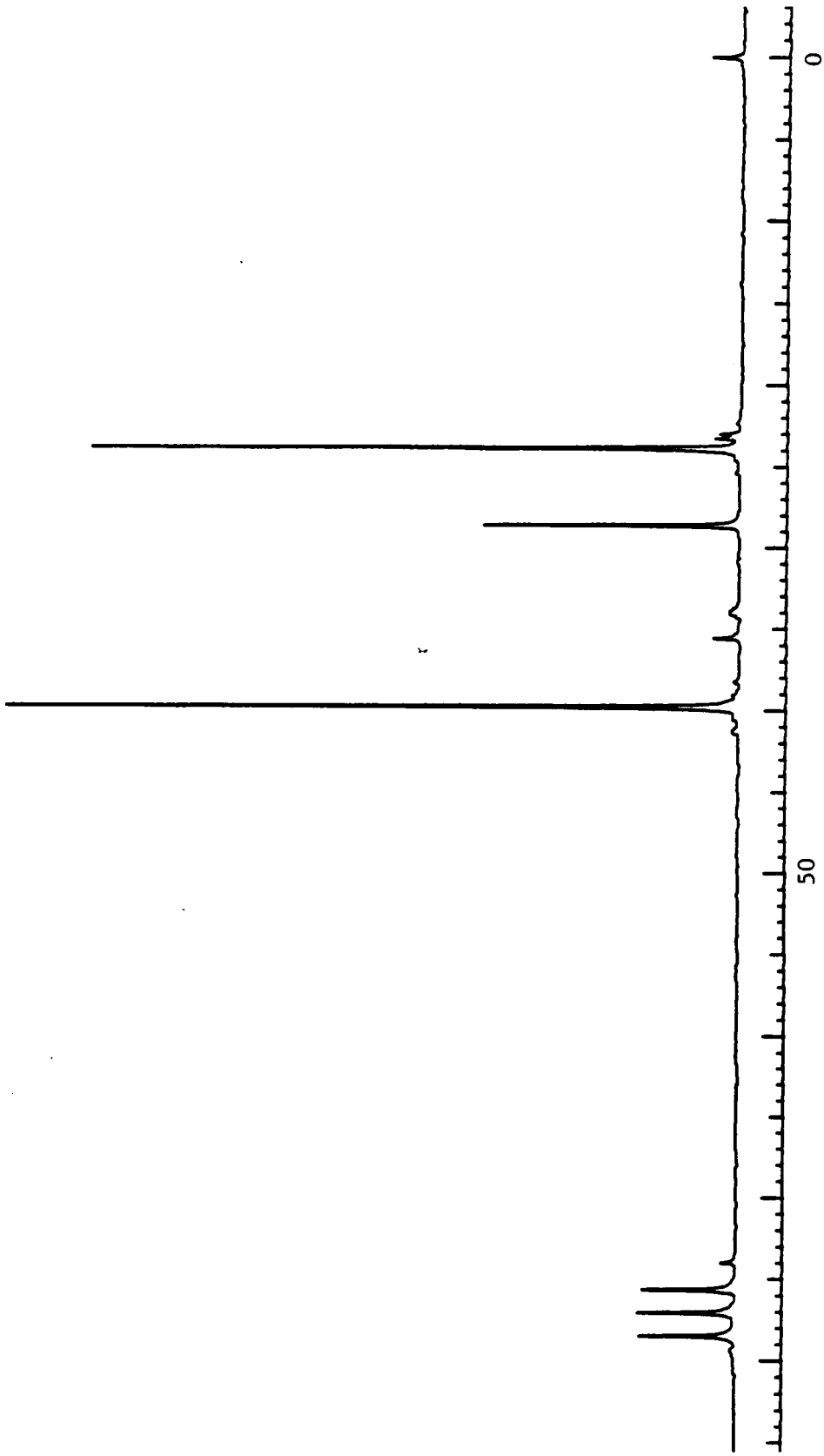


Figure 3. ^{13}C NMR spectrum of standard cyclopentyl iodide.

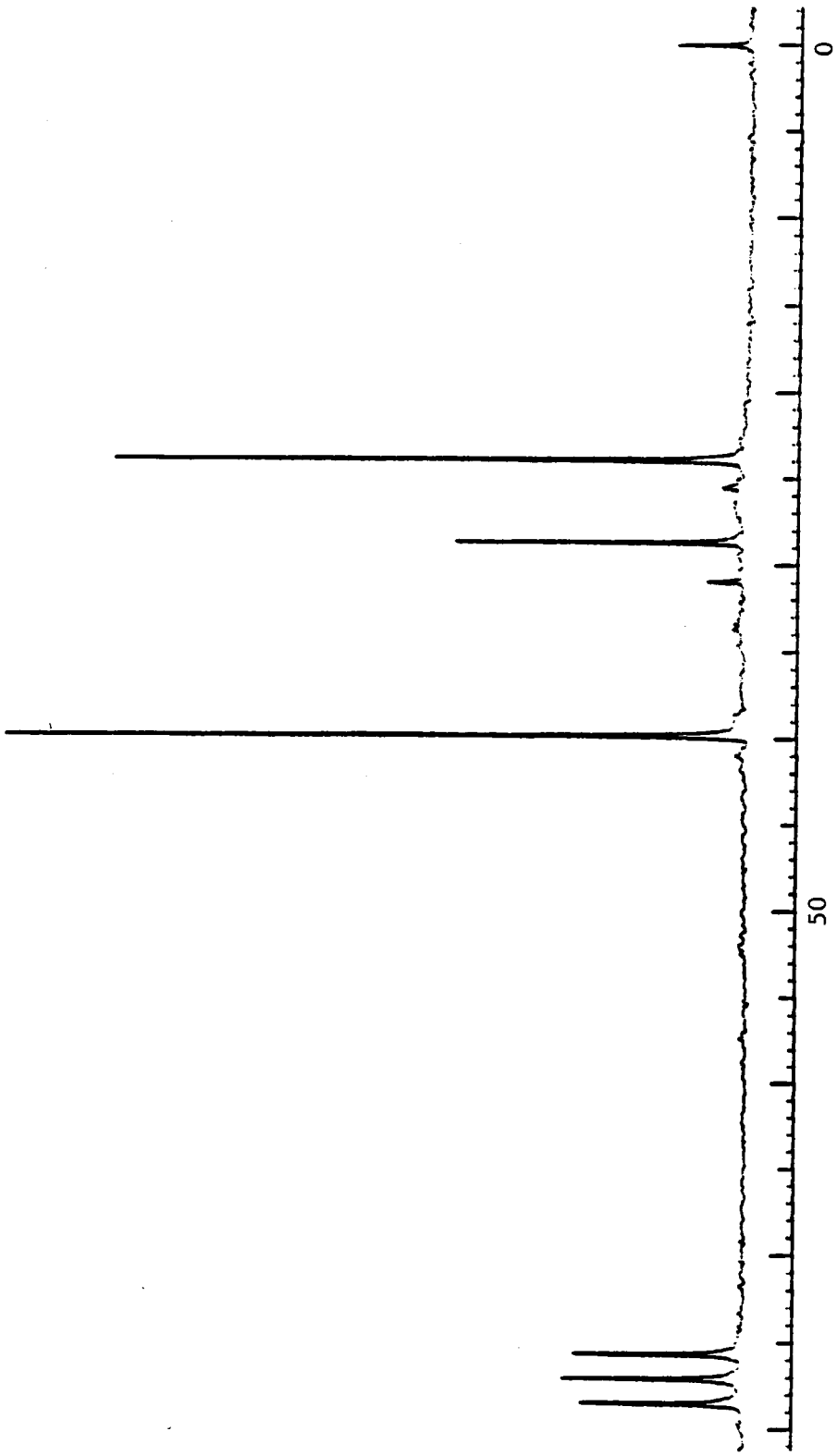
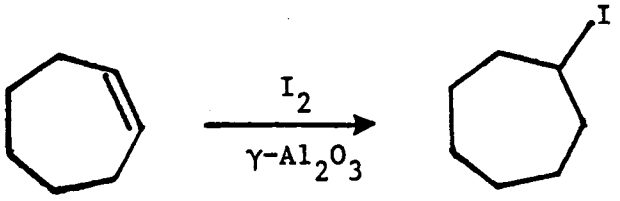


Figure 4. ^{13}C NMR spectrum of cyclopentyl iodide from the alumina reaction.

C. Cycloheptene

Cycloheptene was treated with I_2 using the reaction conditions previously described, and only one iodinated product was obtained. Comparison of authentic material produced in the reaction of cycloheptanol and PI_3 with the product from the alumina reaction proved the latter to be cycloheptyl iodide. See figures 5 and 6.



A 6 hour reaction between cycloheptene and iodine gave a 48.7% yield of the iodinated product.

D. Cyclooctene

Treatment of cyclooctene with I_2, using the reaction conditions previously described, yielded only one iodinated product. Standard cyclooctyl iodide was prepared for comparison to the product formed in the alumina reaction by the reaction of cyclooctanol and PI_3. The ^{1}H and ^{13}C NMR spectra of both the standard material and the reaction product were identical. The ^{13}C NMR spectra are presented in figures 7 and 8.

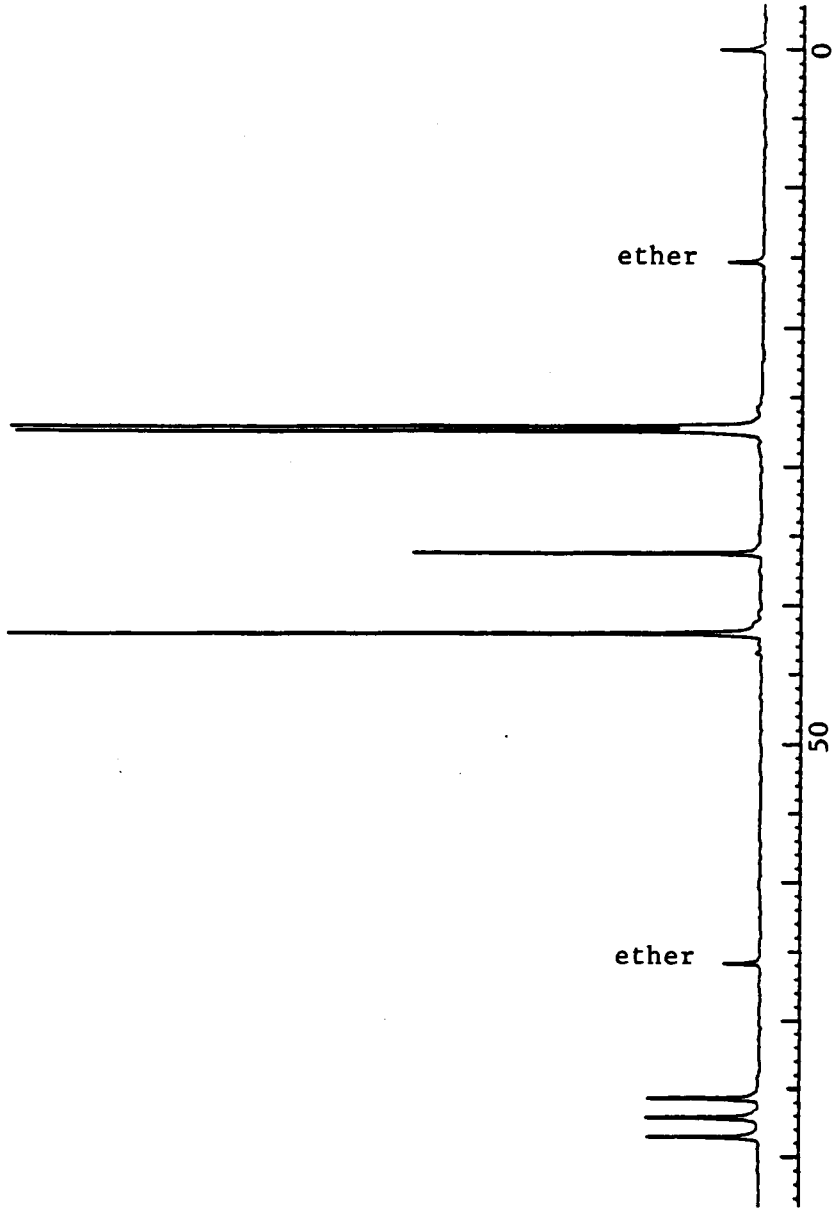


Figure 5. ^{13}C NMR spectrum of standard cycloheptyl iodide.

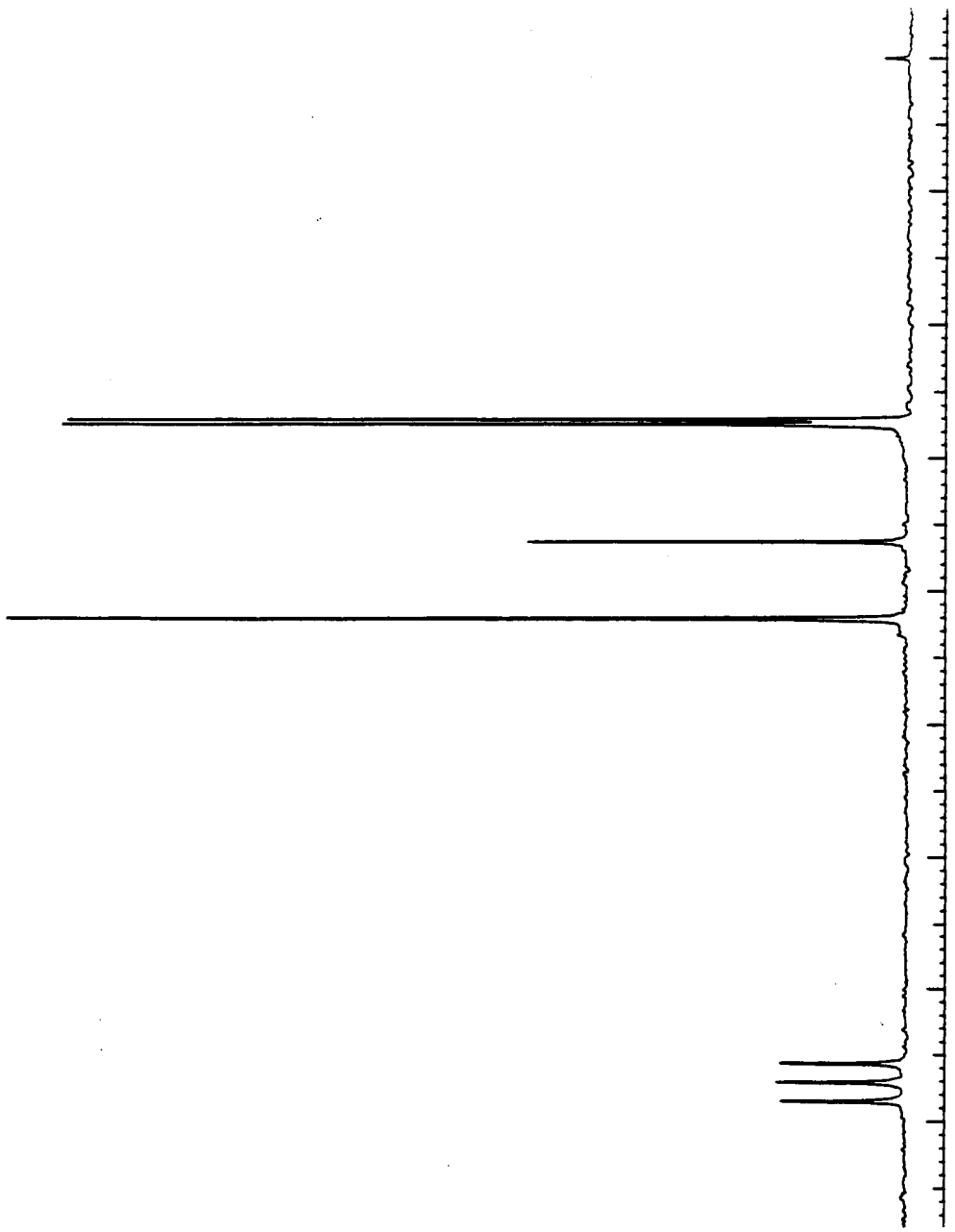


Figure 6. ^{13}C NMR spectrum of cycloheptyl iodide from the alumina reaction.

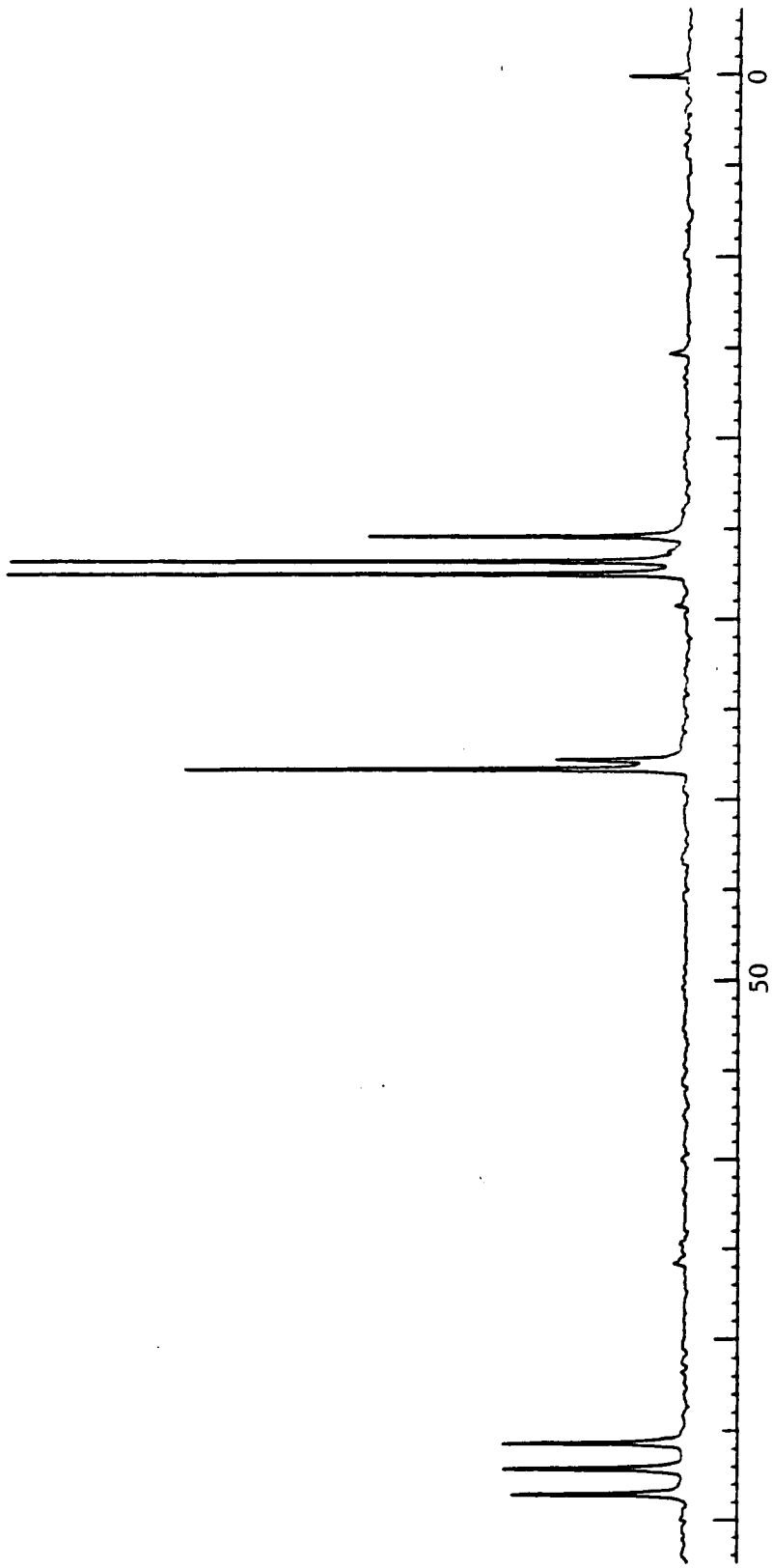


Figure 7. ^{13}C NMR spectrum of standard cyclooctyl iodide.

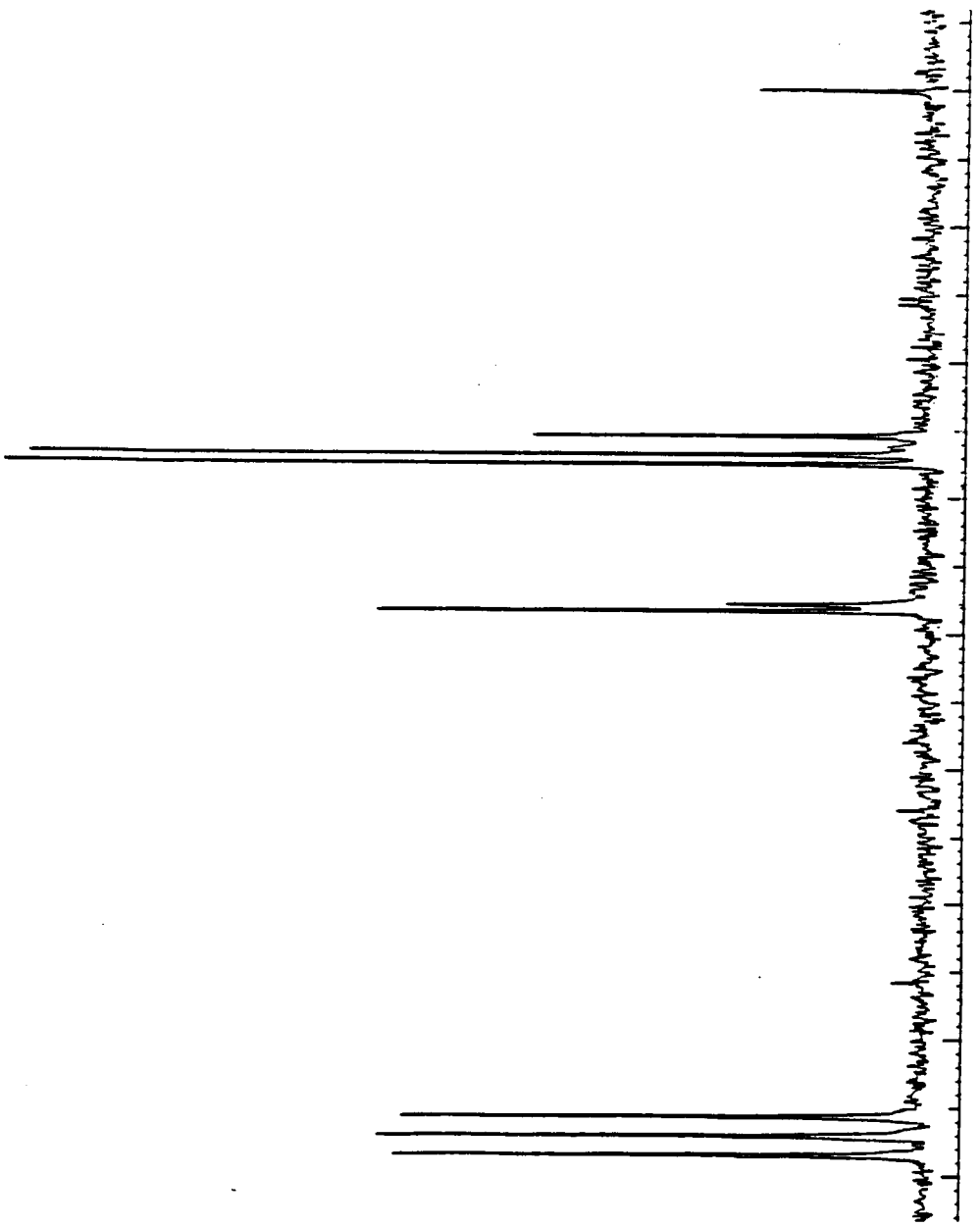
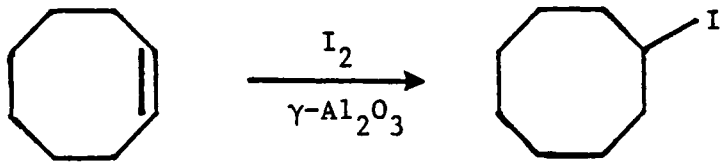


Figure 8. ^{13}C NMR spectrum of cyclooctyl iodide from the alumina reaction.



The cyclooctyl iodide was purified by column chromatography, because the high boiling point of the product made gas chromatography difficult. Column chromatography using silica gel as the stationary phase and petroleum ether and ethyl ether as the mobile phases gave excellent separation of the iodinated product from starting material.

A 32.5 hour reaction between cyclooctene and iodine on alumina at the reflux temperature of petroleum ether gave a 36.5% yield of the iodinated product.

E. 1-Octene

1-Octene was treated with I_2 as described previously, and only one iodinated product, 2-iodooctane, was obtained from the reaction. Reference 2-iodooctane was prepared by the reaction of 2-octanol and PI_3. ^1H and ^{13}C NMR spectra of both the standard and the alumina reaction product showed the compounds to be identical. The ^{13}C NMR spectra are presented in figures 9 and 10.

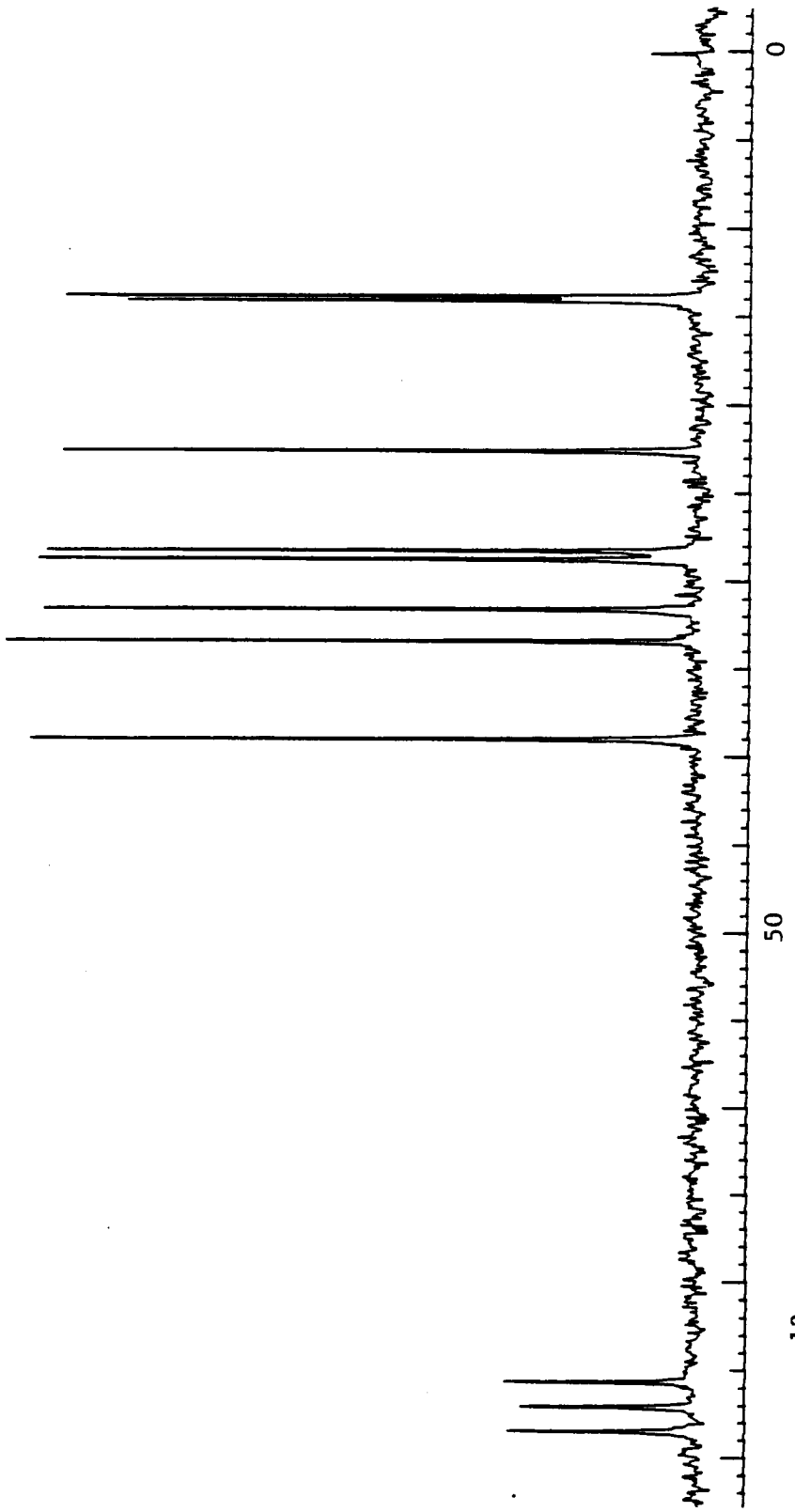


Figure 9. ^{13}C NMR spectrum of standard 2-iodooctane.

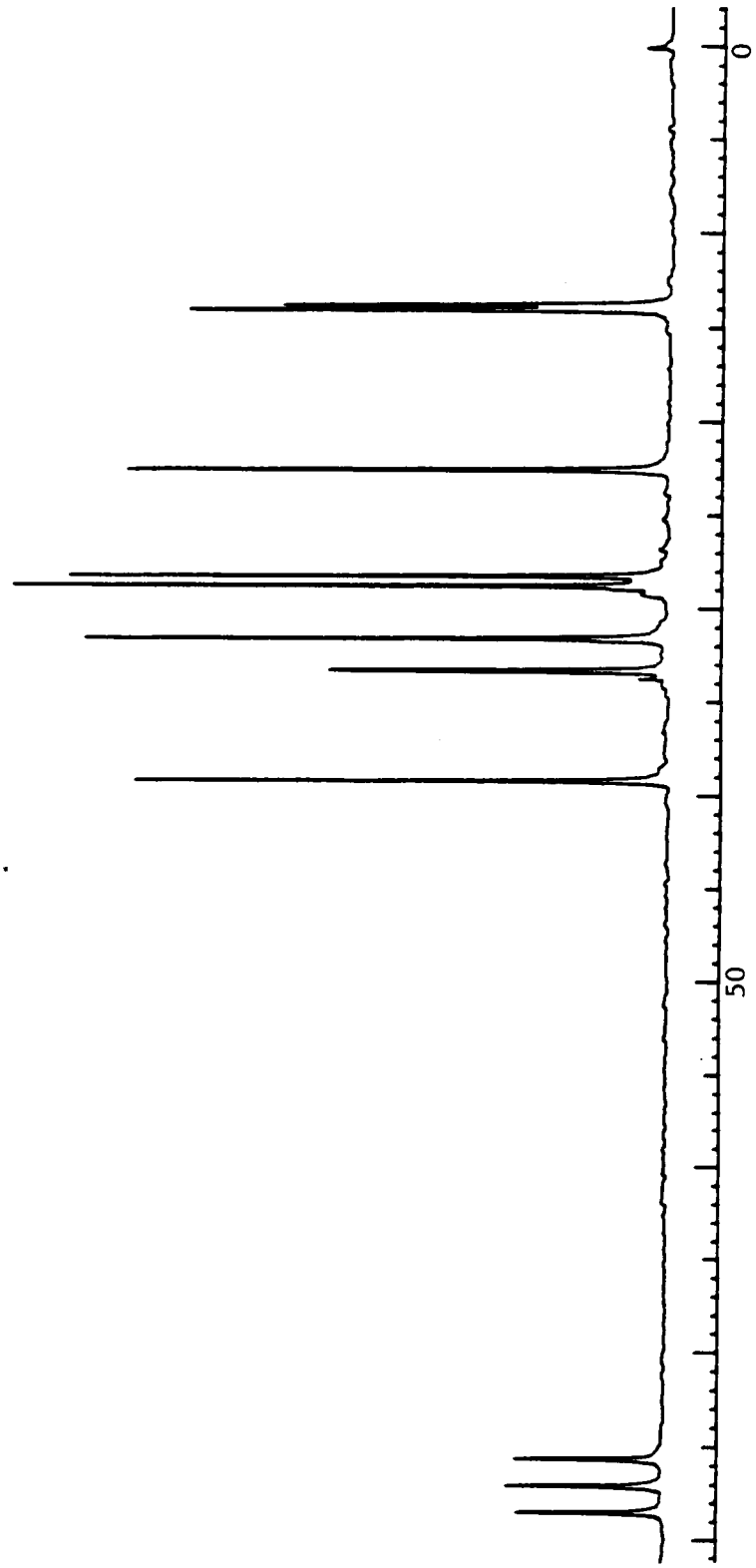
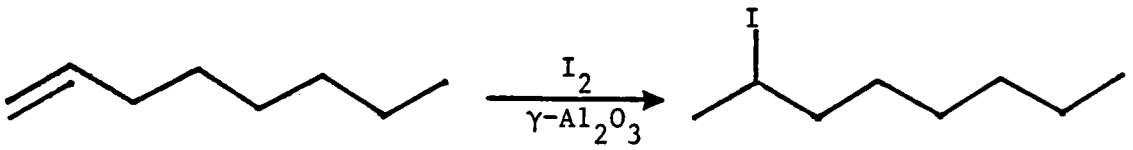


Figure 10. ^{13}C NMR spectrum of 2-iodooctane from the alumina reaction.



Due to the high boiling point of 2-octyl iodide, it was not purified by gas chromatography. The product was purified by removing the starting alkene under vacuum ($\leq$5mm Hg). A 2 hour reaction of 1-octene with iodine at reflux gave an 83.5% yield of the iodinated product.

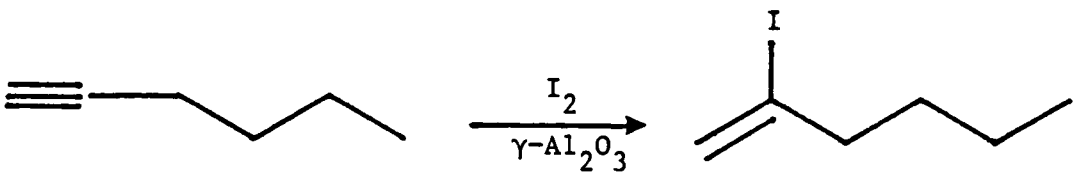
F. Norbornene

Reaction of norbornene with I_2 in a slurry of alumina and refluxing petroleum ether yielded no iodinated products after 8 hours. It was thought that the reaction temperature of 35°C might be too low for the reaction to be successful. The solvent was changed to the higher boiling cyclohexane, boiling point 80°C, and still there was no iodinated product formed after a 6 hour reaction.

G. 1-Hexyne

1-Hexyne was treated as previously described, except that 2 equivalents of I_2 on alumina were used. Only one iodinated product was obtained. It was thought that the excess of iodine in the reaction

mixture would afford the diiodinated product, 2,2-diiodohexane. The ^{1}H spectrum shows a strong singlet at 6.8 ppm, characteristic for vinyl H's alpha to an iodine atom, figure 11. There is also a triplet at 2.5 ppm, corresponding to methylene H's shifted downfield due to the influence of the iodine atom. The ^{13}C spectrum shows two peaks characteristic of a vinyl iodide. The internal vinyl carbon carying the iodine gives a sharp peak at 79 ppm. The other vinyl carbon peak is at 104.5 ppm, due to the external vinyl carbon. Both of the peaks are shifted upfield from where normal vinyl carbons resonate because of the influence of the iodine atom, figure 12. Elemental analysis was also consistent with the product being the vinyl iodide, 2-iodo-1-hexene.



A 2 hour reaction of 1-hexyne with iodine on alumina at reflux gave a 61.8% yield of the iodinated product as determined by gas chromatography.

H. Styrene

A reaction of I_2 and styrene was run using the standard method, and no iodinated product could be isolated from the reaction mixture. The styrene polymerized in the reaction flask during a 4-hour reaction

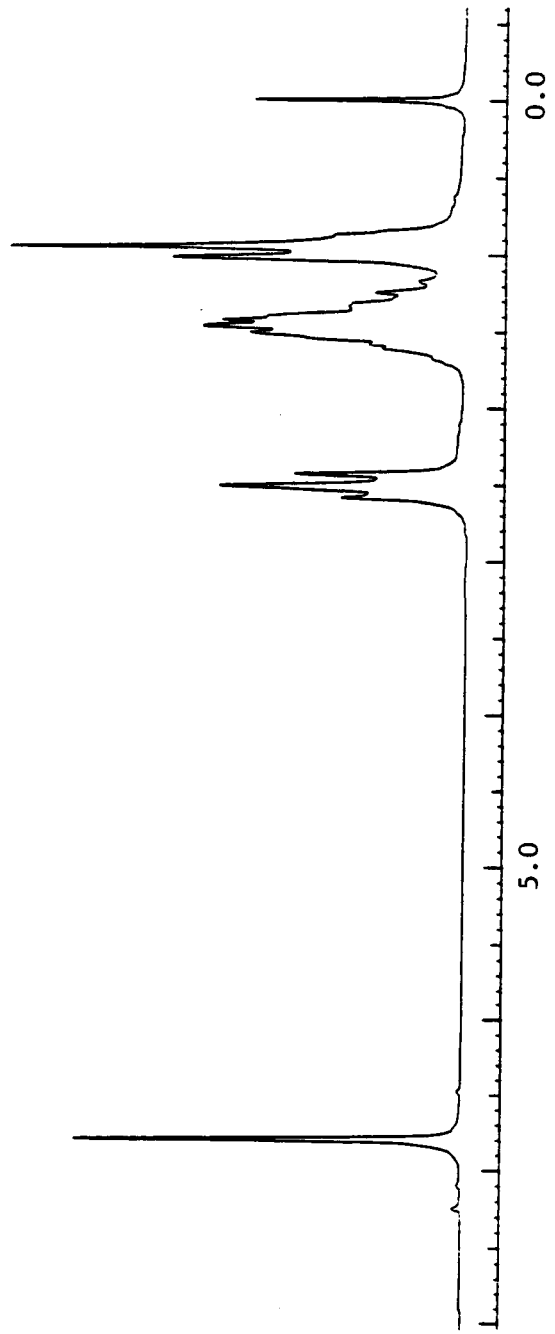


Figure 11. ^{1}H NMR spectrum of 2-iodo-1-hexene from the alumina reaction.

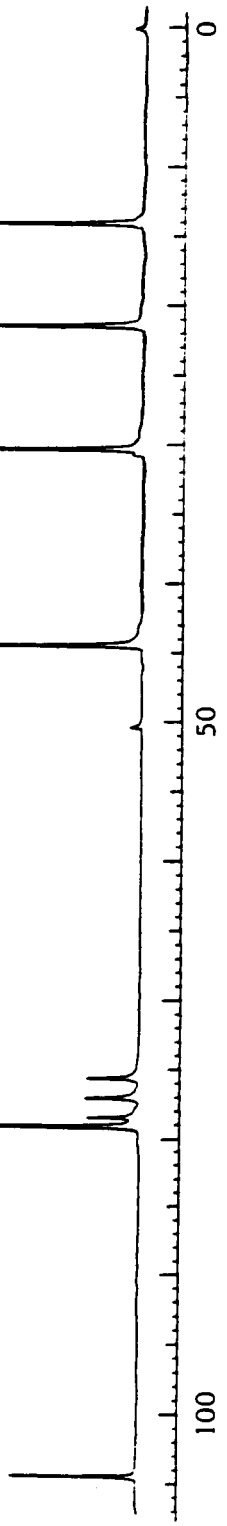


Figure 12. ^{13}C NMR spectrum of 2-iodo-1-hexene from the alumina reaction.

while the solution polymerized upon evaporation of the solvent after a 2-hour reaction. The polymer was dissolved in toluene in an attempt to observe any iodinated product, but ^{1}H and ^{13}C NMR showed only polystyrene and toluene.

I. Trans-Stilbene

Trans-stilbene was treated with I_2 in the usual manner, but no iodinated product was isolated. After a 4 hour reaction time, the solvent was removed from the product mixture by evaporation. Hot ethanol, 15 ml, was added to the product and the mixture allowed to cool. Crystals of trans-stilbene began to form in the flask. These crystals were removed by filtration, and a ^{13}C NMR spectrum of the crystals in $CDCl_3$ showed the crystals to be trans-stilbene. Both ^{1}H and ^{13}C NMR spectra of the resulting ethanol solution showed only solvent and ethanol.

J. 3,3-Dimethyl-1-butene and 2,3-Dimethyl-2-butene

A reaction of 3,3-dimethyl-1-butene with I_2 on alumina gave only one iodinated product. The product of this reaction was compared to the product of the reaction of 2,3-dimethyl-2-butene with I_2 on alumina. ^{1}H and ^{13}C NMR spectra of both products showed them to be identical (Figures 13 and 14). Authentic 2,3-dimethyl-2-iodobutane was prepared by the reaction of 2,3-dimethyl-2-butanol and PI_3 (Figure 15).

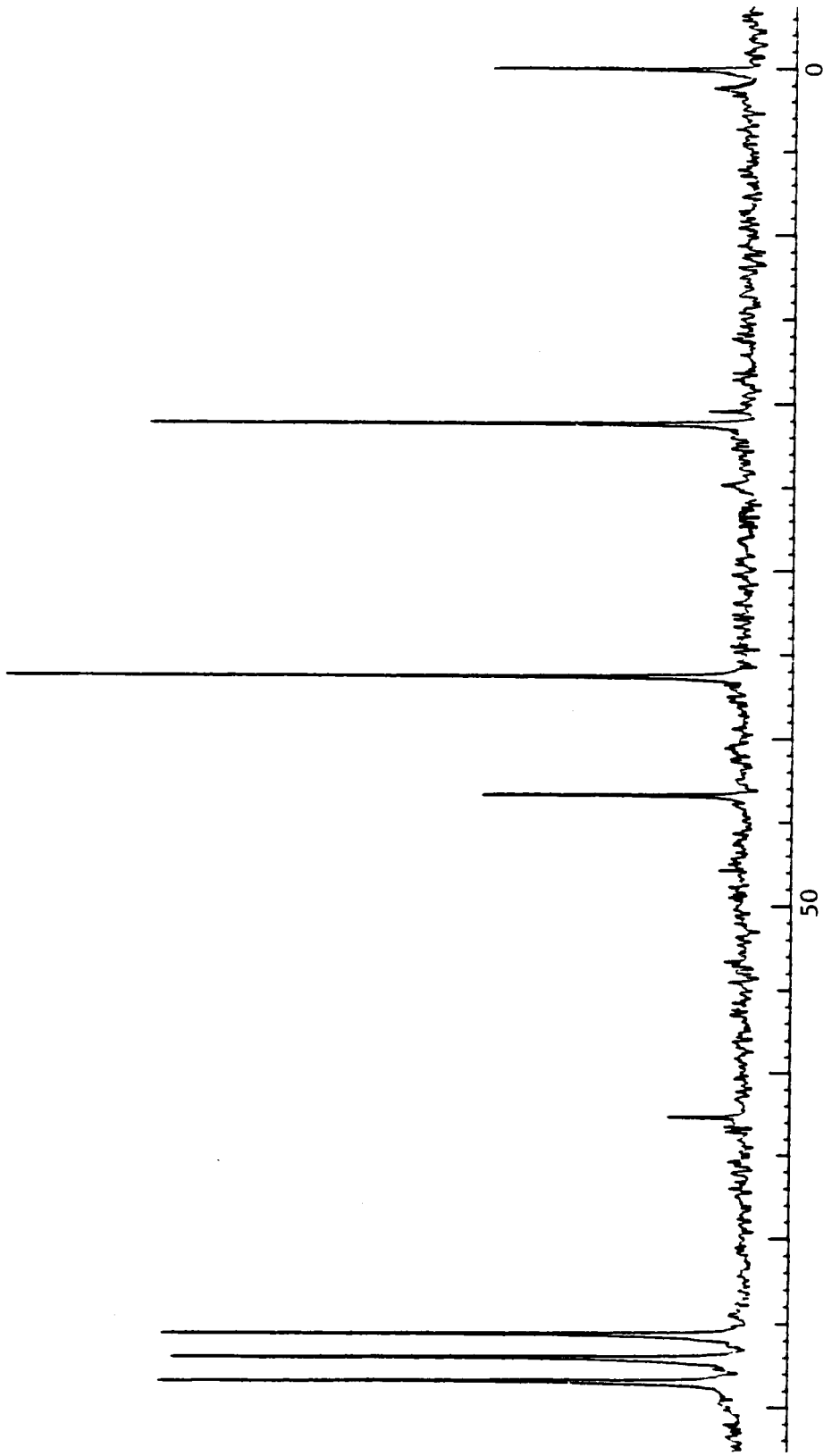


Figure 13. ^{13}C NMR spectrum of 2,3-dimethyl-2-iodobutane from the alumina reaction of 3,3-dimethyl-1-butene.

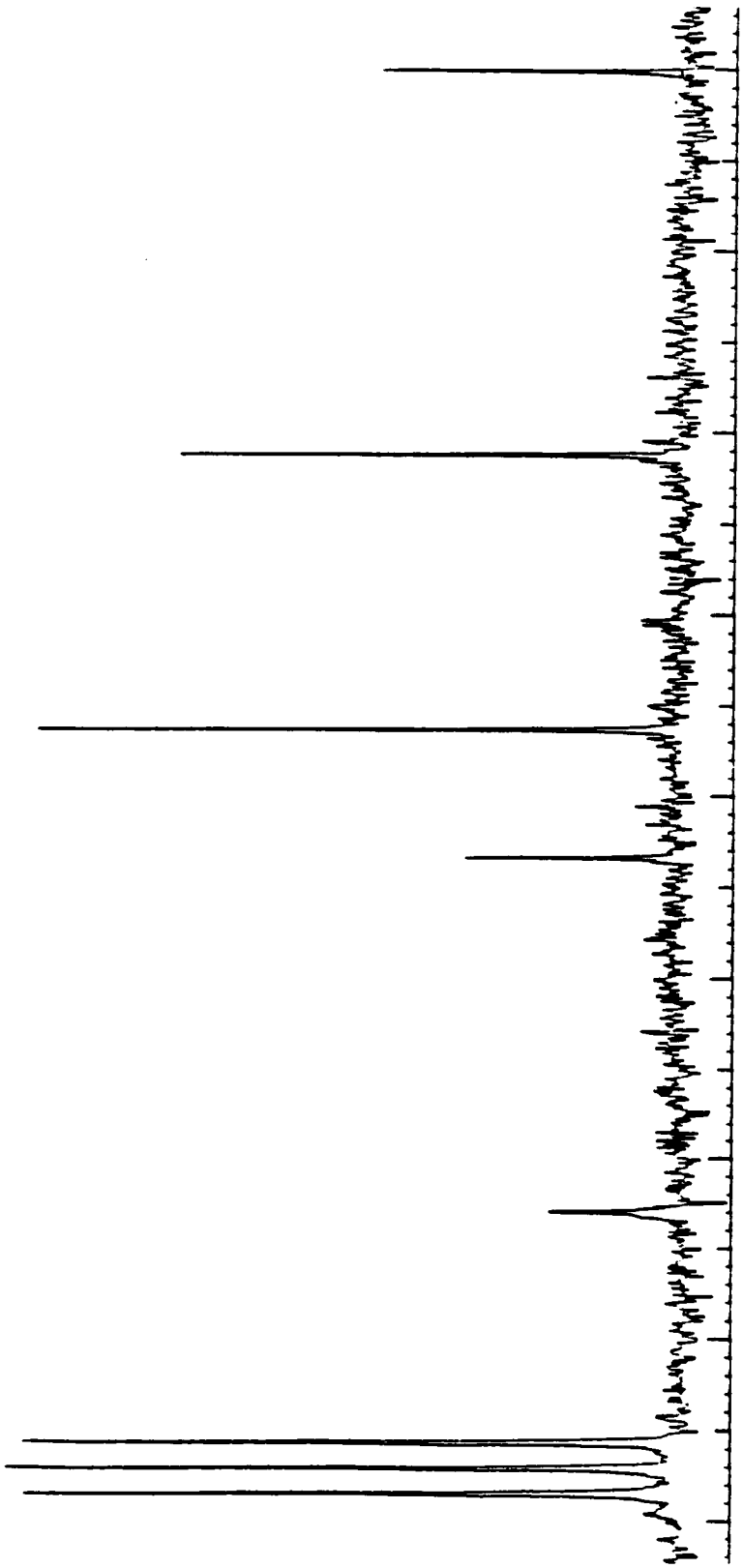


Figure 14. ^{13}C NMR spectrum of 2,3-dimethyl-2-iodobutane from the alumina reaction of 2,3-dimethyl-2-butene.

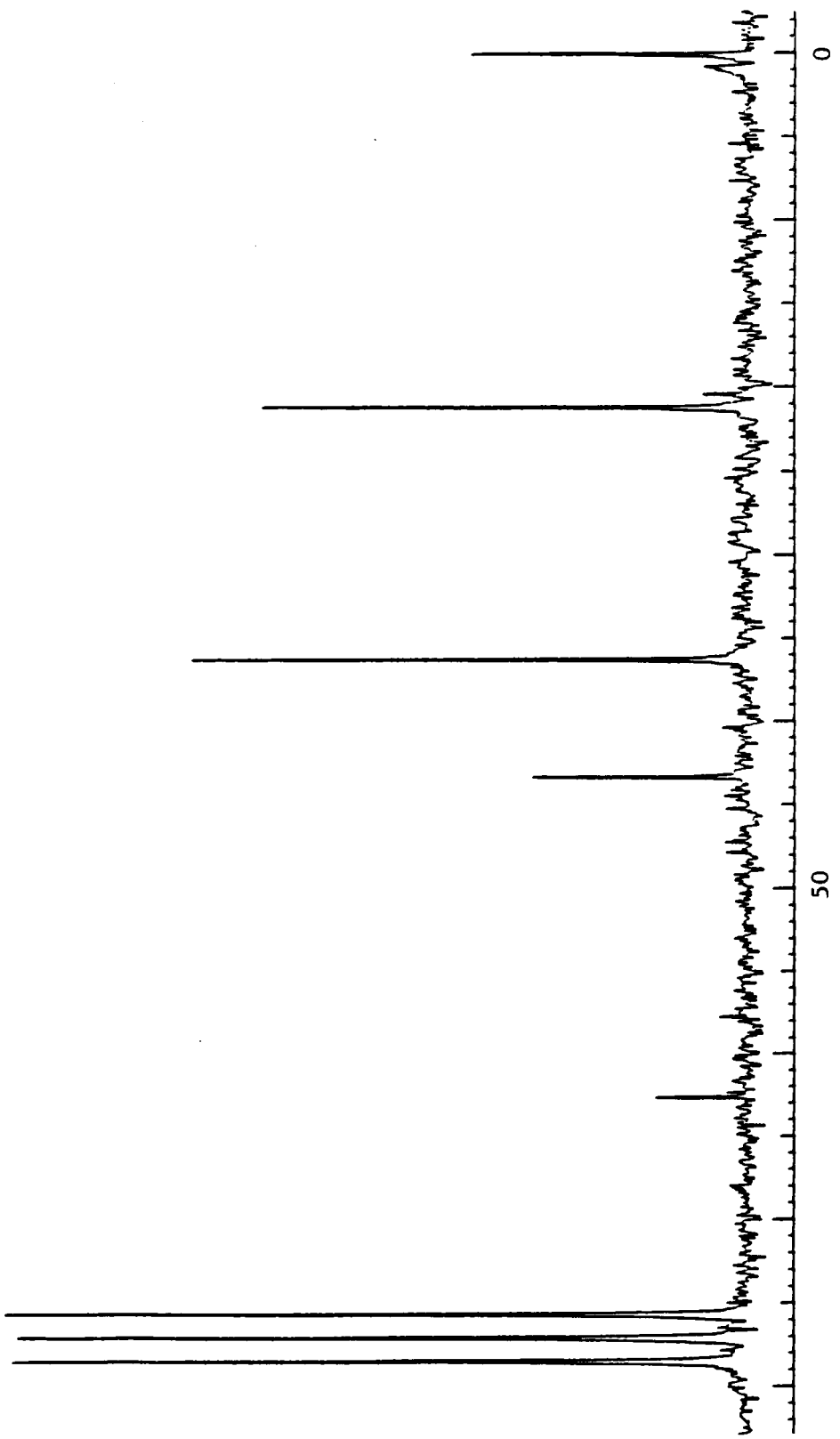
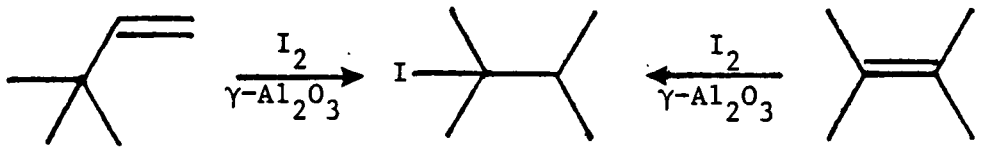


Figure 15. ^{13}C NMR spectrum of standard 2,3-dimethyl-2-iodobutane.



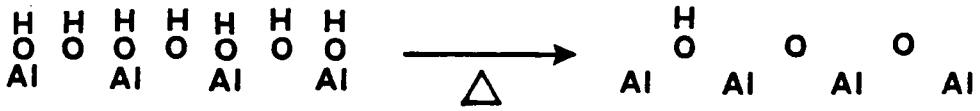
A 2 hour reaction of 3,3-dimethyl-1-butene gave a 30.5% yield of 2,3-dimethyl-2-iodobutane, while a 4 hour reaction of 2,3-dimethyl-2-butene gave a 36.1% yield of the same product.

K. Reaction Studies and Discussion

In an effort to understand the mechanism of the addition of HI to alkenes and alkynes on alumina, several parameters were investigated; these included the degree and effect of dehydration, reaction location, and the use of other surfaces for the reaction. The alkene used for these studies was cyclohexene.

The surface of alumina has been shown to be an excellent place to perform electrophilic iodinations of arenes.[16] This is due to the nature of the surface itself. Before dehydration, the surface of alumina is covered by a layer of hydroxyl groups. Upon heating, many of these hydroxyls react to give water which is driven from the surface. The remaining surface has exposed Al^{+3} ions as well as O^{-2} ions in addition to the hydroxyls that remain on the surface. The quantity

of residual hydroxyls, as well as exposed Al^{+3} and O^{-2}, depends on the dehydration temperature.[18] The remaining surface hydroxyls make these iodinations possible.

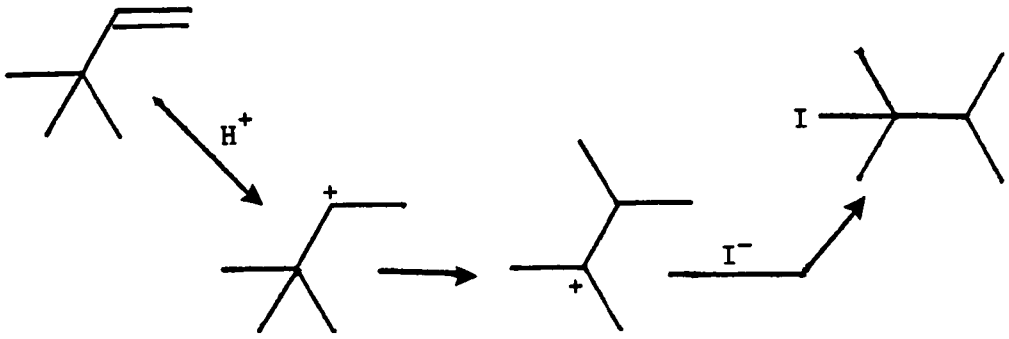


The reaction that is occurring is the reaction between I_2 and the surface hydroxyls to form HI and OI^-.

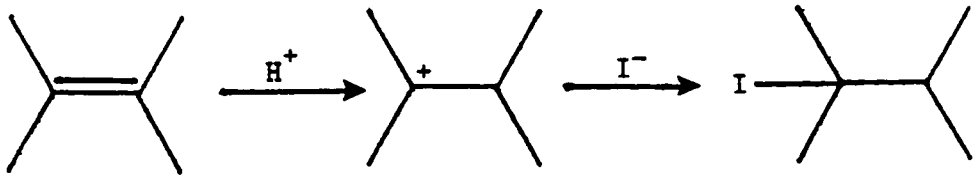
$$OH^- + I_2 \longrightarrow HI + OI^-$$

The evidence for this reaction occurring, in addition to the present examples, is that ethyl ether, when used as a solvent for electrophilic iodinations, is readily cleaved.[19]

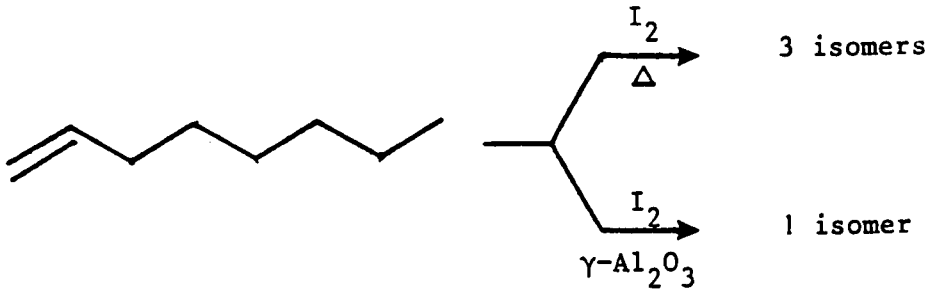
Dewar and Byer have shown that the reaction of HCl and HBr with alkenes goes through carbocation intermediates and, they say, by analogy HI should react with alkenes in the same manner.[20] The reaction of 3,3-dimethyl-1-butene with I_2 on alumina involves a cationic intermediate because the reaction product has a rearranged carbon skeleton. The rearrangement presumably occurs via the protonation of the double bond to form a secondary carbocation followed by migration of a methyl group to form the more stable tertiary carbocation. This species reacts with I^- to give the observed reaction product.



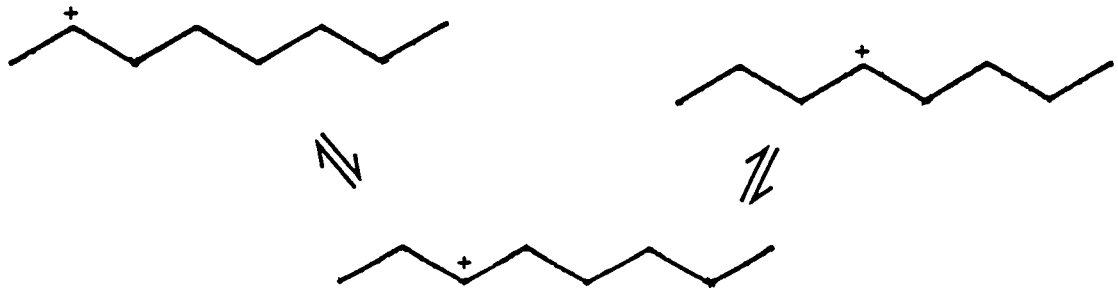
The reaction of 2,3-dimethyl-2-butene with I_2 would not be expected to involve a rearrangement because the cation first formed is the stable tertiary cation. This cation then reacts with I^- to give the observed reaction product.



The reaction of 1-octene with iodine on alumina to give only one iodinated product seems to contradict this argument, because a cationic intermediate in this reaction would be expected to yield traces of 2-iodo, 3-iodo, and 4-iodooctane as by-products. Freidlina and coworkers report that upon heating 1-octene with I_2 at 120°C, a mixture of the 2-, 3-, and 4-iodooctane were found.[21]

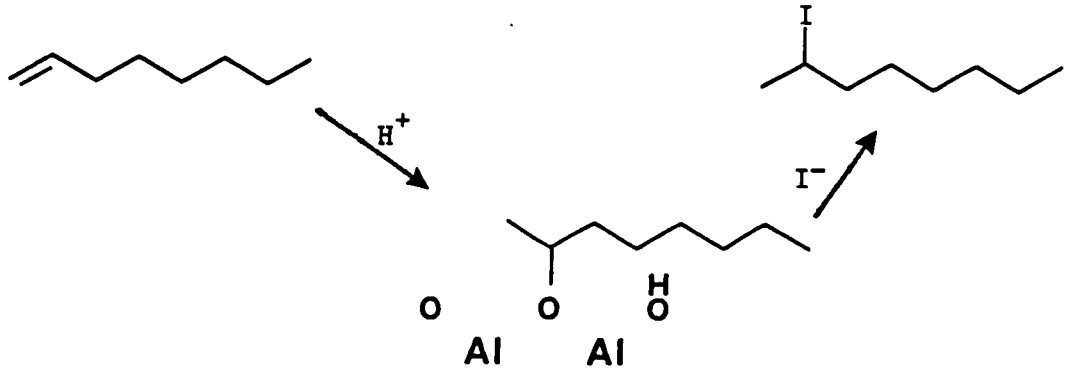


Freidlina's results are consistent with the reaction proceeding through a carbocation intermediate. The energy difference between equivalent secondary carbocations is very small, and the charge could easily move along the carbon chain by a series of 1,2 hydride shifts at these temperatures.[22]

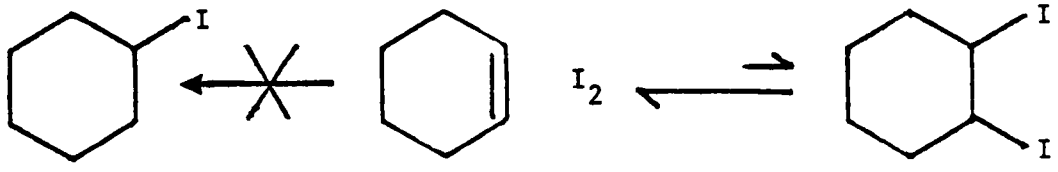


The reaction on alumina gave only one product, 2-iodooctane. This result might be due to coordination between the carbocation and the O^{-2} ions on the surface of the alumina. This coordination could not allow for a hydride migration, but would be able to be displaced by an iodine ion adsorbed onto the surface of the alumina.

The nonpolar solvent, petroleum ether, may also be influential in the reaction by not aiding in the stabilization of a carbocation not on the surface of the alumina. In any event, no isomerization was observed in the reaction.



The first question concerning the reaction itself was: is alumina necessary for the reaction to take place? Refluxing cyclohexene in petroleum ether with I_2 in the absence of alumina gave only recovered cyclohexene. There was evidence, however, for the formation of trace amounts of the diiodinated product in this reaction. The solution, after the excess iodine had been removed, turned purple over time. This suggests that 1,2-diiodocyclohexane had been produced, in very small amounts, and that it gradually lost iodine to regenerate starting material.



The second question concerns the necessity of dehydrating the alumina used in the reactions. Boothe determined that, after dehydration for 17 hours at 400°C, the alumina was sufficiently activated to catalyze the iodination of arenes.[18] The alumina used for all the reactions discussed in this work was activated for at least 17 hours, but the ability of unactivitated alumina to catalyze the iodination of alkenes needed to be studied. A 2 hour reaction of cyclohexene with iodine on activated alumina gave an 85.1% yield of the iodinated product, while a 2 hour reaction of cyclohexene with iodine on unactivated alumina gave only a 39.0% yield of the iodinated product. To examine further the catalytic properties of unactivated alumina, a reaction between cyclohexene and iodine on unactivated alumina was run for 3 hours, and the yield of product increased to 75.8%. There is still an advantage for using activated alumina, because the iodinated products are heat and light sensitive. Longer reaction times using unactivated alumina would lead to lower yields due to degradation of the iodinated product.

The next question examined was: do these reactions take place on the alumina or in solution? Two reactions were carried out to answer this question. Activated alumina was placed in a flask with iodine and petroleum ether. This slurry was allowed to reflux for 2 hours, and then the alumina was removed by filtration. The filtered solution was placed into one flask, while the filtered alumina was placed into another flask with petroleum ether and no iodine. Cyclohexene was added to both of the reaction flasks, and they were refluxed for 2

hours. In the flask with the alumina that had been refluxed with iodine, a 35% yield of the iodinated product was formed. The cyclohexene was apparently iodinated by the HI adsorbed to the surface of the alumina. If HI had been present in the solution, there would have been some product formation in the flask that had the filtered solution. There was no iodinated product isolated from the reaction with the filtered solution. This shows that the reactions occur on the surface of the alumina.

The last point examined was to determine if another solid was capable of catalyzing the addition of HI to alkenes. It has been shown that unactivated alumina catalyzes these reactions, but not as well as the activated solid. Column chromatographic grade silica gel, SiO_2, was examined next. A reaction of cyclohexene and iodine on unactivated silica gel for 4 hours at 35°C gave no yield of any iodinated products. Silica gel was also dehydrated at 400°C for 17 hours, and the reaction between cyclohexene and iodine was repeated using the activated silica gel. No iodinated products were isolated from the reaction.

L. Conclusion

The reaction of I_2 with alkenes and alkynes on alumina is an extremely efficient and simple method for the synthesis of alkyl iodides. The reaction takes place in one flask and uses a catalyst that is easily obtained by dehydration. The absence of competing side

reactions, even though it appears that the intermediate is a carbocation, also makes this an attractive method for iodinations. The reaction is also attractive due to the simplicity of the method and the simple laboratory equipment and reagents required. The ease with which the products can be isolated also add to the synthetic applicability of this method.

Overall, this reaction is a promising synthetic procedure for the rapid and direct production of cyclic and acyclic alkyl iodides. In addition it provides a straightforward synthesis of vinyl iodides from the corresponding alkynes.

TABLE 1

REACTION OF UNSATURATED HYDROCARBONS WITH I_2/Al_2O_3

Hydrocarbon	Product	Yield(%)
Cyclopentene	Iodocyclopentane	42.0
Cyclohexene	Iodocyclohexane	85.1
Cycloheptene	Iodocycloheptane	48.7
Cyclooctene	Iodocyclooctane	36.5
2,3-Dimethyl-2-butene	2,3-Dimethyl-2-iodobutane	36.1
3,3-Dimethyl-1-butene	2,3-Dimethyl-2-iodobutane	30.5
1-Octene	2-Iodooctane	83.5
1-Hexyne	2-Iodo-1-hexene	61.8

CHAPTER III

EXPERIMENTAL

A. Analytical Techniques

Nuclear magnetic resonance spectra were recorded on a 90 MHz JEOL FX-90Q spectrometer. Samples were run in $CDCl_3$ with 1% tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per milliom downfield from TMS.

Gas chromatograms were recorded with a Varian series 1700 Aerograph equipped with a 12 foot by 1/4" column packed with 30% SE-30 by weight on Chromsorb W as the solid support. The carrier gas used was helium.

Mass spectra were recorded with a Perkin-Elmer Model IR-5A GC-Mass spectrometer.

Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

B. Preparation of Alumina

Brockman activity grade 1 neutral alumina, purchased from the Fisher Scientific Company, was used for all the reactions. The alumina was dehydrated by heating under vacuum ($\leq$0.5 mm Hg) for 17 hours at 400°C utilizing the apparatus designed by Pagni et al.[17]

TABLE 2

MANUFACTURERS AND METHODS OF PURIFICATION

OF COMMERCIALLY AVAILABLE CHEMICALS

Chemicals	Manufacturers[a]	Method of Purification[b]
Cyclohexene	F	D
Cyclopentene	F	D
Cycloheptene	A	D
Cyclooctene	A	D
1-Octene	A	D
1-Hexyne	Far.	
3,3-Dimethyl-1-butene	A	
2,3-Dimethyl-2-butene	A	
Norbornene	A	
Trans-stilbene	A	
Cyclohexyl iodide	A	
Phosphorous (III) iodide	A	
Cyclopentanol	A	CaO
Cycloheptanol	A	CaO
Cyclooctanol	A	
2-Octanol	F	CaO
2,3-Dimethyl-2-butanol	A	
Petroleum ether, low-boiling	ASP	D
Ethyl ether	F	

TABLE 2 (continued)

Chemicals	Manufacturers[a]	Methods of Purification[b]
Alumina	F	
Silica gel	Da.	
Iodine, crystals	F	
Cyclohexane	F	D
Chloroform-d_1	A	
Decane	A	
Undecane	A	
Octane	A	
Nitrogen, liquid	ASP	

[a]Manufacturers: (Far.) - Farchan Research Laboratories
(Da.) - Davasil
(F) - Fisher Scientific Company
(A) - Aldrich Chemical Company
(ASP) - American Scientific Products

[b]Methods of Purification:
(D) - Distillation
(CaO) - Dried over CaO

C. Reaction of Cyclohexene

For the reaction of cyclohexene, 120 ml of distilled, low-boiling petroleum was added to I_2 (0.0600 mol, 15.2 grams) in a 250 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser. Dehydrated alumina (50 grams) was slowly added to the solution. Distilled cyclohexene (0.0493 mol, 4.02 grams) was then added to the slurry, and the reflux condenser was attached to the flask. The slurry was refluxed at 35°C for 2 hours. After cooling the mixture, the alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate to remove the excess iodine, dried over $MgSO_4$, and the solvent removed by evaporation. Decane (0.025 mol, 3.5 grams) was added to the residual oil as an internal standard for gas chromatography. The gas chromatograph was calibrated for yield determinations with known mixtures of cyclohexyl iodide and decane. The mixture was chromatographed at 170°C , and only one product peak was observed. The peak with a 2.75 minute retention time was collected for ^1H and ^{13}C NMR analyses. The yield of cyclohexyliodide was determined to be 0.042 moles, or an 85.1% yield of product based on cyclohexene.

Spectral characteristics of cyclohexyl iodide: ^1H NMR δ 1.3-1.8 (6H,m,-CH_2-), 1.9-2.2 (4H,m,-CH_2-CI), 4.2-4.5 (1H,m,-CH-I). ^{13}C NMR δ 25.5, 27.5, 32.0, 39.5.

D. Reaction of Cyclopentene

In a 250 ml round-bottom flask equipped with magnetic stirring and a reflux condenser, 120 ml of distilled, low-boiling petroleum ether was added to I_2 (0.0650 mol, 16.5 grams). Dehydrated alumina (50 grams) was slowly added to the slurry followed by distilled cyclopentene (0.0568 mol, 3.87 grams). The mixture was refluxed at 35°C for 1.75 hours, and allowed to cool. The alumina was removed by vacuum filtration, washed with 2 x 15 ml of ethyl ether, and the excess iodine was destroyed by washing the organic layer with a saturated solution of sodium thiosulfate. The organic layer was separated and dried using $MgSO_4$. The solvent was removed by evaporation and undecane (0.0284 mol, 4.44 grams) was added to the resulting oil as an internal standard. This mixture was chromatographed at 155°C, and only one product peak was observed. The peak with a retention time of 3 minutes was collected for analysis by ^1H and ^{13}C NMR. The product oil was shown to contain 0.0239 moles of cyclopentyl iodide, a 42.0% yield of product based on cyclopentene.

Spectral characteristics of cyclopentyl iodide: ^1H NMR δ 1.6-1.9 (4H,m,-CH_2-), 1.9-2.1 (4H,m,-CH_2-CI), 4.2-4.45 (1H,m,-CH-I). ^{13}C NMR δ 23.5, 28.5, 40.0.

E. Reaction of Cycloheptene

For the reaction of cycloheptene, iodine (0.0500 mol, 12.7 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether in a 250 ml round-bottom flask. Activated alumina (50 grams) was added and

stirring was maintained by means of a magnetic stirrer. Distilled cycloheptene (0.0428 mol, 4.12 grams) was added to the slurry, and it was refluxed at 35°C for 6 hours. After cooling, the alumina was removed by vacuum filtration, and the alumina was washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous sodium thiosulfate solution to remove the excess iodine. The organic layer was dried, and then reduced to a thick oil by evaporation. Undecane (0.0214 mol, 3.34 grams) was added as an internal standard, the mixture was chromatographed at a 190°C, and only one product peak was observed. The peak with a 4 minute retention time was collected for ^{1}H and ^{13}C NMR analyses. The oil was shown to contain 0.0208 moles of cycloheptyl iodide corresponding to a 48.7% yield of cycloheptyl iodide from cyclohexene.

Spectral characteristics of cycloheptyl iodide: ^{1}H NMR δ 1.4-1.65 (8H,s,-CH_2-), 2.1-2.35 (4H,m,-CH_2-CI), 4.3-4.65 (1H,m,-CH-I). ^{13}C NMR δ 26.72, 27.3, 36.3, 42.0.

F. Reaction of Cyclooctene

In a 250 ml round-bottom flask, I_2 (0.0450 mol, 11.4 grams) was dissolved in 120 ml of distilled, low-boiling ether. Activated alumina (50 grams) was slowly added to the mixture so that the stirring would not stop, followed by distilled cyclooctene (0.0383 mol, 4.23 grams). The slurry was refluxed for 32.5 hours at 35°C and then cooled. The alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a

saturated aqueous $Na_2S_2O_3$ solution, and the organic layer was dried over $MgSO_4$. The solvent was removed, and the residual oil was chromatographed by column chromatography using Davisil 61 silica gel as the stationary phase. Low-boiling petroleum ether and ethyl ether were used as the mobile phases in the chromatography. The dark oil obtained after chromatography was shown to contain 0.0139 moles of cyclooctyl iodide, a 36.7% yield of product from cyclooctene.

Spectral characteristics of cyclooctyl iodide: ^1H NMR δ 1.4-1.6 (10H,s,-CH_2-), 2.15-2.35 (4H,m,-CH_2-CI), 4.48-4.75 (1H,m,CH-I). ^{13}C NMR δ 25.25, 26.8, 27.8, 37.5, 38.4.

G. Reaction of 1-Octene

For the reaction of 1-octene, iodine (0.0399 mol, 10.1 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether in a 250 ml round-bottom flask equipped as described earlier. Activated alumina (50 grams) was slowly added to the slurry, followed by distilled 1-octene (0.0319 mol, 3.57 grams). The slurry was heated to 35°C for 2 hours and then allowed to cool. The alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate to remove the excess iodine. The resulting organic layer was dried, and evaporated to give the oil. The oil was placed on a vacuum pump and the pressure was reduced to $\leq$ 5.0 mm Hg for 30 minutes. The remaining oil was shown by mass spectrometry and ^1H and ^{13}C NMR analyses to be pure 2-iodooctane (0.0266 moles, 83.5% yield).

Spectral characteristics of 2-iodooctane: ^{1}H NMR δ 0.8-0.95 (3H,t,CH_3-), 1.2-1.5 (8H,m,-CH_2-), 1.7-2.05 (3H,d,CH_3-CI), 3.55-4.18 (1H,m,-CH-I), 4.18-4.48 (2H,m,-CH_2-CI). ^{13}C NMR δ 13.8, 14.2, 22.5, 28.2, 28.9, 31.5, 33.4, 39.0.

H. Reaction of 1-Hexyne

In a 250 ml round-bottom flask, I_2 (0.0450 mol, 11.4 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Activated alumina (50 grams) was added to the solution, and then hexyne (0.0215 mol, 1.78 grams) was added to the slurry. The slurry was refluxed for 2 hours at 35°C and then cooled. The alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate to destroy the excess iodine. The organic layer was dried and evaporated. Decane (0.017 mol, 2.4 grams) was added to the residual oil, the mixture was chromatographed at 180°C, and three peaks were obtained. The peak with a 4 minute retention time was collected for analysis by ^{1}H and ^{13}C NMR. The oil was shown to contain 0.0133 moles of 2-iodo-1-hexene corresponding to a 61.8% yield of product. The elemental analysis calculated for $C_6H_{11}I$ is 34.3% C, 5.3% H, and the determined ammounts are 33.7% C, 5.6% H.

Spectral characteristics of 2-iodo-1-hexene: ^{1}H NMR δ 0.85-1.0 (3H,t,CH_3-), 1.15-1.65 (4H,m,-CH_2-), 3.38-3.6 (2H,t,-CH_2-CI), 6.8 (2H,s,CH_2=CI). ^{13}C NMR δ 14.1, 21.5, 30.4, 44.5, 79.0, 104.5.

I. Reaction of 3,3-Dimethyl-1-butene

For the reaction of 3,3-dimethyl-1-butene, iodine (0.0450 mol, 11.4 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether in a 250 ml round-bottom flask equipped with a magnetic stirrer and reflux condenser. Activated alumina (50 grams) was slowly added to the mixture so that the stirring could be maintained. 3,3-Dimethyl-1-butene (0.0388 mol, 3.26 grams) was added to the reaction, and the slurry was refluxed for 2 hours at 35°C and then cooled. The alumina removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate to remove the excess iodine and dried using $MgSO_4$. The solvent was removed by evaporation, and octane (0.0194 mol, 2.22 grams) was added to the oil as an internal standard. The mixture was chromatographed at 120°C and only one product peak was observed. The peak with a 3.5 minute retention time was collected for ^1H and ^{13}C NMR analyses. The oil was shown to consist 0.0118 moles (30.5% yield) of the iodinated product, 2,3-dimethyl-2-iodobutane.

Spectral characteristics of 2,3-dimethyl-2-iodobutane: ^1H NMR δ 0.95-1.1 (6H,m,CH_3-), 1.65 (1H,m,CH-CI), 1.9 (6H,s,CH_3-CI). ^{13}C NMR δ 21.1, 36.3, 43.4, 62.6.

J. Reaction of 2,3-Dimethyl-2-butene

In a 250 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser, I_2 (0.0500 mol, 12.7 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Activated alumina

(50 grams) was added to the slurry, followed by 2,3-dimethyl-2-butene (0.0420 mol, 3.54 grams). The slurry was refluxed for 4 hours at 35°C, cooled, and the alumina removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous $Na_2S_2O_3$ solution to remove the excess iodine. The organic layer was collected, dried, and reduced by evaporation. Octane (0.021 mol, 3.4 ml) was added to the oil, the mixture was chromatographed at 120°C, and only one product peak was observed. The peak with a retention time of 3.5 minutes was collected for analysis by ^{1}H and ^{13}C NMR. The oil was shown to contain 0.0152 moles (36.1% yield) of 2,3-dimethyl-2-iodobutane.

Spectral characteristics of 2,3-dimethyl-2-iodobutane: ^{1}H NMR δ 0.95-1.1 (6H,m,CH_3-), 1.65 (1H,m,CH-CI), 1.92 (6H,s,CH_3-CI). ^{13}C NMR δ 21.2, 36.28, 43.4, 62.5.

K. Reactions of Norbornene

For the reaction of norbornene, iodine (0.0500 mol, 12.7 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether in a 250 ml round-bottom flask. Activated alumina (50 grams) was added to the slurry, and then solid norbornene (0.0425 mol, 4.00 grams) was added. The slurry was refluxed for 6 hours at 35°C and then cooled. The alumina was removed by vacuum filtration, and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate, and the organic layer was collected and dried over magnesium sulfate. The layer was evaporated,

and decane (0.0212 mol, 3.06 grams) was added to the oil as an internal standard. The mixture was chromatographed at 175°C, and no iodinated products were identified in the product oil. The reaction was repeated using distilled cyclohexane as the solvent and refluxed at 82°C for 4 hours, and again no iodinated products were identified.

L. Reactions of Styrene

In a 250 ml round-bottom flask, iodine (0.0500 mol, 12.7 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Activated alumina (50 grams) was added to the mixture, followed by styrene (0.0436 mol, 4.54 grams). The slurry was refluxed for 4 hours at 35°C and a solid formed in the reaction flask. The solid was determined by ^{1}H NMR analysis to be polystyrene. The procedure was repeated, and after a reflux time of 2 hours the reaction was halted. The alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The excess iodine was destroyed by washing with a saturated aqueous solution of sodium thiosulfate, and the organic layer was collected and dried. Upon removal of the solvent by evaporation, a solid formed in the flask. The solid was determined by ^{1}H and ^{13}C NMR analyses to be polystyrene. The polymer was dissolved in toluene in an attempt to isolate any iodinated products from the polymer, but ^{1}H and ^{13}C NMR analysis showed no iodinated products to be present.

M. Reaction of Trans-Stilbene

For the reaction of trans-stilbene, iodine (0.0299 mol, 7.61 grams) was dissolved in 120 ml of distilled, low-boiling petroleum

ether in a 250 ml round-bottom flask. Activated alumina (50 grams) was added to the mixture so that the stirring is not interrupted. Trans-stilbene (0.022 mol, 4.0 grams) was then added to the reaction slurry. The slurry was refluxed for 4 hours at 35°C and allowed to cool. The alumina was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of $Na_2S_2O_3$, and dried over $MgSO_4$. The solvent was removed by evaporation and, during the evaporation, crystals began to form in the flask. The crystals were dissolved into hot ethanol. As the ethanol began to cool, white crystals began to form in the beaker. The crystals had a melting point of 124.5°C and ^{13}C NMR analysis showed them to be trans-stilbene. The ethanol was analyzed by ^{1}H and ^{13}C NMR, but no iodinated products were present.

N. Synthesis of Standard Cyclopentyl Iodide

Standard cyclopentyl iodide was prepared by the reaction of cyclopentanol and PI_3. Cyclopentanol (99%) and PI_3 were purchased from the Aldrich Chemical Corporation. The alcohol was dried over CaO for 3 days before it was used.

PI_3 (0.0243 mol, 10.0 grams) was placed in a 100 ml round-bottom reaction flask equipped with a side arm and septum, magnetic stirrer, and reflux condenser. The flask was cooled to 0°C by an ice and water bath. Cyclopentanol (0.0729 mol, 6.27 grams) was slowly added by syringe through the septum. The water bath was removed after 15 minutes and the reaction was allowed to warm to 25°C. After 1

hour at 25°C, 10 ml of water was added to destroy any remaining PI_3 in the flask. The mixture was transferred to a 250 ml separatory funnel where 50 ml of ethyl ether was added. The contents of the separatory funnel were washed with a 1.0 M aqueous solution of $NaHCO_3$ until there was no apparent gas evolution. The aqueous layer was discarded and the organic layer dried over $MgSO_4$. Removal of the ether by evaporation gave a thick oil that was shown by mass spectral analysis as well as ^1H and ^{13}C NMR analyses to be cyclopentyl iodide. The spectral characteristics of this compound were identical to those obtained for the product of the cyclopentene reaction with iodine on activated alumina.

O. Synthesis of Standard Cycloheptyl Iodide

Standard cycloheptyl iodide was prepared by the reaction of 98% cycloheptanol with phosphorous (III) iodide, both purchased from the Aldrich Chemical Corporation. The alcohol was dried over CaO for 3 days before it was used in this reaction.

PI_3 (0.0243 mol, 10.0 grams) was placed into a 100 ml round-bottom reaction flask equipped as described earlier. The flask was cooled to 0°C, and cycloheptanol (0.0729 mol, 8.32 grams) was slowly added to the reaction flask by syringe. After 15 minutes, the mixture was allowed to warm to 25°C. After stirring for 1 hour, 10 ml of water was added to destroy any excess PI_3 remaining. The reaction mixture was placed into a 250 ml separatory funnel, 50 ml of ethyl ether was added, and

the contents were washed with a 1.0 M aqueous solution of sodium bicarbonate until there was no further gas evolution. The ether layer was collected and dried, and then the ether was removed by evaporation. The resulting oil was analyzed by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy and showed to be cycloheptyl iodide. The spectral characteristics of this compound were identical to those obtained from the product of the reaction of cycloheptene with iodine on activated alumina.

P. Synthesis of Standard Cyclooctyl Iodide

Cyclooctyl iodide was prepared by the reaction of cyclooctanol and PI_3. Cyclooctanol (99%) and PI_3 were both purchased from the Aldrich Chemical Corporation. The alcohol was used without drying over CaO.

PI_3 crystals (0.0243 mol, 10.0 grams) were placed into a 100 ml round-bottom reaction flask equipped as described earlier. The crystals were cooled to $0^{\circ}C$ by an ice and water bath. Cyclooctanol (0.0729 mol, 9.34 grams) was slowly added by means of a syringe through the side arm. The mixture stirred for 15 minutes at $0^{\circ}C$, the ice bath was removed and the flask was allowed to warm to $25^{\circ}C$ and stirred for 1 hour. 10 ml of water was added to destroy any remaining PI_3, and the reaction mixture was placed into a 250 ml separatory funnel. Ethyl ether (50 ml) was added, and the entire mixture was washed with a 1.0 M aqueous $NaHCO_3$ solution until there was no evidence of gas evolution. The ether layer was collected and dried over $MgSO_4$. The ether was

removed by evaporation, and the resulting oil was analyzed by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The oil was shown to be pure cyclooctyl iodide. The spectral properties of this compound were the same as the product of the reaction between cyclooctene and iodine on activated alumina.

Q. Synthesis of Standard 2-Iodooctane

Standard 2-iodooctane was made by the reaction of 2-octanol and PI_3. The 2-octanol (97%) was purchased from the Fischer Scientific Company, while PI_3 was purchased from the Aldrich Chemical Corporation. The alcohol was dried over CaO for 3 days before it was used.

PI_3 crystals (0.0243 mol, 10.0 grams) were placed into a 100 ml round-bottom reaction flask equipped as described earlier. The flask was cooled to $0^{o}C$, and 2-octanol (0.0729 mol, 9.49 grams) was slowly added by syringe. The reaction was stirred at $0^{o}C$ for 15 minutes and then allowed to warm to $25^{o}C$ while stirring for 1 hour. Water (10 ml) was added, and the entire reaction mixture was placed into a 250 ml separatory funnel. Ethyl ether (50 ml) was added, and the mixture was washed with a 1.0 M aqueous solution of sodium bicarbonate until there was no further evidence of gas evolution. The ether layer was collected, dried and reduced by evaporation. The remaining oil was shown by ^{1}H NMR to be contaminated with some unreacted alcohol, so the mixture was chromatographed at $180^{o}C$. The peak with a retention time of 3.2 minutes was collected for analysis by ^{1}H and ^{13}C NMR and shown to

be pure 2-iodooctane. Mass spectral analysis also indicated the product was 2-iodooctane. The spectral properties of this compound were compared to those of the product of the reaction between 2-octene and iodine on activated alumina, and they were identical.

R. Synthesis of Standard 2,3-Dimethyl-2-Iodobutane

The synthesis of standard 2,3-dimethyl-2-iodobutane was carried out by the reaction of 2,3-dimethyl-2-butanol with phosphorous (III) iodide. 2,3-Dimethyl-2-butanol (99%) and PI_3 were both purchased from the Aldrich Chemical Corporation and used without further purification.

PI_3 (0.0243 mol, 10.0 grams) was placed into a 100 ml round-bottom reaction flask equipped as described earlier. The flask was cooled to $0^{\circ}C$, and 2,3-dimethyl-2-butanol (0.0729 mol, 7.44 grams) was slowly added to the reaction flask by syringe. The mixture was stirred a $0^{\circ}C$ for 15 minutes, then was warmed to $25^{\circ}C$ and stirred for 1 hour. Water (10 ml) was added to destroy any remaining PI_3, and the reaction mixture was then placed into a 250 ml separatory funnel. Ethyl ether (50 ml) was added, and the mixture was then washed with a 1.0 M aqueous solution of sodium bicarbonate until there was no evidence of gas evolution. The ether layer was collected, dried, and evaporated. The remaining oil was analyzed by ^{1}H and ^{13}C NMR and shown to be contaminated with unreacted alcohol. The mixture was chromatographed at $120^{\circ}C$ and one product peak was observed. The peak with a 3.5 minute retention time was collected for further analysis by ^{1}H and ^{13}C NMR. This

was shown to be pure 2,3-dimethyl-2-iodobutane. The spectral properties of this compound were compared to the properties of the product of the reaction between 2,3-dimethyl-2-butene and iodine on activated alumina, and the reaction of 3,3-dimethyl-1-butene with iodine on activated alumina. The spectral properties of each of the products were identical to the other products.

S. Reaction of Cyclohexene and Iodine Without Alumina

In order to determine if alumina was necessary for these iodinations to take place, cyclohexene was refluxed with iodine in the absence of alumina.

In a 250 ml round-bottom reaction flask equipped with a reflux condenser, iodine (0.0600 mol, 15.2 grams) was dissolved into 120 ml of of distilled low-boiling petroleum ether. Cyclohexene (0.0493 mol, 4.02 grams) was added to the reaction and the mixture was refluxed at 35°C for 2 hours. The excess iodine was removed by washing the organic layer with a saturated aqueous solution of sodium thiosulfate. As the solvent was being removed by evaporation, the solution began to turn purple, indicating the presence of iodine. The organic layer was again washed with the thiosulfate solution and evaporated again. The purple color returned quickly, and the evaporation was halted. ^{1}H and ^{13}C NMR analyses were done on the organic layer without any further evaporation, but the only compound that could be identified was cyclohexene. There was no evidence that any cyclohexyl iodide was being formed, but

the returning purple color due to iodine indicated that there were small ammounts of 1,2-diiodocyclohexane being formed.

T. Reaction of Cyclohexene and Iodine on Unactivated Alumina

In order to determine if unactivated alumina has the ability to catalyze the iodination of cyclohexene uding I_2, a reaction was done using unactivated Brockman Activity Grade 1 alumina.

In a 250 ml round-bottom reaction flask equipped with a magnetic stirrer and reflux condenser, I_2 (0.0600 mol, 15.2 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Unactivated alumina (50 grams) was slowly added to the reaction flask, followed by distilled cyclohexene (0.0493 mol, 4.02 grams). The reaction was refluxed at 35°C for 2 hours and then cooled. The alumina was removed by vacuum filtration, and the alumina was washed with 2 x 15 ml of ethyl ether. The combined filtrate was washed with a saturated aqueous solution of sodium thiosulfate to remove the excess I_2. The organic layer was collected, dried and the solvent was removed by evaporation. Decane (0.025 mol, 3.5 grams) was added to the oil as an internal standard. The mixture was chromatographed at 170°C, and 3 peaks were observed. The peak with a 2.75 minute retention time was collected for analysis by ^{1}H and ^{13}C NMR. The oil was shown to contain 0.0195 moles (39.0% yield) of cyclohexyl iodide. The reaction was repeated, lengthing the reaction time to 3 hours, and .0374 moles (75.8% yield) of cyclohexyl iodide was obtained.

U. Reaction of Cyclohexene and Iodine on Silica Gel

In order to determine if silica gel would catalyze the iodination of cyclohexene using iodine, Davisil 61 Chromatographic Grade silica gel was used in place of alumina.

In a 250 ml round-bottom reaction flask equipped with a magnetic stirrer and reflux condenser, iodine (0.0600 mol, 15.2 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Silica gel (50 grams) was added to the reaction mixture. Cyclohexene (0.0493 mol, 4.02 grams) was then added, and the reaction was refluxed at 35°C for 2 hours. The silica was removed by vacuum filtration and washed with 2 x 15 ml of ethyl ether. The combined organic layers were collected and washed with a saturated aqueous solution of $Na_2S_2O_3$ to remove the excess iodine. The organic layer was dried, and the solvent removed by evaporation. The product after evaporation was determined by ^1H and ^{13}C NMR to be cyclohexene. The reaction was repeated using 50 grams of silica that had been dehydrated at 400°C for 17 hours, but there were no iodinated products formed in the reaction.

V. Reaction to Determine Product Formation Site

In order to determine where the products of these iodinations are formed, two reactions were performed.

In a 250 ml round-bottom reaction flask equipped with a magnetic stirrer and reflux condenser, I_2 (0.0600 mol, 15.2 grams) was dissolved into 120 ml of distilled, low-boiling petroleum ether. Activated alumina (50 grams) was added to the reaction. The slurry was

refluxed at 35°C for 2 hours and then cooled. The alumina was removed by vacuum filtration and placed into another 250 ml reaction flask with 120 ml of distilled petroleum ether and no iodine. The filtrate was placed into another 250 ml flask. Cyclohexene (0.0493 mol, 4.02 grams) was added to both of the reaction flasks, and they were heated at 35°C for 2 hours. The alumina was removed from the flask containing it and was washed with 2 x 15 ml of ethyl ether. The organic layers of both of the reaction flasks were washed with a saturated solution of sodium thiosulfate to destroy the excess iodine. In the reaction flask that contained the filtrate of the original reflux of iodine and alumina, no cyclohexyl iodide was found. In the reaction flask that contained the filtered alumina and no iodine, 0.0189 moles (38.4% yield) of cyclohexyl iodide was formed.

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