A Study of the Preparation of Tricyclo[4, 1, 0, $0^{3,7}$]heptane and the 6-Halofulvenes

Thesis by

Joseph R. Bruckner

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ABSTRACT

The literature synthesis, with some modifications, of tricyclo [4, 1, 0, $0^{3,7}$] heptane was undertaken. While considerable difficulty was encountered in the final reaction involving a sodium borohydride reduction, far more successful results were obtained when lithium aluminum hydride was used instead as the reducing agent. The hydrocarbon can be stereospecifically deuterated at various points in the reaction sequence and once labeled, can be pyrolyzed and its products studied to determine the extent of orbital symmetry restrictions on the pyrolytic rearrangement process.

ABSTRACT

In efforts to produce the mono- and diadducts of dichloro- and dibromocarbene to cyclopentadiene, it was found that the respective 6-halofulvenes were being produced instead. Depending upon the conditions used, varying amounts of halobenzene and 1, 1-dihalo-2, 2-dimethylcyclopropane could be produced as other major reaction products. The fulvenes were obtained in best yield using haloform as the dihalocarbene precursor and potassium tert-butoxide as the base. Ethyl trichloroacetate and phenyl (bromodichloromethyl) mercury were also used with various bases to generate dichlorocarbene, but these methods were unsuccessful in producing the 6-chloro-fulvene.

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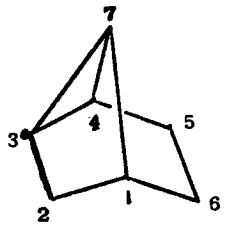
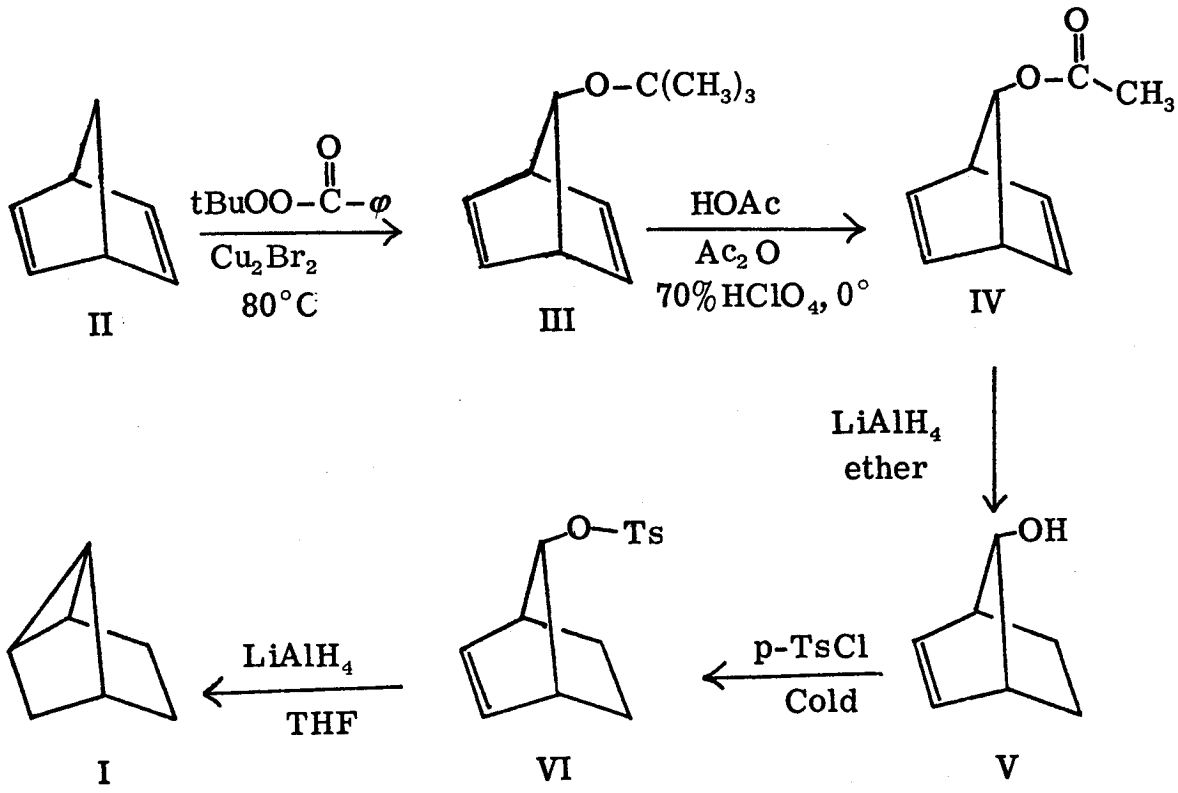
INTRODUCTION

The synthesis of compound I, tricyclo-[4, 1, 0, $0^{3,7}$]-heptane, was undertaken in order that its behavior under pyrolytic conditions could be evaluated.

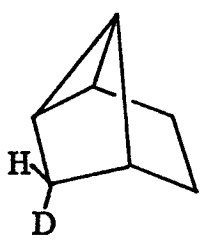


The hydrocarbon can be prepared in five steps, with conditions as discussed later, starting with norbornadiene, II.

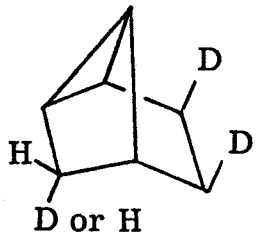


Of the methods of preparation available, this series of reactions was reported to give the maximal yield of the tricyclic heptane (8.2% overall) in the fewest number of steps and also allowed stereospecific deuteration of the ring system.

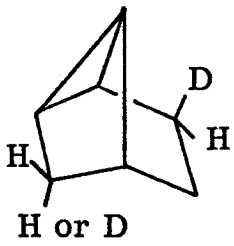
Deuterium labels could be placed in the endo-2 position by reduction of the tosylate VI with $LiAlD_4$, and/or in both the exo-5, 6 positions or the exo-5 position alone, at the alcohol V stage, according to a procedure developed by Franzus and Snyder.[1] The resulting compounds would be, respectively, I(a), (b), and (c).



I(a)

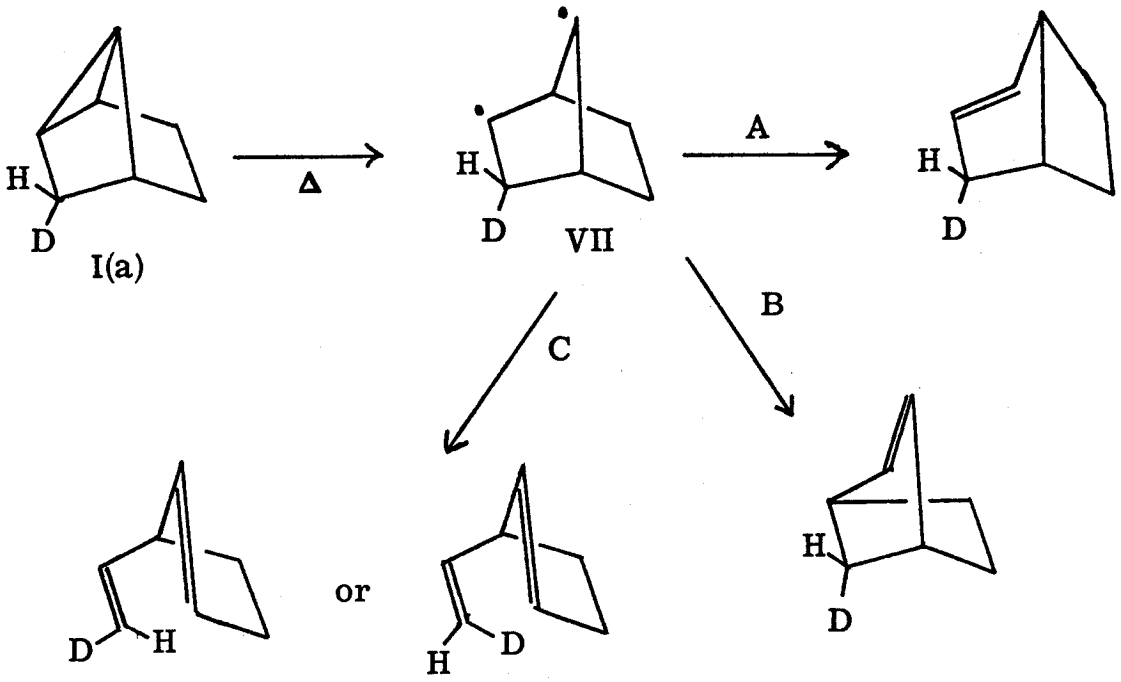


I(b)



I(c)

If I is then viewed essentially as a strained, disubstituted bicyclo-[2, 1, 0]-pentane ring system, 3, 7 bond cleavage would be expected to be the most facile at elevated temperatures. Using compound I(a) as an example, the resulting diradical VII would be expected to yield three products. In this case, the pathway C stereochemistry may depend upon restrictions imposed by orbital symmetry with regard to the conrotatory or disrotatory sense of the ring opening at the C1–C2 bond.



conrotatory disrotatory

Similarly, by examining the stereochemistry of the appropriate pyrolysis products of the other suitably deuterated tricycloheptanes, the extent of the orbital symmetry restrictions can be determined for pathways A and B as well.

EXPERIMENTAL

1. Preparation of 7-t -butoxy-bicyclo-[2, 2, 1]-hepta-2, 5-diene:

The preparation of this compound, as well as the acetate and alcohol, was carried out using a procedure developed by P. Story[2] with various modifications. A 500 ml quantity of benzene was mixed with 300 grams (3.26 moles) of norbornadiene and 0.65 gram (0.0046 mole) of cuprous bromide. The flask and its contents were heated to reflux under a nitrogen atmosphere. To this mixture was then added 245 grams (1.26 moles) of tert-butyl perbenzoate dissolved in 100 ml of benzene slowly, with stirring, over a one-hour period. It was found that the addition time could be varied from 30 to 60 minutes without affecting the yield of the ether. The solution changed color immediately upon addition of the perester, going from a light green to a deep blue-green. Heating to maintain reflux was continued for 1/2 hr more after all the perester had been added.

After the mixture was cooled to room temperature, it was washed three times each with 300 ml volumes of a saturated sodium chloride solution and a 10% aqueous sodium carbonate solution. The original procedure suggested using a sodium hydroxide solution, but it was found that this led to the formation of emulsions requiring as long as 6 hours to separate. The organic layer was washed once again with 150 ml of a saturated brine solution and then dried over sodium sulfate.

A fractional distillation was performed after the solution was transferred to a 2-liter flask. A 30 cm Vigreux column was suggested for use, but best results were obtained using a 50 cm tantalum wire column. After the majority of the benzene was removed at 45° to 50°C and 200 mm pressure, the pressure was gradually lowered to 10 to 15 mm. A small amount of product and benzene was collected before almost pure product distilled over. The distillation was monitored by VPC rather than by temperature, since the distillate temperature never reached the 80° to 85°C reported at the lower pressure. Distillation was continued until nothing further came over at a pot temperature of 125°C and 5 mm pressure. A VPC taken of the thick residue indicated that no product was present.

This procedure gave typical yields of 50 grams (25%) of the 7-t-butoxy norbornadiene, $\geq 95\%$ pure, with the chief contaminants benzene and unreacted norbornadiene. The spectra obtained agree well with those in the Story reference.(Figs. 1 and 2).

2. Preparation of 7-Acetoxy-bicyclo[2, 2, 1]hepta-2, 5-diene:

A mixture of 15 grams (92 mmoles) of the 7-t-butoxy norbornadiene, 150 ml of glacial acetic acid, and 30 ml of acetic anhydride, after standing together at room temperature for 1/2 hour, was poured into 20.3 grams of 70% aqueous perchloric acid which had been cooled to 0°C in an ice bath. The solution immediately turned a bright yellow on mixing (not red as reported), and then brown as it was swirled for 1 minute at 0°C. The mixture was quenched in 500

ml of ice and water, extracted several times with methylene chloride, and the combined organic extracts washed with saturated sodium bicarbonate, water, saturated brine, and then dried over sodium sulfate.

The product was purified by fractional distillation using a 50 cm tantalum wire column, the acetate fraction collected at 95°C and 20 mm pressure. Ten grams (73%) was a typical yield of product which VPC analysis showed to be 90-95% pure, the major impurity being methylene chloride. The product spectra (Figs. 3 and 4) agree with those reported by Story.

3. Preparation of Bicyclo[2, 2, 1]hept-2-ene-anti-7-ol:

The best results for the reduction of the acetate were obtained when the reaction was performed on a relatively small scale. When the proportions used were double the ones given, there was as much as a 33% decrease in the yield of the alcohol. The alcohol was prepared by adding, over a 15-minute period, 2.00 grams (13 mmoles) of the norbornadienyl acetate dissolved in 40 ml of dry ether, to a stirred solution of 0.70 gram (19 mmoles) of lithium aluminum hydride in 40 ml of dry ether under a nitrogen atmosphere. The reaction mixture was allowed to stir for 30 minutes more and was quenched by slow dropwise addition of a saturated sodium sulfate solution until a granular precipitate of lithium and aluminum salts had formed. Addition of water alone or too rapid an addition of the salt solution led to the formation of a gelatinous precipitate and

decreased the yields. The ether extracts of the reaction mixture were worked up in the usual way and dried over sodium sulfate. The ether was removed slowly under vacuum to yield approximately 2.2 grams of a gelatinous substance containing 1.40 grams (95%) of the alcohol. Attempts to remove more of the ether by pulling a stronger vacuum resulted in a loss of product, which sublimes at 5 mm pressure at room temperature.

The anti-7-norbornenol is most easily isolated from the mixture impurities, mainly methylene chloride, ether, and a higher boiling alcohol, as indicated by isolation of these substances through VPC analysis, by recrystallization from pentane. At all times, a minimum amount of pentane was used to effect solution. All vessels involved in transfers were rinsed with pentane and these washings worked up to yield further crops of alcohol crystals. For initial recrystallizations, the pentane solutions must be cooled to acetone-dry ice temperatures before the alcohol will crystallize. There is some loss of alcohol initially present, perhaps due to its high volatility. The melting point of the white crystalline alcohol was 117°-118°C which agrees well with the value of 117°-118°C reported in the Story reference cited.(Figs. 5 and 6).

4. Preparation of Bicyclo[2, 2, 1]hept-2-ene-anti-7-yl tosylate:

The tosylate of the anti-7-norbornenol was initially made using the unrecrystallized gelatinous form of the alcohol. Approximately 4.40 ml of dry pyridine were used to dissolve 0.70 gram (5.5

mmoles) of the impure alcohol and to the solution was added 1.16 grams (6.11 mmoles) of recrystallized p-toluenesulfonyl chloride. After the mixture was allowed to react in the cold for 24 hours, an aliquot taken was analyzed by VPC and indicated that essentially all of the alcohol had reacted. The reaction was quenched by pouring the mixture into ether-ice water, washing the ether layer several times with cold 2% aqueous hydrochloric acid to remove the pyridine, rinsing with saturated sodium bicarbonate and saturated sodium chloride solutions, and then drying over sodium sulfate. Rapid removal of the ether at room temperature and 20 mm pressure yielded 1.09 grams (65%) of another semi-solid which the infrared spectrum showed to be mostly (>80%) the tosylate. No attempts were made to recrystallize this material and it was later used directly in the hydrocarbon synthesis.

Somewhat more successful results were obtained when the recrystallized alcohol was used to make the tosylate. Using the same procedure and workup as before, yields of the tosylate up to 80% were attained. Neither a variation in reaction time from 18 to 48 hours, nor the presence of up to a 20% excess of the acid chloride had any apparent effect on the yield of the product. When the pure alcohol was used, the tosylate initially obtained upon evaporation of the ether was a light tan solid melting at 54° to 55°C. Recrystallization from pentane, again using dry ice-acetone cold, gave a white crystalline solid melting at 60.5° to 61.0°C, in good agreement with the literature value.[3]

The tosylate is unstable at room temperature in the air and decomposes within a few hours, but it may be stored safely, with no apparent decomposition, for several weeks in a freezer. No spectral data for the compound are reported in the literature.(Figs. 7 and 8).

5. Preparation of Tricyclo[4, 1, 0, $0^{3,7}$]heptane:

Method I: Reduction of the anti-7-norbornenyl tosylate by sodium borohydride in diglyme. -- S. Winstein and others reported[4] that the tricyclic heptane could be prepared in 95% yield by the borohydride reduction of the anti-7-tosylate in dry diglyme at 50°C. Amounts of reactants, time of reaction, and other specific details were not given.

Initial attempts to make the hydrocarbon involved heating 11 ml of a diglyme solution 1.5 M in sodium borohydride at 50°C in an oil bath. About 1.00 gram (3.8 mmoles) of the tosylate was added directly as the solid, over several minutes to the stirred solution. In later experiments, the tosylate was dissolved in a minimal amount of diglyme solvent before being added.

The reaction times were varied from 1 hour to 72 hours, the latter reaction run at 30°C instead of 50°C, and were run both open to the air as well as under an inert nitrogen atmosphere. The presence of added water (1 to 2 ml) in some cases had no effect on the reaction, though according to Winstein's paper, the presence of water in the medium was supposed to reduce the hydrocarbon yield to about 15%. At no time during the course of any of the borohydride-

diglyme reductions, was there any more than a few milligrams (less than a 1% yield) of the hydrocarbon produced. The major products, identified by VPC isolation and infrared spectra, were 2-norbornene and norbornane. The two to three other products from the reaction were present in mg quantities and were not able to be characterized from their infrared spectra alone.

The reactions were monitored by VPC and IR. The IR was used to determine when all of the tosylate had reacted by indicating the gradual lessening in intensity and eventual disappearance of the very characteristic tosylate absorptions at 1291 and 1281 cm^{-1}. Workup of the reaction mixture was usually effected by pouring the product solution into pentane-water, followed by extraction of the pentane layer several times with water to remove diglyme solvent. VPC analysis showed that no products had been lost in the water washings. Most of the pentane was removed by a fractional distillation at atmospheric pressure using a Vigreux column.

When it was found that the hydrocarbon was not being produced at all (or in very low yield), the reagents used were checked. Sodium borohydride from two sources was used and was recrystallized from diglyme before use. The diglyme itself had come from freshly opened bottles, was dried over molecular sieves, and was twice distilled from lithium aluminum hydride. Even when these reagents and the recrystallized tosylate were used, there was no effect on the tricyclic hydrocarbon yield.

On the possibility that the workup was affecting the results, a more elaborate apparatus for isolation of the products was employed involving a nitrogen flow system. After the tosylate solution had been added and reacted, the pressure in the system was reduced to about 500 mm with no nitrogen flow. The material that distilled over and condensed in an acetone-dry ice cooled receiver, was found to be by VPC analysis only diglyme. Nitrogen was then bubbled through the reaction mixture while maintaining the same pressure, but diglyme was still the only material coming over. The pressure was lowered gradually to 100 mm, but nothing besides diglyme distilled over. Distillation was continued until only a small amount of liquid remained in the pot. Before rinsing once with a minimal amount of water, the sample was checked by VPC and found to contain only a very small amount ($<1\%$) of the hydrocarbon desired. 1.00 gram of the anti-7-norbornenyl tosylate had been predicted to yield 0.339 gram (3.6 mmoles) of the tricyclo heptane. The yields obtained never exceeded 2.5 milligrams (0.7%) of the tricyclic material.

Method II: Reduction of the anti-7-norbornenyl tosylate by lithium aluminum hydride in tetrahydrofuran. -- With the small amount of material remaining, it was decided to try a tosylate reduction reported by H. C. Brown and his co-workers,[5] not used earlier because of its lower yield of hydrocarbon (60%). To 12.5 ml of tetrahydrofuran (THF), which had been twice distilled from lithium aluminum hydride was added 0.71 gram (18.6 mmoles) of lithium aluminum hydride giving a solution approximately 1.5 M in the

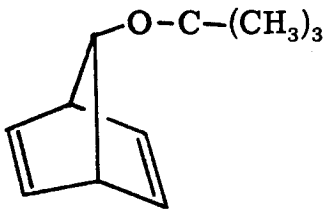
reducing agent. To this stirred solution was added slowly dropwise, 1.23 grams (4.7 mmoles) of the tosylate dissolved in a minimal amount of THF. The reaction was carried out at room temperature, though the mixture heated slightly during the addition of the tosylate, and some effervescence was noted as each drop of the tosylate solution was added. VPC and IR were again used to monitor the reaction which was complete after one hour. The mixture was allowed to stir one hour more and was then quenched using the sodium sulfate-water technique. A pentane-water workup followed to remove as much of the THF as possible.

After drying over sodium sulfate, the hydrocarbon layer was distilled at atmospheric pressure using a Vigreux column. Distillation was continued until the pot temperature reached 70°C and some products began coming over. Of the 0.632 gram of material isolated, VPC analysis showed 29.5% of this to be products. As reported, there were only two major products from the reaction. The expected yield of the lesser product, norbornylene, was 34%; the actual yield obtained was 15.3%. The anticipated yield for the tricyclic hydrocarbon was 0.262 gram (60%); the yield obtained was 0.120 gram (27.6%).

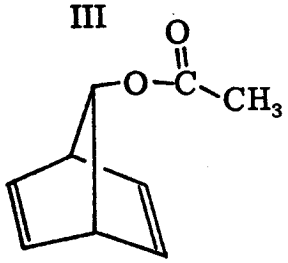
It was partly on the basis of the ratio of these two products that the tricyclic structure was assigned to the second product, since the only other positive identification has been made on the basis of three absorptions in the aliphatic region of the infrared.[6] The lower yield can be partly attributed to the fact that in the quenching, the wet

sodium sulfate was added too quickly and a gelatinous precipitate was formed with the probable inclusion of some organic products. A proper quenching may have led to an increased hydrocarbon yield.

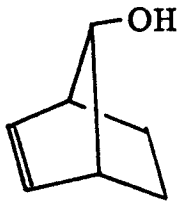
All VPC analyses were done on a 5' × 1/4" column of 3% SE 30 on Chromosorb P. Retention times for the various compounds were (minutes):



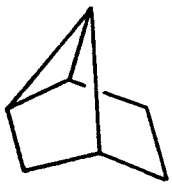
III 1.45



IV 1.56



V 1.18



I 0.80

Column temperature: 105°C

Injector temperature: 152°C

Flow rate: 100ml/min

The sodium borohydride used was from Ventron Corporation and Alfa Inorganics.

Figure 1. IR Compound III.

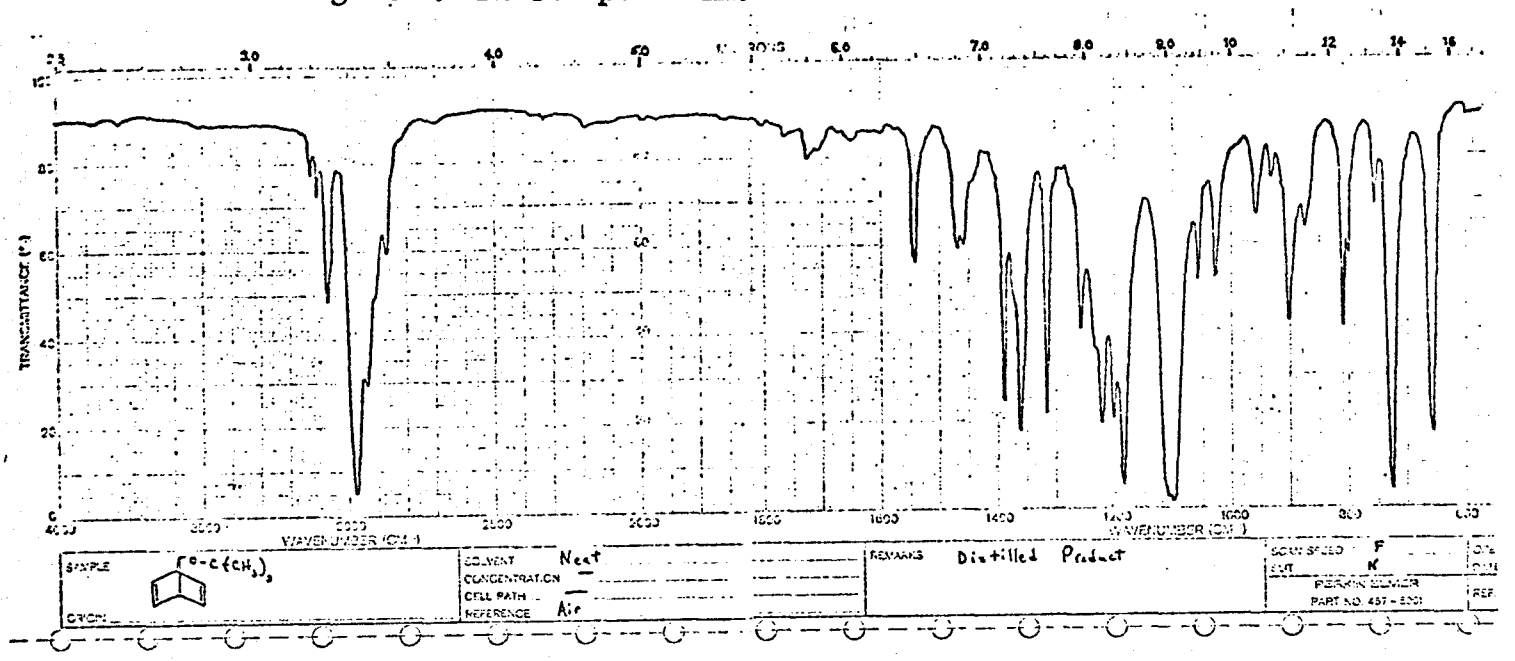


Figure 2. NMR Compound III.

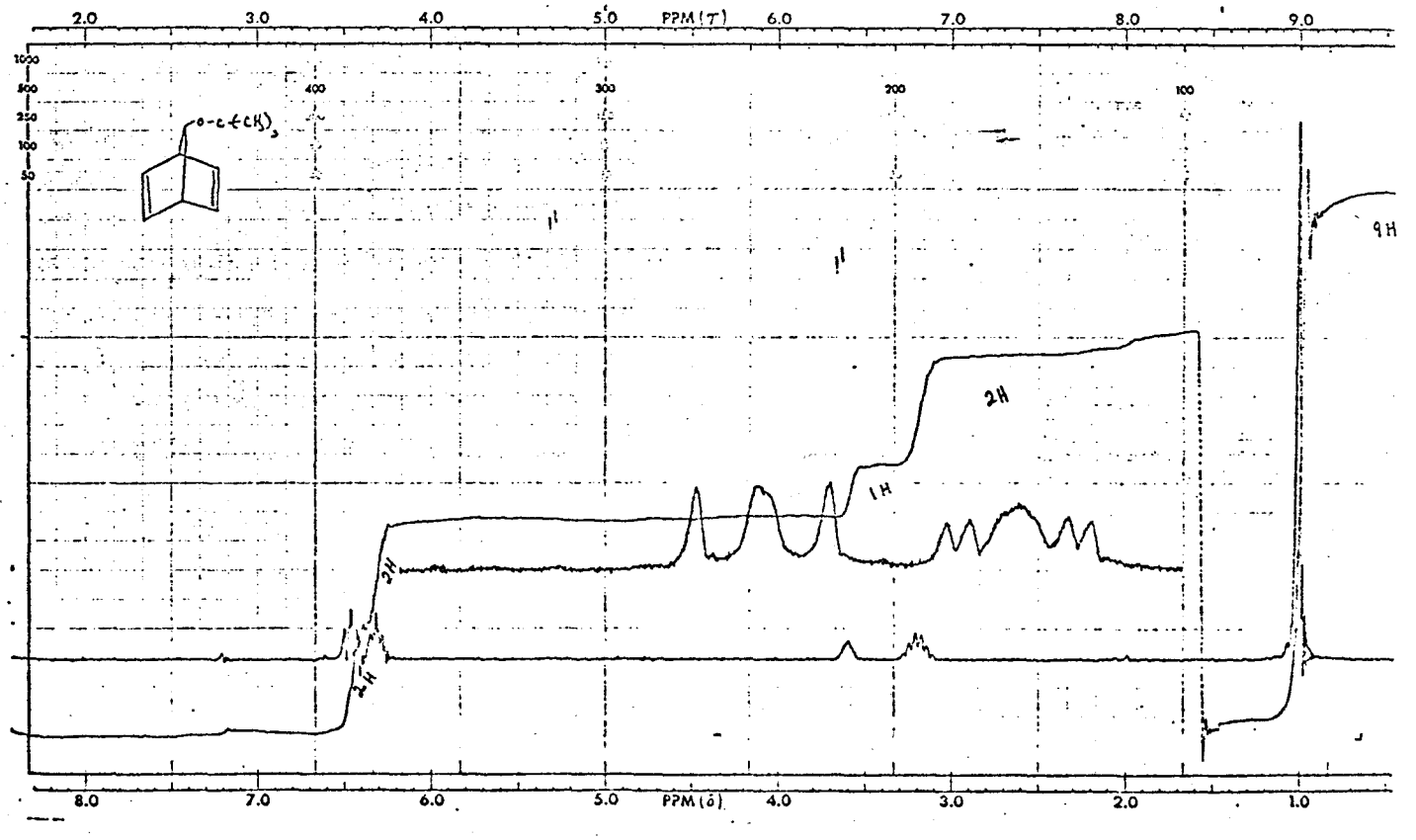


Figure 3. IR Compound IV.

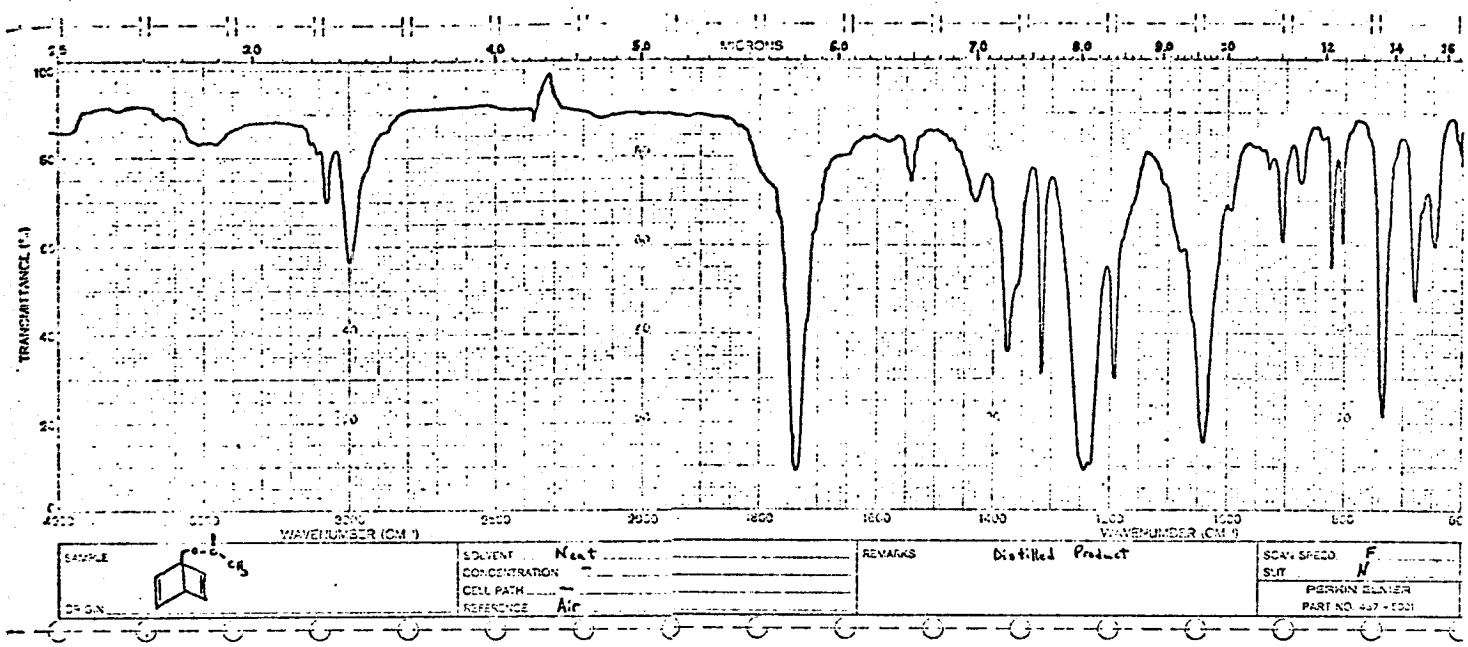


Figure 4. NMR Compound IV.

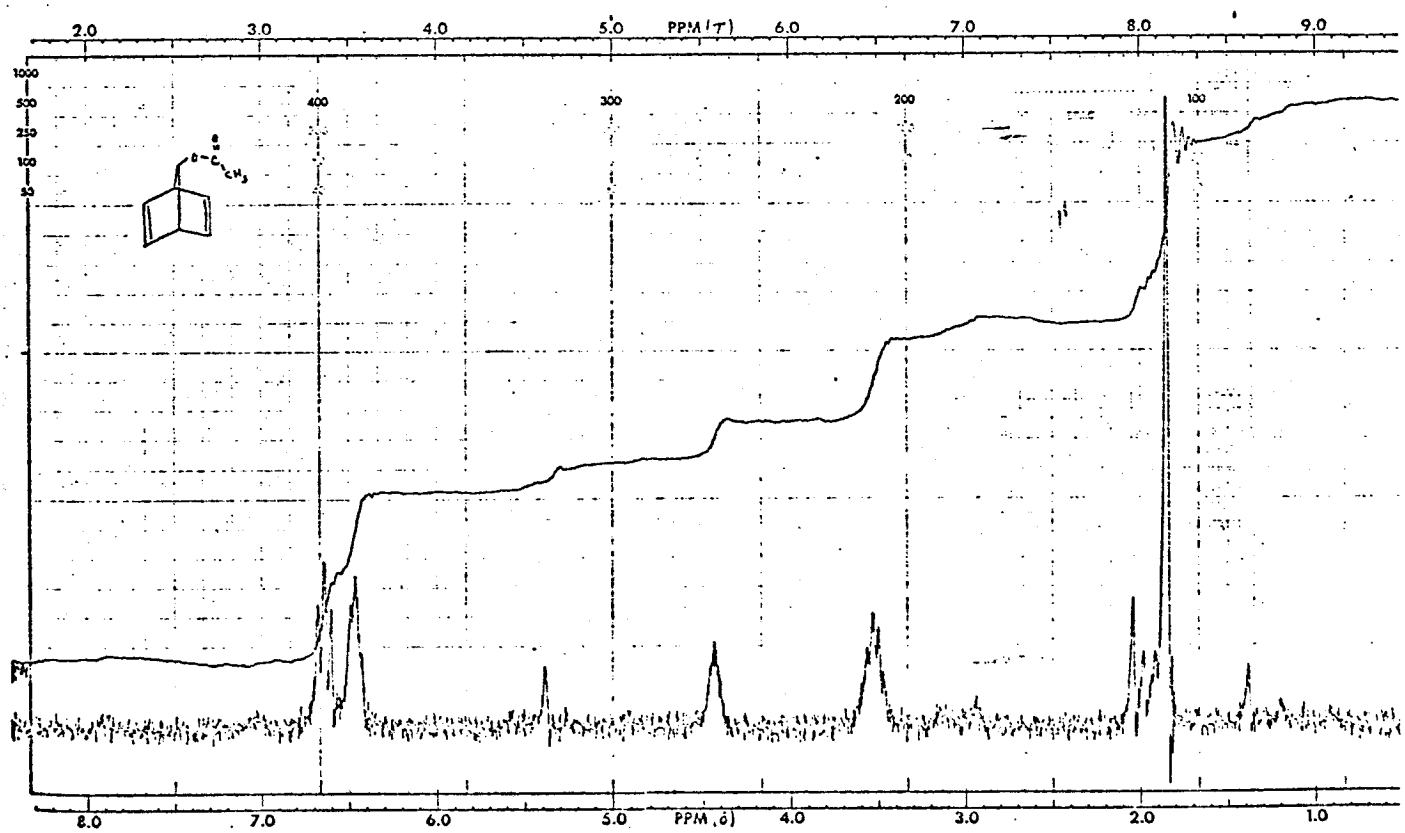


Figure 5. IR Compound V.

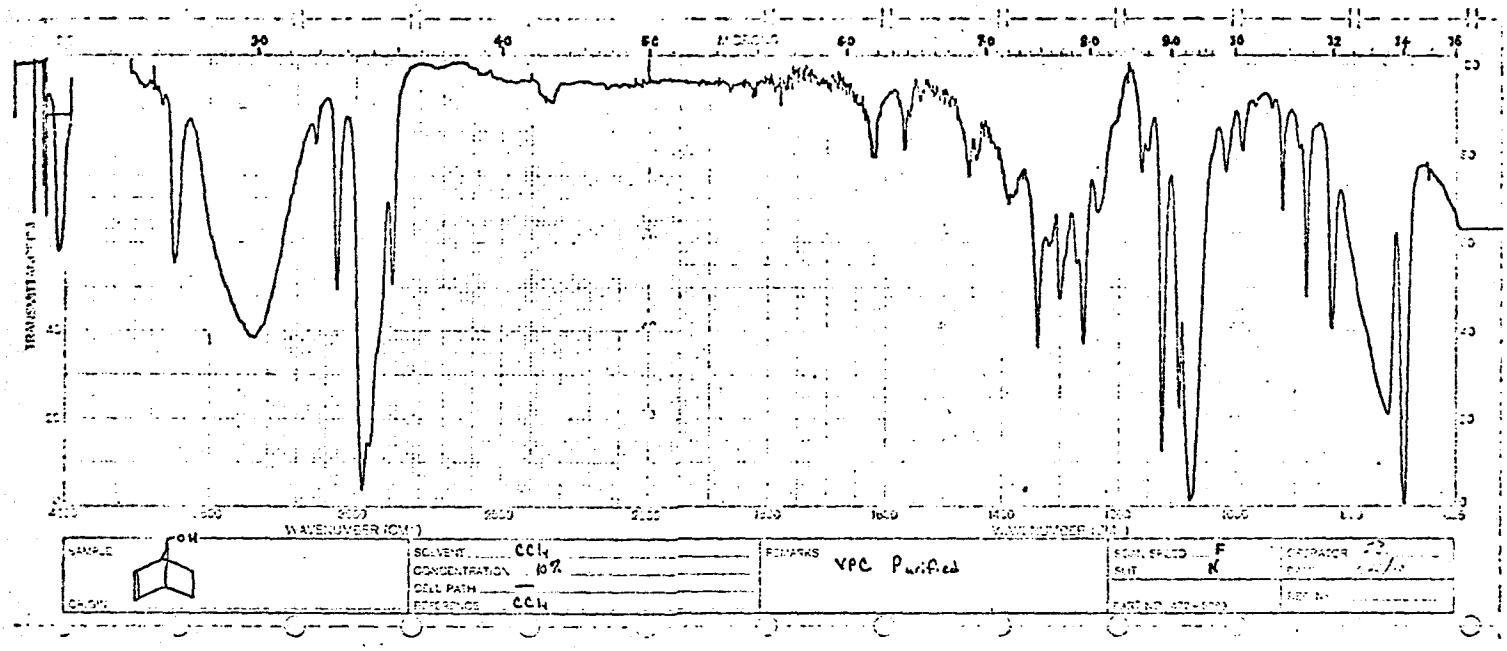


Figure 6. NMR Compound V.

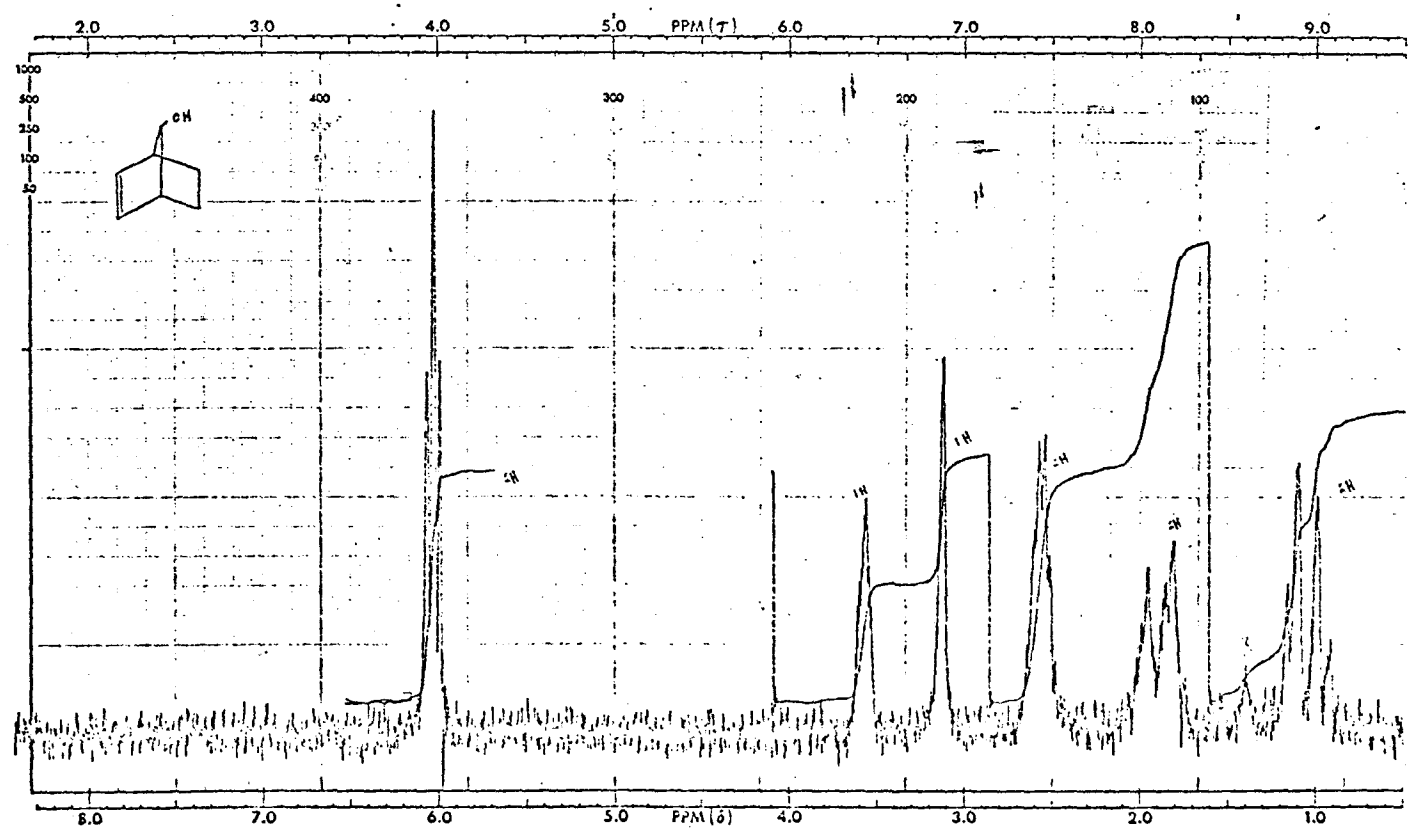


Figure 7. IR Compound VI.

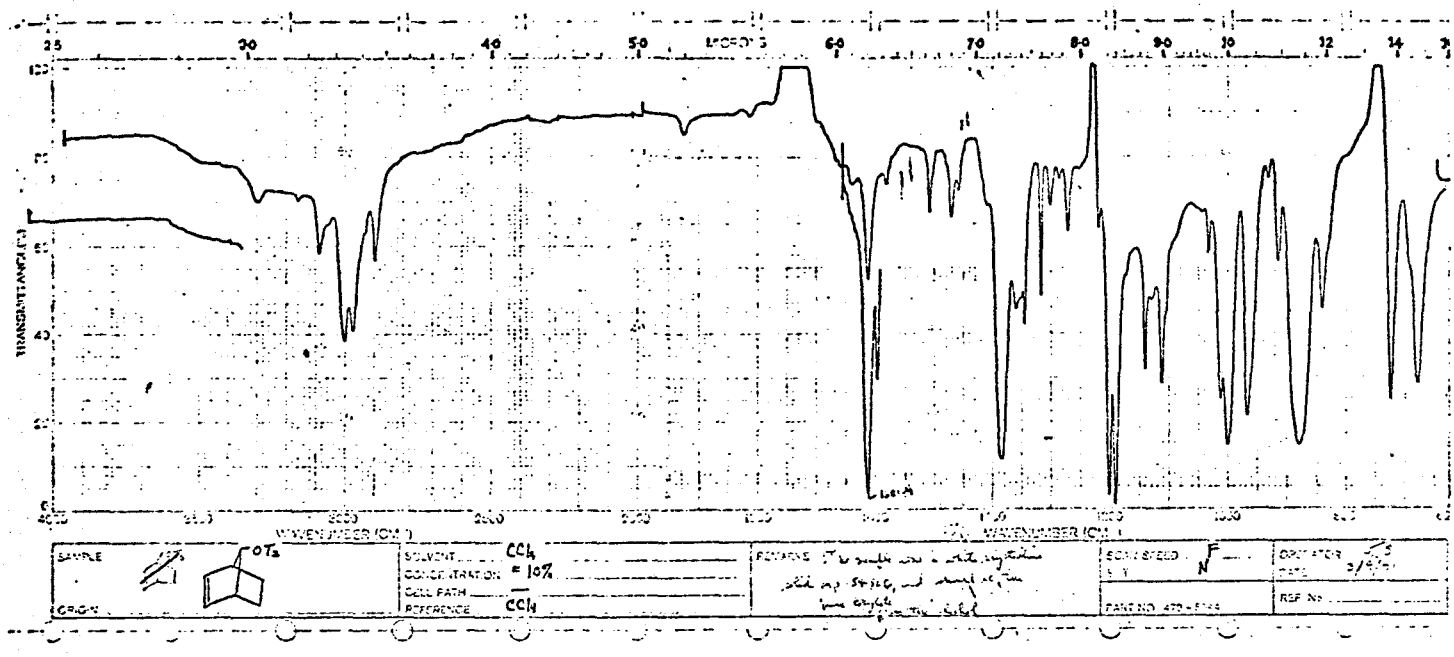


Figure 8. NMR Compound VI.

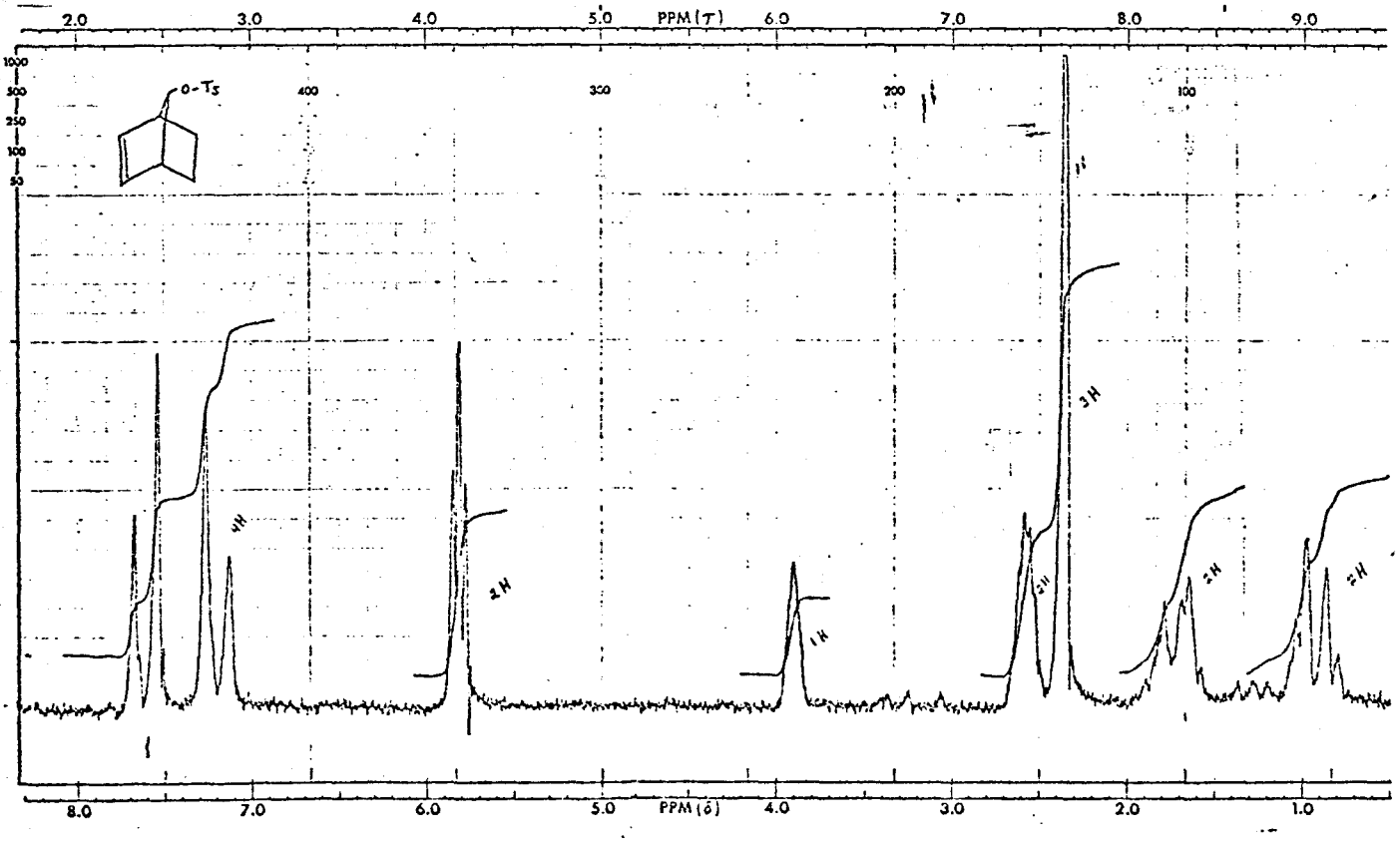
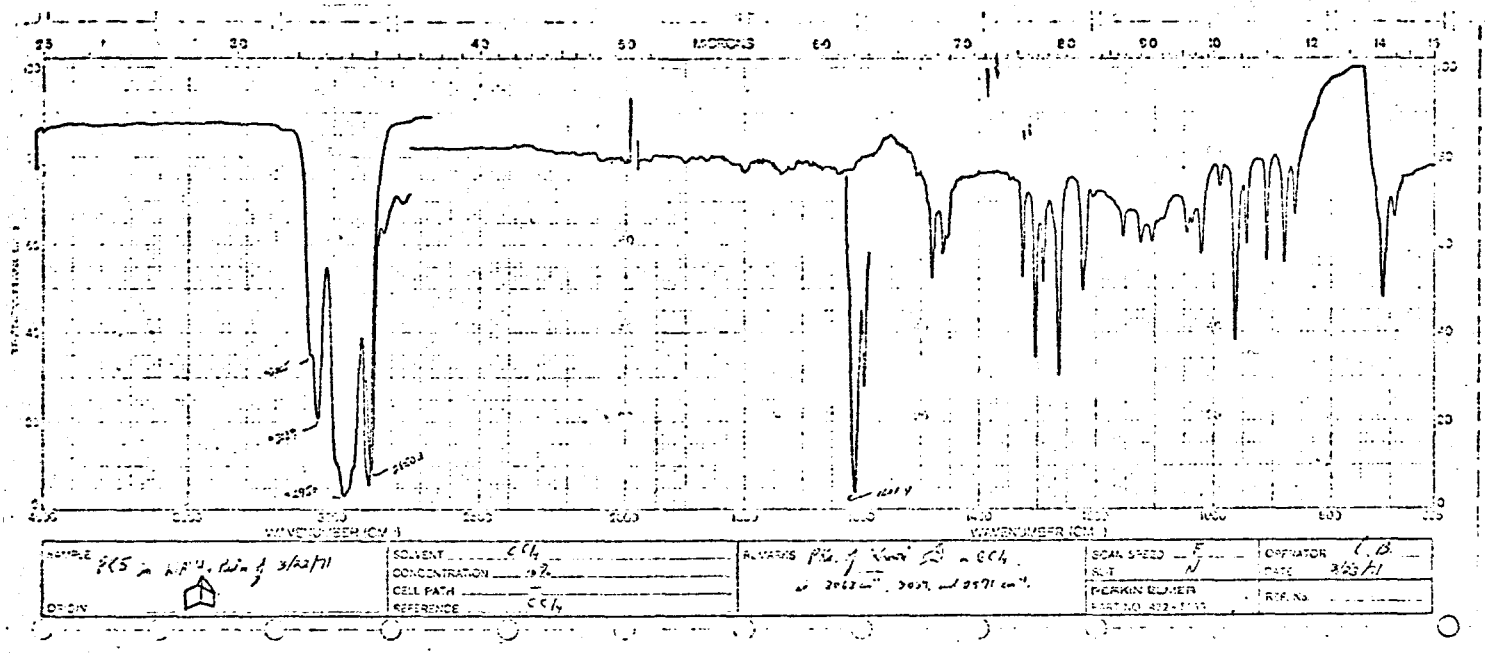


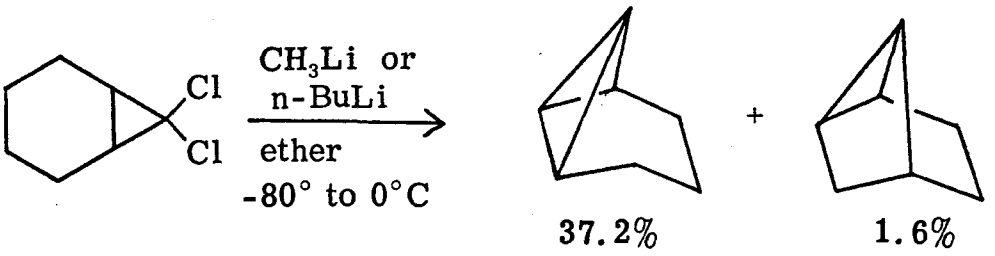
Figure 9. IR Compound I.



DISCUSSION

From the experiments performed, it would appear that the lithium aluminum hydride reduction method is to be preferred over the sodium borohydride method. All due precautions regarding reagents and reaction conditions were taken for the Winstein reduction without positive results. The parameters of time, temperature, and reactant concentrations were varied over a wide range of values without successfully increasing the yield of tricycloheptane above 1%, indicating that the value of this method of its preparation is questionable at best. For future attempts to prepare the hydrocarbon, the lithium aluminum hydride--THF method is strongly recommended.

A search of the literature revealed that tricyclo[4, 1, 0, $0^{3,7}$]-heptane has been made in only one other way. In addition to the two methods outlined experimentally, it has also been isolated by Moore, Ward, and Merritt as a byproduct of the following reaction:[6]



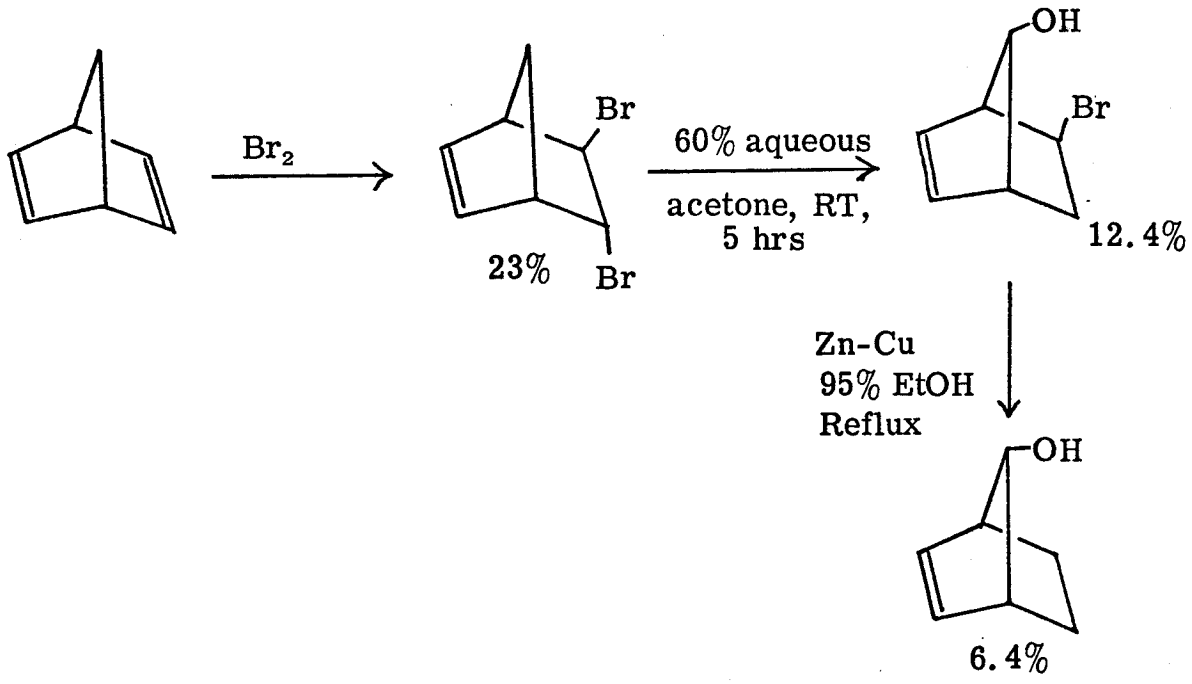
37.2% 1.6%

+ others

1.2%

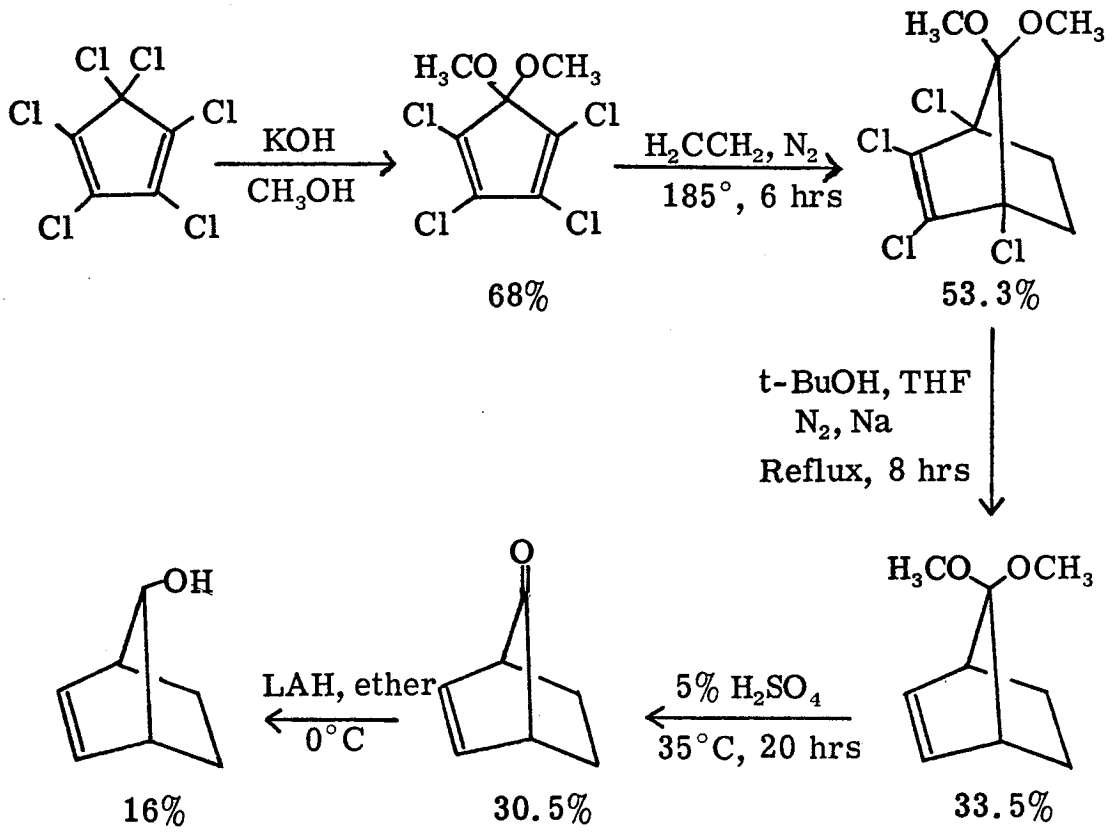
The overall calculated yield of tricyclic hydrocarbon from norbornadiene starting material was 13% by Winstein's method and 8.2% using H. C. Brown's reduction, which was why the borohydride-diglyme method was attempted first. However, on the basis of the experiments carried out, the former method gives $\ll 1\%$ overall yield, while the lithium aluminum hydride method, tried only once, gave a 3.8% yield.

Besides the method outlined, there were essentially two other ways to make the bicyclic alcohol. The method used was chosen because it produced the alcohol with the maximal overall yield, 17%, with the fewest number of steps, 3, and because no serious drawbacks were encountered while carrying out the series of reactions. A second method involved one developed by S. Winstein and his co-workers.[7] All yields are overall yields based on the initial amount of norbornadiene used.



This method had the disadvantage that it had a yield only about 1/3 that of the method used and required working with the highly toxic brominated intermediates.

The other method involved a series of reactions developed by P. Gassman and others[8] with yield as overall yields based on hexachlorocyclopentadiene.



While the yields for this method and Story's method were comparable, this method involved isolation of two more intermediates and the several rather lengthy reflux periods it required made it considerably more time consuming. In all three methods however, the final reduction is done on small amounts of material, presumably to maintain better yields of the alcohol.

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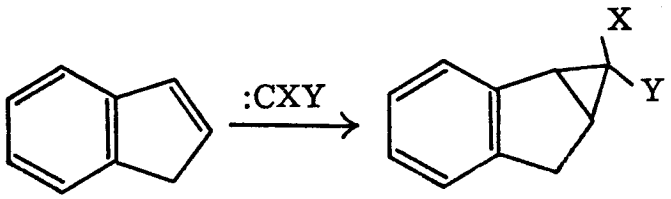
INTRODUCTION

Work on the syntheses of 6-bromofulvene and 6-chlorofulvene resulted initially from attempts to prepare the mono- and diadducts of dihalocarbenes to cyclopentadiene. Parham and others[1-3] have carried out reactions involving the addition of dichloro-, dibromo-, and various mixed halocarbenes to the indene system, I. The mono-adduct, II(a), was obtainable in yields up to 70%, with lesser yields reported for compounds II(b)-(d).

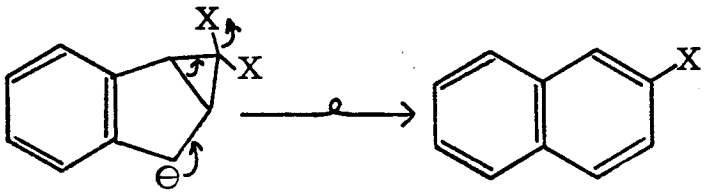


I II

a) X = Y = Cl c) X = Cl Y = F

b) X = Y = Br d) X = Cl Y = Br

Further reaction of II(a) and (b) in base gave good yields of the respective 2-halonaphthalenes, III(a) and (b).

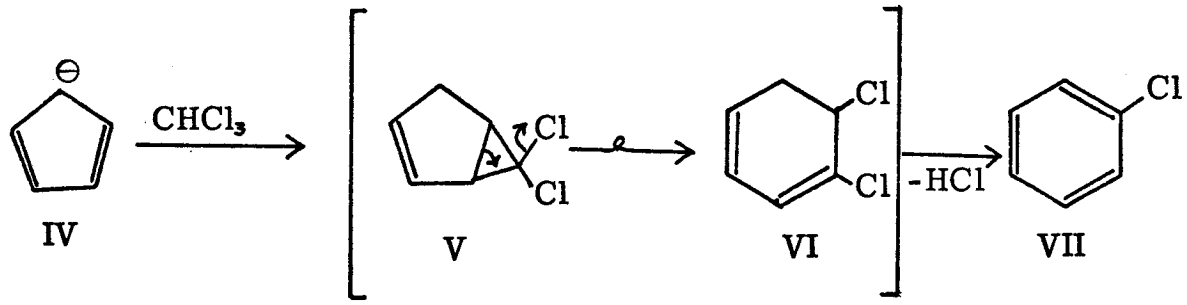


a) X = Br

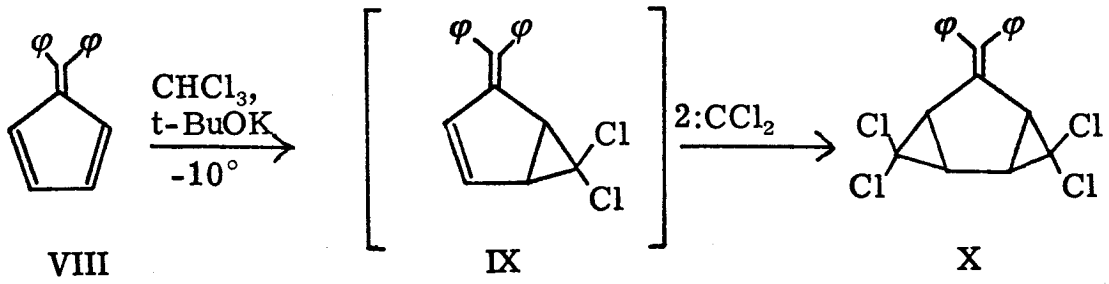
b) X = Cl

Parham reported that his attempts to add dichlorocarbene to cyclopentadiene were unsuccessful without mentioning what types of products he had obtained. A. F. Bickel and A. P. ter Borg reported,[4]

however, that they were able to obtain chlorobenzene, VII, in yields up to 23% by the addition of dichlorocarbene, generated from chloroform, to the sodium salt of cyclopentadienyl anion. They assumed, without isolating it, that the intermediate in the reaction was the monoadduct to cyclopentadiene, V, which spontaneously rearranged to give VII.

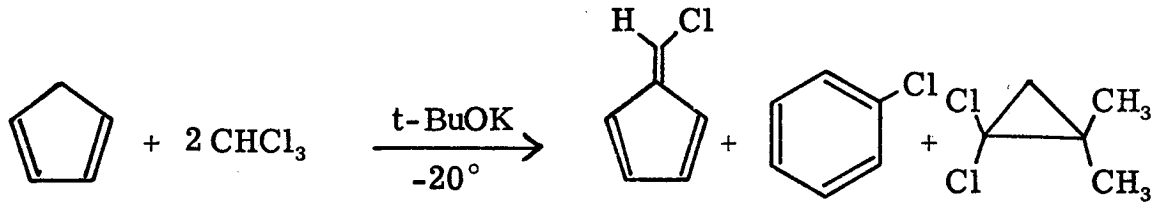


More recently, [5, 6] two equivalents of dichlorocarbene have been successfully added to the 6, 6-diphenylfulvene system, VIII, to give compound X in a 57% yield.



Attempts to isolate the intermediate, IX, though, have thus far been unsuccessful.

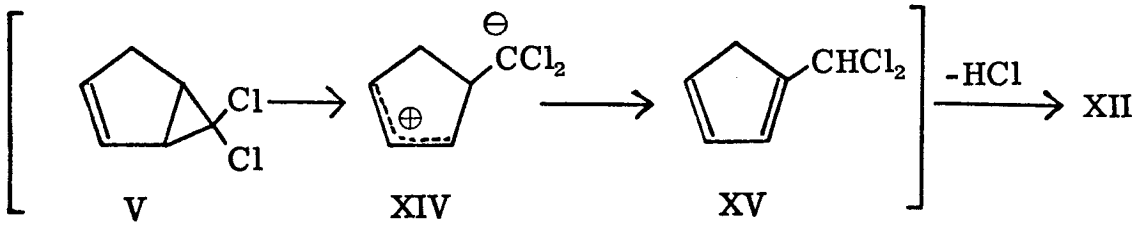
In efforts to prepare and isolate dichlorocarbene adducts to cyclopentadiene in our laboratories, it was found[7] that in the reaction of chloroform, with potassium tert-butoxide as base, the principle product isolated was 6-chlorofulvene, XII.



XI XII VII XIII

10% 2% 4%

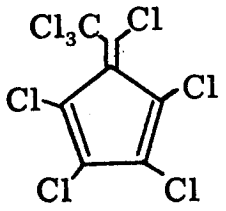
Because some chlorobenzene was formed, it was thought that the monoadduct V might be an intermediate in the reaction. Instead of rearranging and going to VII,then, V could give rise to a zwitterionic intermediate XIV, which would in turn go on to XII.



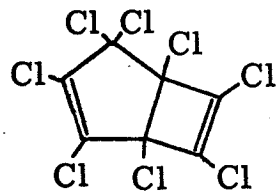
V XIV XV

The possibility that a mechanism involving sodium cyclopentadienide could be responsible for the reaction was ruled out, since neither chlorobenzene nor the chlorofulvene was formed on reaction of the salt with chloroform.

A review of the fulvene literature[8-11] revealed that none of the relatively simple 6-halofulvenes had previously been prepared. Reports[12, 13] that the perchlorofulvene XVI, had been synthesized



XVI



XVII

were later shown to be in error, the actual compound made being XVII, as determined by spectral means.[14]

The research described here was directed toward obtaining other 6-halofulvenes using the haloform-base technique, varying the experimental parameters to maximize the yields obtained, and toward investigating other possible methods for synthesizing the 6-halofulvenes, and if possible, the dihalocarbene adducts to cyclopentadiene.

EXPERIMENTAL

1. Preparation of 6-Chlorofulvene (XII) Using $CHCl_3$ and t-BuOK:

To a stirred mixture of 1.00 gram (15.2 mmoles) of cyclopentadiene obtained by thermal decomposition of the dimer, 3.70 grams (33.0 mmoles) of potassium tert-butoxide, and 15 ml of pentane solvent was added dropwise over 1/2 hour 3.60 grams (33.0 mmoles) of chloroform. During the addition, the temperature of the reaction mixture was maintained at -18° to -22°C. The mixture was then allowed to stir for 15 minutes more with the temperature held at -12° to -16°C. The entire reaction was carried out under a nitrogen atmosphere.

The reaction was quenched by pouring the mixture of products, a dark reddish-brown solution, into cold pentane, filtering, and washing the brown solid with pentane until the wash was clear. The solid was then dissolved in 30 to 40 ml of cold water and extracted several times with pentane. The combined pentane solutions were washed with water and saturated brine solution and then dried over anhydrous sodium sulfate overnight in the cold.

Removal of the pentane at room temperature and 20 mm pressure left a dark orange-red oil. Distillation of this material at 0.1 mm pressure gave typically a solution containing 0.204 gram of the 6-chlorofulvene (12%), 34 to 68 mg of chlorobenzene (2-4%), and small amount of 1, 1-dichloro-2, 2-dimethyl cyclopropane as the major products.

Spectra of the 6-chlorofulvene, a deep orange liquid at room temperature, were obtained by prep VPC of the reaction mixture using a 5' × 1/4" 3% SE 30 column. The fulvene had a retention time of 2.9 minutes with an injector temperature of 145°C, a column temperature of 75°C, and a flow rate of 50 ml/min. Both IR and NMR spectra were taken as 10% solutions of the compound in CCl_4.

The IR spectrum had strong absorptions at 1615, 1608, 1480, 1364, and 1085 cm^{-1}, medium absorptions at 3090, 1654, and 1271 cm^{-1}, and weak lines at 1448 and 1322 cm^{-1}. The NMR gave three groups of peaks: a singlet at 6.78 δ (1H), a multiplet at 6.58 δ (3H), and a multiplet at 6.17 δ (1H). The UV*, taken in cyclohexane, had 4 major peaks: at 261 mμ ($\log \epsilon = 4.4$), at 268 mμ ($\log \epsilon = 4.2$), at 277 mμ ($\log \epsilon = 4.2$), and at 371 mμ ($\log \epsilon = 2.5$).

To establish the existence of the 6-chlorofulvene by chemical means, the known 6-piperidinofulvene derivative was made. This was prepared by taking 1.00 gram of the distilled reaction solution containing about 0.200 gram of the chlorofulvene and adding to it, with stirring at room temperature, about 1.0 ml of freshly distilled piperidine. Fuming and mild bubbling were noted as the amine was added. The addition was complete after 2 minutes and shortly afterwards, the formation of a thick, silky precipitate was observed. The solution, which had gone from a bright yellow to a deep red, was allowed to stir ten minutes more in a stoppered flask.

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*M. D'Amore's values.

The reaction mixture was then poured into a beaker with 10 ml of pentane, swirled, and filtered. The brown solid filtered off was washed several times with pentane and recrystallized from hot water with charcoal to yield several milligrams of a fine white crystalline precipitate. This water soluble compound melted at 246°-247°C, in good agreement with the reported value[15] for piperidinium chloride of 246°-247°C. The dark red filtrate was stripped down under vacuum to remove the pentane and excess piperidine until only a thick, oily residue remained. This residue was taken up in 2-4 ml of cyclohexane, boiled with charcoal for 1-2 minutes, filtered, and again stripped down leaving a red-orange semi-solid. This material was recrystallized a number of times from pentane to yield several milligrams of a light tan, crystalline precipitate. The material melted at 66°-67°C, in excellent agreement with the reported value[16] for 6-piperidinofulvene of 67°C. The IR and NMR spectra of the 6-piperidinofulvene were taken as 10% solutions in CCl_4. The IR for the compound had strong absorptions at 2940, 1612, 1400, and 1356 cm^{-1}, with medium absorptions at 2860, 1454, 1258, 1222, 1079, and 915 cm^{-1}, and weak absorptions at 3080 and 1308 cm^{-1}. The NMR gave a singlet at 6.62 δ (1H), a multiplet at 6.13 δ (2H), a multiplet at 5.90 δ (2H), a multiplet at 3.41 δ (4H), and a broad singlet at 1.60 δ (6H). The UV in hexane had a λ_{max} at 323 mμ (log ϵ = 4.40).

2. Preparation of 6-Bromofulvene from Bromoform and t-BuOK:

The bromo compound was prepared in essentially the same manner as the chloro derivative. In this case 1.00 gram (15.2 mmoles) of cyclopentadiene, 8.30 grams (33.0 mmoles) of bromoform, and 3.70 grams (33.0 mmoles) of potassium tert-butoxide were reacted and worked up in the manner described earlier, maintaining a reaction temperature of -15° to -20°C. The typical yield of 6-bromofulvene, a bright yellow oil, from the reaction was 0.0156 gram (0.7%). Among the other products, bromobenzene and 1, 1-dibromo-2, 2-dimethylcyclopropane were the principle ones produced in yields which varied depending upon how the reaction conditions were varied.

The 6-bromofulvene was characterized as a reaction product by comparison of its infrared spectrum (10% in CCl_4) with that of the chlorofulvene and by converting it to 6-piperidinofulvene. The bromofulvene IR had strong absorptions at 1611, 1477, 1358, 1257, and 1080 cm^{-1}, medium absorptions at 3070, 1311, 1145, and 903 cm^{-1}, with a weak absorption at 1705 cm^{-1}. The mixed melting point of the piperidinofulvene obtained from the bromo and chloro sources was 66°-67°C showing no melting point depression. The piperidinium bromide produced in the reaction melted at 236° to 237°C in good agreement with the value for the salt produced from piperidine and hydrogen bromide which melted also at 236° to 237°C.

3. Attempts to Prepare 6-Chlorofulvene by Other Methods:

A. Generation of dichlorocarbene from methyl trichloroacetate and base. -- In an effort to increase the yield of chlorofulvene and possibly to produce the mono- or diadduct of the dichlorocarbene to cyclopentadiene, a method for carbene generation reported by Parham and Schweizer[17] was investigated.

In the initial experiments, sodium methoxide was used as the base. The relative amounts of the ester and base initially present were kept constant for all the experiments, while times of reaction, temperature, and the concentration of cyclopentadiene were varied. Since the reported reactions were run with a large excess of olefin, this method was tried first. The presence or absence of pentane as solvent was found to have no effect on the types or amounts of products formed. Tetrahydrofuran was rejected as a solvent because it formed a very viscous, unstirrable mixture in the presence of diene and base.

To a stirred solution of 6.60 grams (100 mmoles) of cyclopentadiene, 0.87 gram (16 mmoles) of sodium methoxide, and 10 ml of pentane cooled to -30°C, was added over 1 to 2 minutes, under nitrogen, 2.2 grams (12.5 mmoles) of methyl trichloroacetate. After all the ester had been added, the stirred mixture was kept at -20° to -25°C. An aliquot analyzed by VPC 1 1/2 hours later indicated that no reaction had occurred, so the temperature was gradually raised to -10°C. After remaining several minutes at this temperature, the solution became a light orange and the base, previously a loose

powder in solution, became thick and sticky. Another aliquot taken indicated reaction had still not occurred. When the mixture was warmed to and maintained at 0° to 5°C for 20 to 25 minutes, the ester finally reacted gradually as monitored by VPC, and the solution had turned a dark reddish brown.

After work up as in the chlorofulvene reaction, the distilled product mixture was analyzed and found to contain 3 product peaks on the VPC. The major product was chlorobenzene with a yield of 44 mg (2.5%). Lesser amounts of two other substances were formed. One was definitely identified as dimethylcarbonate, but the other, with an infrared spectrum similar to the one of chlorobenzene, remains unidentified. There may have been trace amounts of 6-chlorofulvene produced, since the chlorobenzene collected had a faint yellow color, but the amount was undetectable by IR, NMR, and VPC.

The reaction using sodium methoxide as base was also run with a stoichiometric amount (12.5 mmoles) of cyclopentadiene. The ester was added over 10 minutes this time with the other reaction conditions as before. After two hours, essentially no reaction had occurred, so the temperature was raised to -10° to -15°C. The reaction mixture went from a light orange to a dark red after 20 to 25 minutes at the warmer temperature, and the base had again become sticky, though the solution remained fluid. The VPC was used to monitor the course of the reaction and after 1 hour at the warmer temperature, reaction was complete.

Workup and analysis of the reaction mixture followed. Dimethyl carbonate was the major product (20%), with a somewhat lesser yield of chlorobenzene, 9.8 mg (0.7%), and an even smaller amount of the unidentified material. No chlorofulvene was detected as a reaction product.

Reactions were also carried out using potassium tert-butoxide as base. A mixture of 7.50 grams (115 mmoles) of cyclopentadiene, 3.58 grams (32 mmoles) of potassium tert-butoxide, and 15 ml of pentane solvent was cooled to -30°C; 4.46 grams (25 mmoles) of methyl trichloroacetate was added over a 30 minute period with stirring under nitrogen as the temperature was maintained at -22° to -28°C. After an additional half hour, no reaction had yet occurred. The mixture, after 2 1/4 hours more at the same temperature, had still not reacted. When kept at -10° to -12°C for 1/2 hour, the amount of ester decreased slightly and one product peak began to appear. A little more of the ester had reacted after 1/2 hour at -5° to 0°C. The mixture was cooled to -20°C, small amounts of excess base were added, and the mixture allowed to warm again slowly to 0°C. The reaction was quenched and the usual workup followed.

VPC analysis of the distilled material indicated a complex mixture of reaction products; no indication of either the chlorofulvene or chlorobenzene was found. The major portion of the 0.962 gram of product mixture isolated was t-butanol (75%). The two other identified product peaks were cyclopentadiene dimer, 29.8 mg, and unreacted ester, 8.6 mg. Four of the peaks have not yet been positively

identified, though two of the products have been tentatively identified as trichloroacetic anhydride and tert-butyl trichloroacetate on the basis of their infrared spectra.

When the reaction was carried out using a stoichometric amount (25 mmoles) of cyclopentadiene, a similar array of products resulted in approximately the same relative amounts with the exception of the cyclopentadiene dimer which did not form in this reaction. The overall reaction conditions were similar to those maintained for the case where the olefin was present in large excess; however, the temperature at which the ester was added was kept at -5° to -10°C, during the course of the reaction, the temperature was never raised above 0°C nor lowered below -15°C, and no excess base was added. In spite of the narrower and generally warmer temperature range maintained, there were no apparent effects on the product yields or distribution. Again, no chlorofulvene or chlorobenzene had been formed in the reaction.

B. Generation of dichlorocarbene from the thermal decomposition of ϕ-Hg-CCl_2Br.--A reaction was carried out using phenyl (bromodichloromethyl) mercury as the source of dichlorocarbene to determine how it would react with cyclopentadiene. In the reaction, 2.00 grams (4.5 mmoles) of the mercury compound were dissolved in 20 ml of benzene together with 0.300 gram (4.5 mmole) of cyclopentadiene. Since the reaction was carried out at 80°C, the reflux temperature of benzene, a calculation was made to insure that the cyclopentadiene would not dimerize too rapidly at the temperature

and concentration used. In this case, the diene half life was found to be 29.5 hours.

After the reactants had been mixed together under a nitrogen atmosphere, the temperature was kept at 35°C for the first half hour. A VPC aliquot analyzed after this period indicated that no reaction had yet occurred. The temperature was then raised gradually to 80°C and maintained there for one hour. After the hour, analysis showed no reaction had taken place. After one hour more at 80°C, the reaction mixture became a cloudy white and within 5 minutes, went from a pale yellow, to green, and finally to a deep blue-green, at which point a precipitate of phenyl mercuric bromide appeared and no further reaction was noted.

A qualitative analysis was carried out on the reaction products. After the φ-Hg-Br had been filtered off and most of the benzene had been stripped from the filtrate, a VPC taken of the remaining solution gave two peaks. One component was identified as benzene and the other as chlorobenzene from comparison of infrared spectra. In order to isolate the material which gave the solution the blue color, the liquid products were distilled off cleanly at room temperature and 0.1 mm pressure. As the temperature was slowly raised to 100°C, nothing further distilled over and only a small amount of a dark blue solid remained. Since the solid had not volatilized during the VPC analysis even at 280°C, it was suspected to be an organo-mercury complex. The solid was dissolved in a warm 1:1 mixture of concentrated nitric acid and water. A solution of sodium sulfide was added

and gave a dark grey precipitate characteristic of mercuric sulfide, identical to one produced by similar treatment of a known sample of phenyl mercuric bromide. The blue solid was a minor product (several mg only) of the reaction, with chlorobenzene as the major product. No chlorofulvene was found at any point in the analysis.

DISCUSSION

From the experiments performed, it was concluded that the most facile and productive way to produce the 6-halofulvenes was through the use of haloform as the dihalocarbene source and potassium tert-butoxide as the base. The reaction gave the best yields when a stoichiometric amount of cyclopentadiene was present and went with very poor yield ($<1\%$) or not at all as increasing amounts of excess diene were used.

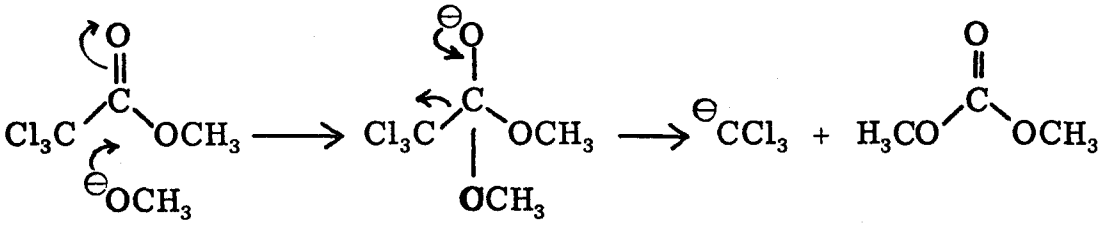
The bromofulvene reaction was carried out with many variations in the temperature, concentrations of reactants, and other conditions. In almost all the cases, the bromoform failed to react completely with the initial base present, even when there was a threefold excess of base. When sodium methoxide was used, no reaction at all occurred even up to a temperature of 10°C. The presence or absence of a nitrogen atmosphere had no effect on the reaction outcome. The order and time sequence of addition of the various reactants were inconsequential. The best solvent for the bromofulvene reaction was found to be pentane, though t-butanol and tetrahydrofuran were also tried. Tetramethylethylenediamine (TMEDA) was added in catalytic and larger amounts with no effect on the reaction outcome.

The yields of the other two major products formed in both the bromofulvene and chlorofulvene reactions, the halobenzene and the 1,1-dihalo-2,2-dimethylcyclopropane, could be manipulated by varying the reaction conditions. Addition of excess base after all the

haloform had been added, reacting the mixture longer than one hour, or raising the temperature above -5°C all contributed to a substantial increase (1500-2000%) in the amounts of the two byproducts produced with a slight diminishing of the halofulvene yield.

With regard to the other two methods tried, it appeared that neither would be suitable for the production of halofulvenes. In the case of the phenyl(bromodichloromethyl)mercury reaction, the major product was chlorobenzene, which perhaps could have resulted here, as in the other reactions where it was produced, from the rearrangement of the short-lived monoadduct V, as discussed earlier. There was no evidence in this or in any of the other reactions that either the mono- or the diadduct of dihalocarbene had been among the product mixtures isolated.

The methyl trichloroacetate reactions using sodium methoxide as base, produced, besides chlorobenzene, dimethyl carbonate XVIII which could have been formed in the following way:



XVIII

When potassium tert-butoxide was the base, all the products with the exception of t-butanol and one unidentified peak, had carbonyl absorptions in their infrared spectra. The tert-butyl trichloroacetate

produced could have resulted from a base catalyzed transesterification reaction with tert-butoxide serving as base. Because there was neither chlorofulvene nor chlorobenzene in the products, it was considered doubtful that either the mono- or diadduct of dichlorocarbene to cyclopentadiene was formed during this reaction.

Future work might be directed at the synthesis of the 6-iodo- and 6-fluorofulvene compounds using the haloform-tert-butoxide method. Based on the work done thus far, it might be predicted that the iodo derivative would be formed with relative difficulty compared to the fluoro compound, though the latter might be expected to form even more readily than 6-chlorofulvene.

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