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The Syntheses of Benzo-(2.2)-Paracyclophane, 2, 15-Dithia-(3.3)-Napthalenophane, and Hexamethylbenzene Dichloride

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The Syntheses of Benzo-(2.2)-paracyclophane, 2,15-dithia-(3.3)-napthalenophane, and Hexamethylbenzene dichloride

by

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ABSTRACT

The purpose of this study was the preparation by a novel approach of benzo-(2.2)-paracyclophane. Also synthesized were the syn- and anti- isomers of 2,15-dithia(3.3)-napthalenophane. The results of these synytheses are supported by spectral studies.

In preparation for future study of the ruthenium complexes of these cyclophanes, hexamethylbenzeneruthenium dichloride was also synthesized.

I would like to dedicate this work to my grandfather, Harold L. Lisenby, who showed me what an inquiring mind could accomplish.

In the course of this work, I have become indebted to many people for their support and assistance, without which this study would never have been completed.

I would first like to thank Professor Virgil Boekelheide for offering me the opportunity to do research as a member of his research group this past summer. I would also like to thank him for his timely and insightful suggestions.

I would also like to thank the members of Professor Boekelheide's group, and especially Doctor Steffan Fittkau, for their invaluable guidance in this work. Most importantly, I would like to thank them for showing me how much fun research is.

An heartfelt thanks goes to the General Electric Corporation for providing the necessary funding for this project. I feel the G.E. Expanded Horizons is a very worthwhile and commendable program.

Lastly, and most importantly, I would like to thank Professor William B. Martin. In the past year, not only has he taught me a great deal of chemistry, he has taught me how to learn and investigate on my own. He has showed me how chemistry relates to the "real world". His knowledge and love of science are almost as vast as his love for the world.

David G. Barnett

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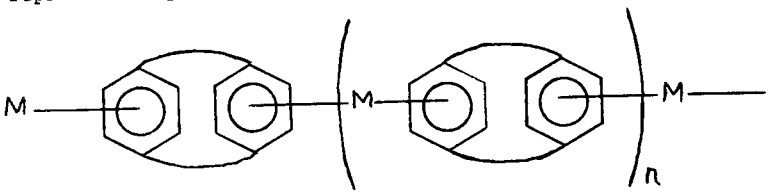
INTRODUCTION

A cyclophane is defined as any compound containing bridged aromatic rings(1). Due to the close proximity of the rings, cyclophanes have many unique characteristics. Gerson showed by the use of ESR that the radical anion of (2.2)-paracyclophane contains eight equivalent protons(2). This is due to the delocalization occurring between the two rings, and is consistent with the belief that (2.2)paracyclophane is a one pi-electron cloud system. The existence of this system has sparked interest in cyclophane-transition metal complexes in an attempt to produce an organic polymer of the form shown below, where M represents any transition metal(3).



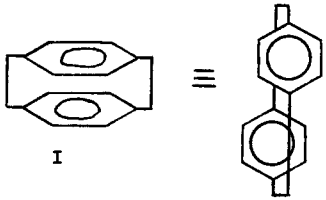
It is hoped that this structure will also be a one pi-electron cloud system. If a compound of this type can be synthesized, it may have very useful conductive properties.

In efforts to produce a compound of this type, many cyclophanes and their transition metal complexes have been synthesized, and their electrochemical properties studied.

Most work to this date concerns the iron and ruthenium metal complexes of the cyclophanes(4).

The first reported synthesis of a cyclophane was by Pellegrin in 1899(5). He synthesized (2.2)-metacyclophane via the Wurtz coupling of m-xylylene dibromide. However, a greater interest in cyclophane chemistry did not occur until the late 1940's, when Brown and Farthing were able to extract di-p-xylylene from a linear polymer produced by the pyrolysis of p-xylylene(6). However, they were unable to prepare this compound by any planned synthetic route.

The first reported synthesis of (2.2)-paracyclophane(I) was by Cram and Steinberg in 1951(7). They were able to prepare the cyclophane via the Wurtz coupling of 1,2-bis(4'-bromomethylphenyl)ethane. They also introduced the cyclophane nomenclature, in which each bridge is designated by a number in brackets, corresponding to the number of substituents in the bridge. The locations of the bridges on the aromatic rings are indicated in the normal manner. That is, the words ortho-, para-, or meta- can be used to indicate the respective positions of the bridges. Another option is the use of numbers placed in parenthesis after the first set. For example, the name (2.2)(1,4)-cyclophane(I) indicates that the bridges are at the one and four positions on the ring, and that both bridges consist of two substituents.



I

In 1976, Begley and Martin produced 2,11-dithia-benzo(3.3)paracyclophane(VII) in an attempt to produce benzo-(2.2)paracyclophane(XIV)(8). The method they pursued was first introduced by Vogtle in 1969. Following this procedure, they first brominated p-xylene(II) in the presence of N-bromosuccinamide. The resulting 1,4-bis-(bromomethyl)-benzene(IV) was then treated with thiourea to produce the 1,4-bis-(mercaptomethyl)-benzene(VI). 1,4-dimethylnapthalene(III) was then brominated in like fashion to give the 1,4-bis-(bromomethyl)-napthalene(VI). This was then coupled with the 1,4-bis-(mercaptomethyl)-benzene(IV) in a basic methanol solution, yielding the 2,11-dithia-benzo-(3.3)-paracyclophane(VII) in excellent yield.(see Fig.2)

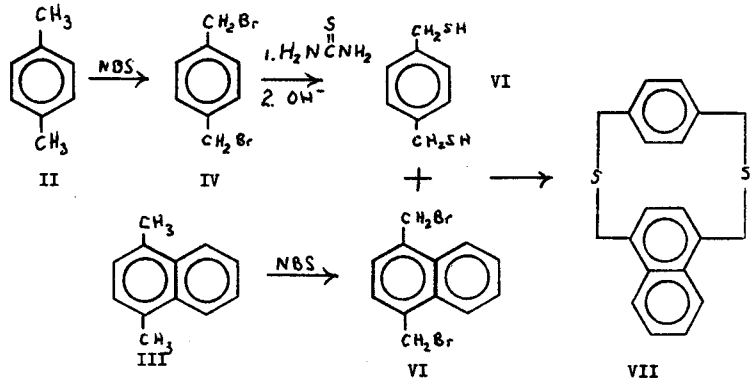


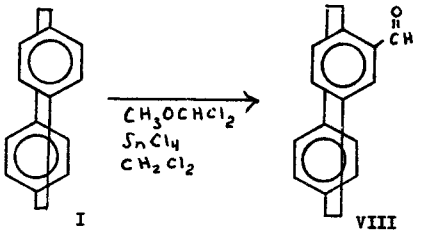
FIG.2

An attempt at sulfur extrusion was unsuccessful, as reported in the thesis; however, Bruhin completed the photoextrusion of the sulfur in trimethylphosphite in good yield, for both the normal and octadeuterated benzo-(2.2)-paracyclophane as reported by Martin, Gerson and Bruhin(9). Boekelheide and others have enjoyed great success employing a similar procedure(10). In this process, the dithiacyclophane is dissolved at very low concentration in either neat degassed trimethylphosphite or in a degassed solution of the trimethylphosphite in benzene. It is then irradiated with ultraviolet light while being agitated by dry, pure nitrogen gas. After irradiation, the solution is hydrolyzed by boiling under reflux with 18% hydrochloric acid. The aqueous solution is then extracted with chloroform, producing the cyclophane in good yield.

As shown above, most approaches to the synthesis of cyclophanes concern themselves with the creation of the bridges between the aromatic decks. The method used by Begley will be applied to the synthesis of the napthalenophanes. However, a novel method will be taken toward the synthesis of benzo-(2.2)-paracyclophane(XIV). The precursor for this synthetic scheme, (2.2)-paracyclophane will already contain the necessary bridges. Through a three-step scheme involving a Rieche formulation reaction, a Wittig reaction, and a photocyclization reaction, it will be shown to be possible to prepare

benzo-(2.2)-paracyclophane(XIV). A ruthenium capping agent will also be synthesized.

EXPERIMENTAL



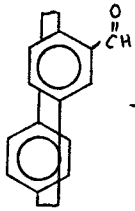
I VIII

ϕ_3P + CH_2CHCH_2Br $\xrightarrow[\text{XYLENE}]{\triangle}$ $[\phi_3\overset{+}{P}CH_2CHCH_2]\,Br^-$

XI XII

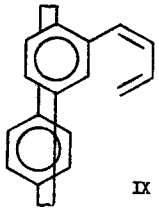
(ϕ = phenyl)

X



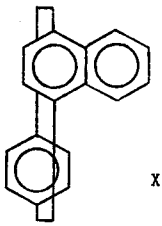
VIII

+ $[\phi_3\overset{+}{P}CH_2CHCH_2]\,Br^-$ (XII) $\xrightarrow[\text{THF}]{\text{K-t-butoxide}}$



IX

$\xrightarrow[I_2, O_2]{h\nu}$ BENZENE



XIV

FIG. 3

Approximately five grams(24mmol) of (2.2)-paracyclophane(I)[19] were placed in a 300ml three-necked round bottom flask equipped with a nitrogen inlet and a dropping funnel. The flask was flushed with nitrogen, and 200ml of dry methylene chloride* was added to dissolve the paracyclophane(I). The flask was then placed in an ice bath, and the solution was stirred. When the temperature approached 0°C, eight milliliters(70mmol) of anhydrous tin(IV)chloride were injected. This was accomplished using a gas-tight syringe to prevent the reaction of the tin(IV)chloride with water in the air. Eleven milliliters(122mmol) of dichloromethyl methyl ether were then added dropwise from the dropping funnel. The mixture was then stirred at 0°C for 70 minutes, and then at room temperature for 45 minutes.

The reaction mixture was then poured into a 1000ml round bottom flask containing a mixture of ice and aqueous sodium bicarbonate solution. Additional bicarbonate solution was then added until the mixture tested neutral or slightly basic to pH paper. The mixture was then extracted with 600ml of methylene chloride, and the organic layer was separated. This was then washed with water, and dried. The methylene chloride was then distilled off using a Buchi rotavaporator, leaving approximately five grams of an off-white powder,

whose NMR spectrum showed it to be 4-formyl-(2.2)-paracyclophane(VIII), containing traces of starting material(I).

On the first run, column chromatography was used to separate the two materials. A silica gel column using benzene as the eluent provided a successful separation. However, due to the nature of the synthetic scheme, it was found that this was an unnecessary purification, and was omitted in future runs.

The first run yielded 5.4198g(95.475%) of product(VIII) from 5.0038g of cyclophane(I). The second run yielded 5.7818g(about100%) of product(VIII) from 5.0792g of cyclophane(I). The third run resulted in the production of 5.1900g(93.825%) of the aldehyde(VIII) from 4.8759g of cyclophane(I).

*The methylene chloride was predried over molecular sieves, and then refluxed over phosphorous pentoxide under an nitrogen atmosphere. It was then distilled off. The first quarter of the distillate was discarded to ensure complete dryness(11).

SYNTHESIS OF 3-(1-BUTA-1,3-DIENYL)(2.2)-PARACYCLOPHANE(IX)

The first part of this synthesis involved the formation of allyltriphenylphosphonium bromide(XII). A solution of

12.7365g(48.5606mmol) of triphenylphosphine(X) and 4.20ml(48.5mmol) of allyl bromide(XI) in xylene was refluxed with stirring for twelve hours. The reaction mixture was then allowed to cool to 60°C. The resulting white precipate was then filtered, washed with xylene and dried in a vacuum oven to constant mass, yielding 17.0859g(91.9%) of product(IX).

This reaction was carried out twice. The second run yielded 17.93g(96.3%) of product(XII) from 12.7446g(48.5904mmol) of salt(X) and 4.20ml(48.5mmol) of allyl bromide(XI).

The first attempt to react the salt above(XII) with the cyclophane(VIII) was unsuccessful. First ethanol was rigorously dried. Approximately 50-75ml of commercially dry ethanol was placed in a dry 1000ml roundbottom flask equipped with a condensor and drying tube. Five grams of magnesium and 0.5g of iodine were then added, and the mixture was warmed until the iodine disappeared. The mixture was then allowed to reflux until all the magnesium was converted to the ethanolate. An additional 900ml of ethanol were then added and refluxed for 30 minutes. The ethanol was then distilled off into a storage vessel containing molecular sieves. Great care was taken to maintain rigorously dry conditions(12).

0.712g(103mmol) of lithium ribbon was then added to 500ml of the absolute ethanol in an attempt to produce a lithium ethoxide solution. This was stored under nitrogen gas.

A solution of 2.6296g(11.127mmol) of 4-formyl-(2.2)-paracyclophane(VIII) and 4.5062g(11.758mmol) of the allyltriphenylphosphonium bromide salt(XII) in 200ml of ethanol was prepared under a nitrogen atmosphere. To enhance the solubility of the cyclophane(VIII), 25ml of methylene chloride were added. 55.6ml(14.73mmol) of the lithium ethoxide solution were then added via a syringe. No noticeable reaction occurred.

In an attempt to find the cause of the problem, a mock reaction was designed, using formaldehyde as the aldehyde in place of the cyclophane(VIII). However, under the same conditions, no reaction occurred. It was decided to try a different base. When the mock reaction was attempted using potassium t-butoxide in tetrahydrofuran, an immediate reaction occurred. Therefore, potassium t-butoxide was used as the base for further reactions.

In the first successful attempt to synthesize the diene(IX), 0.5378g(4.793mmol) of potassium t-butoxide was placed in a 50ml three-necked round bottom flask, while in a nitrogen glove bag. A nitrogen line was attached to the flask, and 15ml of THF were added to dissolve the base. 1.8302g(4.775mmol) of the salt(XII), and 1.1260g(4.765mmol) of 4-formyl-(2.2)-paracyclophane(VIII) was subsequently added. Upon addition of the salt(XII), the previously clear solution became a brilliant red. Upon addition of the 4-formyl-(2.2)-paracyclophane(VIII) the solution became yellow. After stirring for twelve hours, the reaction

mixture was washed with water,and extracted with methlene chloride. The organic layer was then separated from the aqueous layer, dried, and concentrated using a Buchi rotavaporator.

The reaction yielded several products, as shown by thin-layer chromatography on silica plates using benzene as the eluent. A column was then run, yielding a first fraction of 0.3135g(1.2425mmol) of the desired product(IX), as shown by NMR analysis. However, the yield was only 26.08%.

In subsequent attempts, a five-fold excess of base and salt(XII) was used to increase the yield. The second attempt yielded 0.5337g of diene(IX) from 0.7000g(2.9622mmol) of the aldehyde(VIII), a 69.20% yield. The third attempt yielded 0.6653g of the slightly yellow solid(IX) from 1.0009g(4.235mmol) of the cyclophane(VIII), a 60.33% yield.

SYNTHESIS OF BENZO-(2.2)-PARACYCLOPHANE(XIV)

In the first two attempts, an apparatus consisting of a quartz cooling-jacket fitted with a pyrex reaction vessel was charged with equimolar amounts of iodine and 3-(1-buta-1,3-dienyl)-(2.2)-paracyclophane in benzene. These were then irradiated with an Hanovia lamp, while being bubbled through with air. Workup involved the addition of an large excess of a saturated aqueous sodium thiosulfate solution to remove excess iodine. The aqueous and organic layers were then separated. The aqueous layer was extracted

with several methylene chloride fractions. These fractions were then added to the organic layer, washed with several fractions of water, dried and concentrated using a Buchi rotavaporator. The resulting extract was a brown tarry substance.

The first attempt involved the irradiation of 0.3081g(1.1183mmol) of the diene(IX) and 0.3276g(1.2907mmol) of iodine in approximately 150ml of benzene. The irradiation period was 48 hours. TLC on silica gel with benzene as the eluent was used to follow the reaction. Unfortunately, this method was unable to separate the products from the reactants, due to the large Rf of the diene(IX). An NMR spectrum indicated a loss of allylic protons, but separation and purification by column chromatography on a silica gel column with benzene as the eluent proved impossible. A mass spectrum of the mixture showed no parent ion peak at 258amu.

The second attempt involved the irradiation of 0.6653g(2.555mmol) of the diene(IX) and 0.7020g(2.766mmol) of iodine for a four hour period. At the end of this time, it was noted that a slightly yellowed precipitate had coated out on the wall of the cooling jacket only where the light struck directly. This substance was dissolved in d-dimethylsulfoxide and an NMR spectrum was taken. The results were very inconclusive, as not enough material was obtained. Workup of the remaining material resulted in a

brownish tar much like the one reported above. An NMR spectrum showed the loss of allylic protons, and was quite similar to the first attempt. No further work was done on this substance.

The third and final attempt at ring closing made use of the same apparatus as in the first two. However, in an attempt to eliminate possible side-reactions with benzene, this apparatus, minus the lamp, was placed inside a Rayonet Photochemical Reactor. 0.3392g(1.303mmol) of the diene(IX) was irradiated through the pyrex reaction vessel instead of the quartz cooling jacket. The reaction was followed by UV-visible spectroscopy using a Perkin-Elmer Lamda-3 spectrophotometer. The diene spectrum had one maximum at 284.8nm. No iodine was initially added. After 30 minutes with no reaction, less than 0.10g of iodine was added. To eliminate the iodine absorption from the reaction mixture spectra, an iodine in benzene blank was prepared. Its UV-vis spectrum was taken, stored on a disk using the 660 data station, and subtracted electronically from the other spectra. After 24.5 hours, a new peak appeared at 279.2nm, while the old one disappeared. Upon work up a yellow solid was obtained. An NMR spectrum suggested the loss of the bridging protons. The allylic and aromatic protons remained.

SYNTHESIS OF THE SYN- AND ANTI- ISOMERS OF 2,15-DITHIA-(3.3)-NAPTHALENOPHANE(XVII,XVIII)(15)

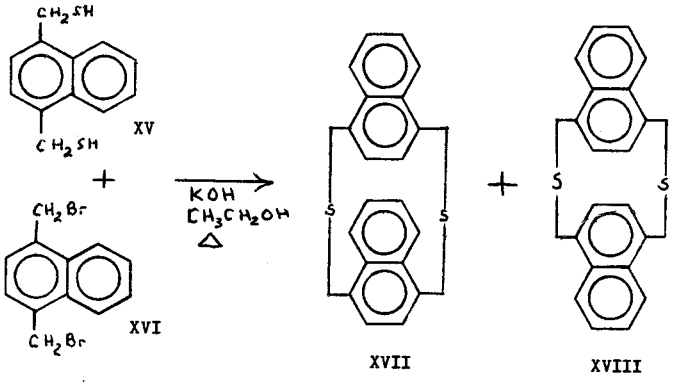
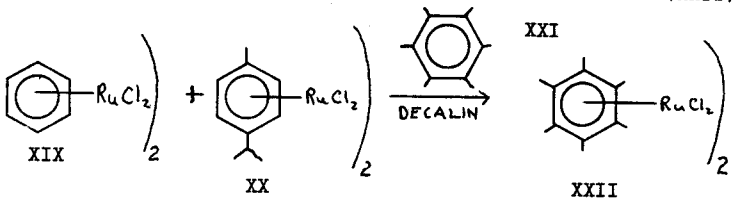


FIG. 4

A solution of 1,4-bis(mercaptomethyl)napthalene(437.6mg)(XV)(18) and 1,4-bis(bromomethyl)napthalene(634.6mg)(XVI)(16) in 400ml of degassed benzene was added dropwise via a 50ml gas-tight syringe and a syringe pump to 2000ml of refluxing potassium hydroxide/ethanol solution over a three day period. The solution was refluxed under an argon atmosphere. The reaction mixture was then concentrated using a Buchi rotavaporator, and the residue was extracted with chloroform. This was then concentrated, and the extract was then run over

a silica gel column with chloroform as the eluent. The first fraction yielded a not highly pure mixture of both the syn- and anti isomers(XVII,XVIII), as shown by NMR. Recrystalization from hot chloroform by the slow addition of pentane or hexanes proved to be partially successful in further purification.

SYNTHESIS OF HEXAMETHYLBENZENERUTHENIUM DICHLORIDE(XXII)(17)



XIX XX XXII

A solution of 18.1810g(59.4mmol) of benzeneruthenium dichloride(XIX), 8.1103g(32.43mmol) of cymeneruthenium dichloride(XX), and 297.7g(1834mmol) of hexamethylbenzene(XXI) in 292ml of decalin was refluxed for six hours at 185C. Due to the large scale of the reaction, a heavy duty stirrer provided mixing. NMR spectra were taken in dimethylsulfoxide every hour until no evidence of starting material remained. After allowing the flask to cool slightly, and the material to settle out, the supernatant liquid was decanted off. The resulting precipitate was then washed with boiling heptane and transferred to a soxlet extraction thimble. It was soxlet extracted with heptane in two fractions. The first fraction was extracted for five

the second for three, to remove the excess hexamethylbenzene. Upon drying in a vacuum oven, 26.0344g(84.9%) of a brownish orange solid was recovered, whose NMR spectrum showed it to be the desired product(XXII)

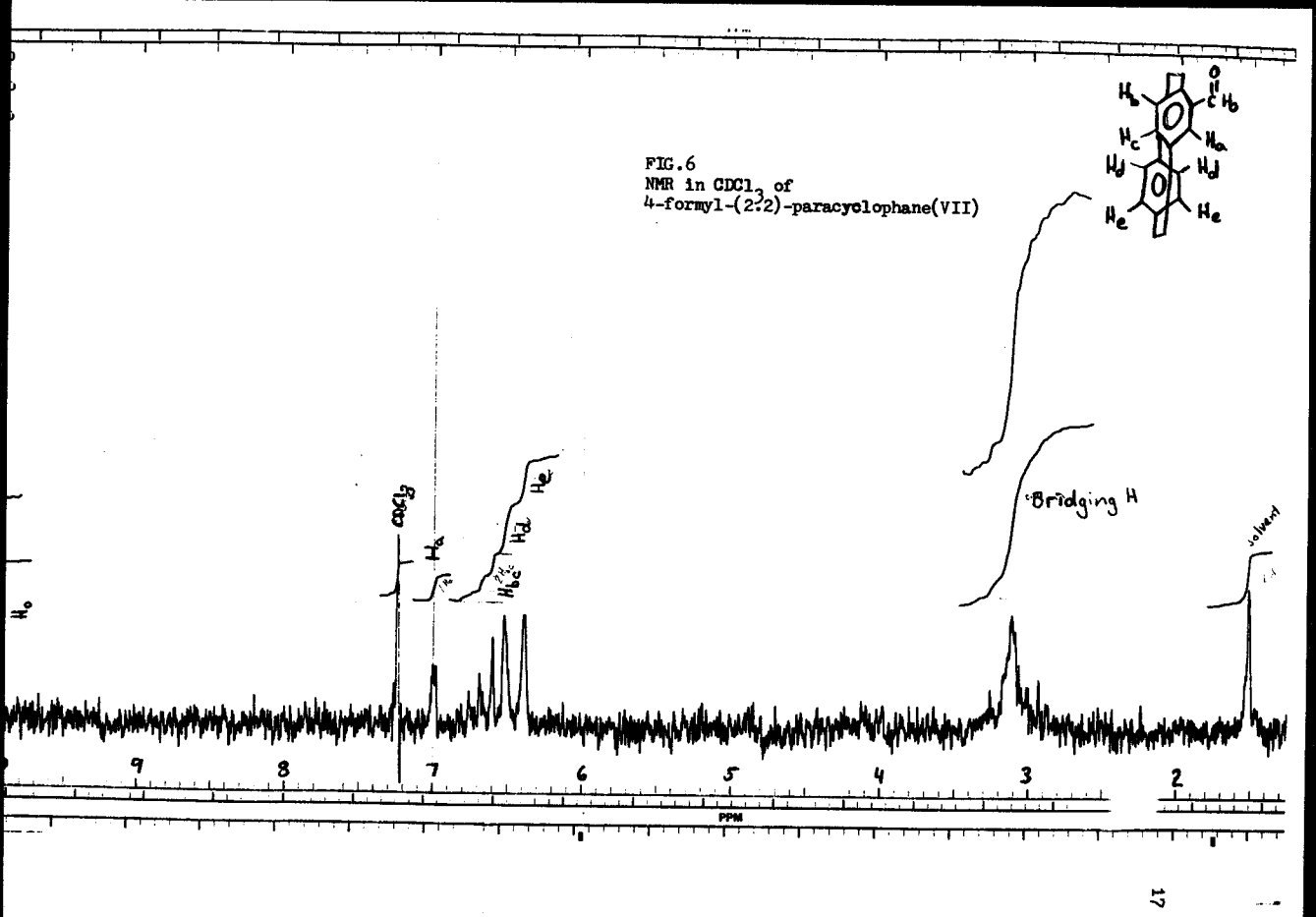


FIG.6
NMR in $CDCl_3$ of
4-formyl-(2.2)-paracyclophane(VII)
H_b
H_c
H_a
H_d
H_e
Bridging H
Solvent
PPM
9
8
7
6
5
4
3
2

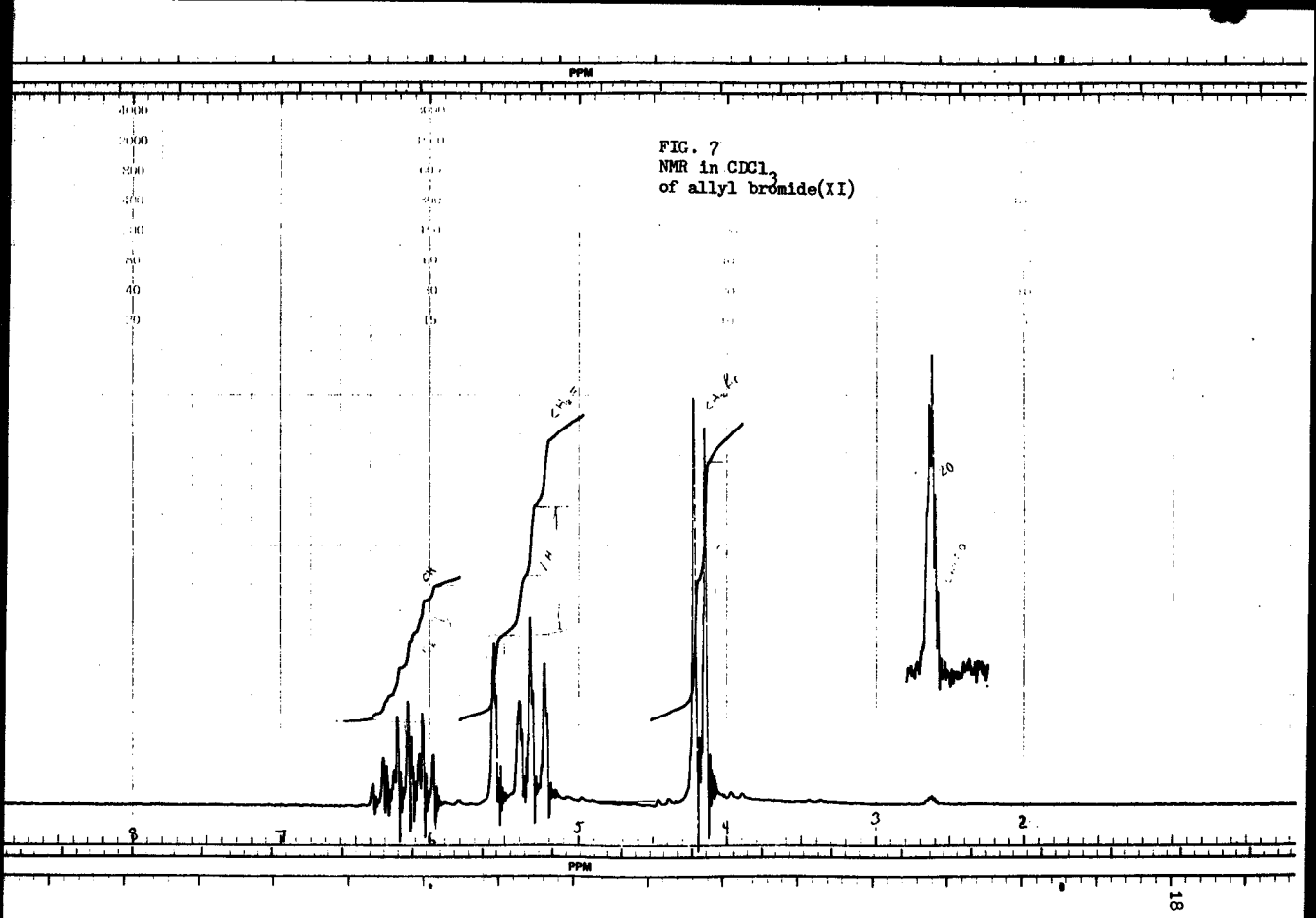


FIG. 7
NMR in $CDCl_3$
of allyl bromide(XI)

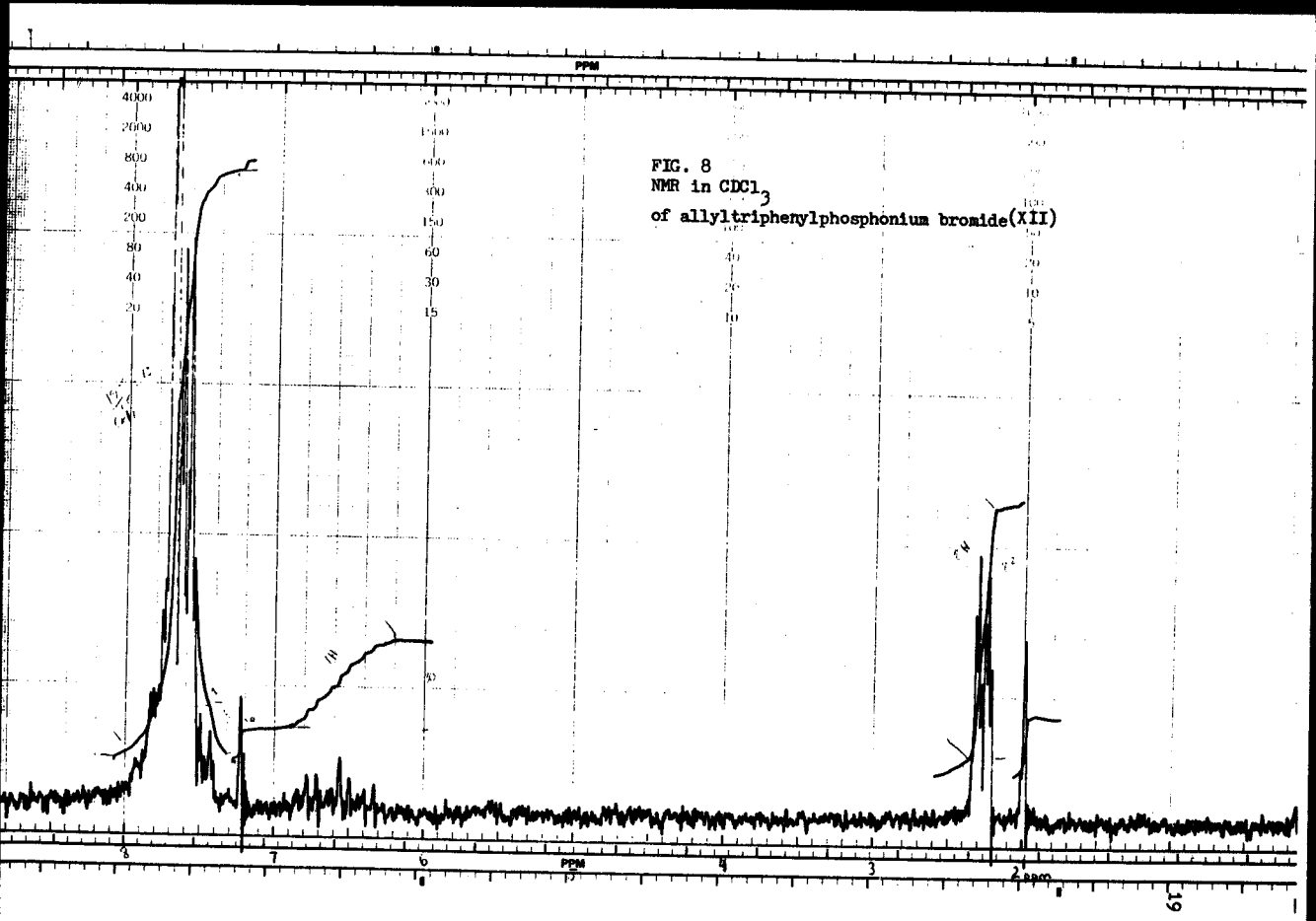


FIG. 8
NMR in $CDCl_3$
of allyltriphenylphosphonium bromide(XII)

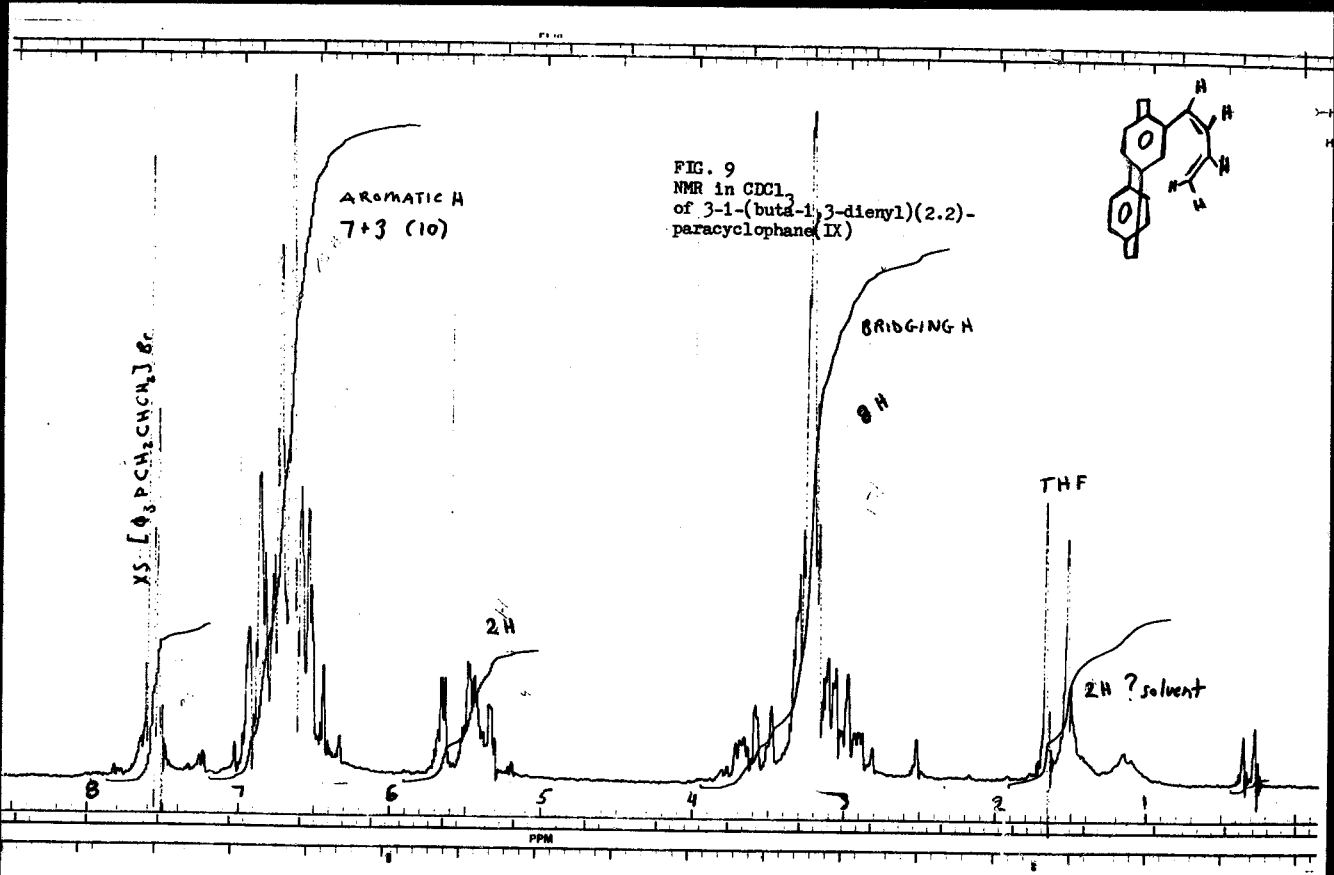


FIG. 9
NMR in $CDCl_3$
of 3-1-(buta-1,3-dienyl)(2.2)-paracyclophane (IX)

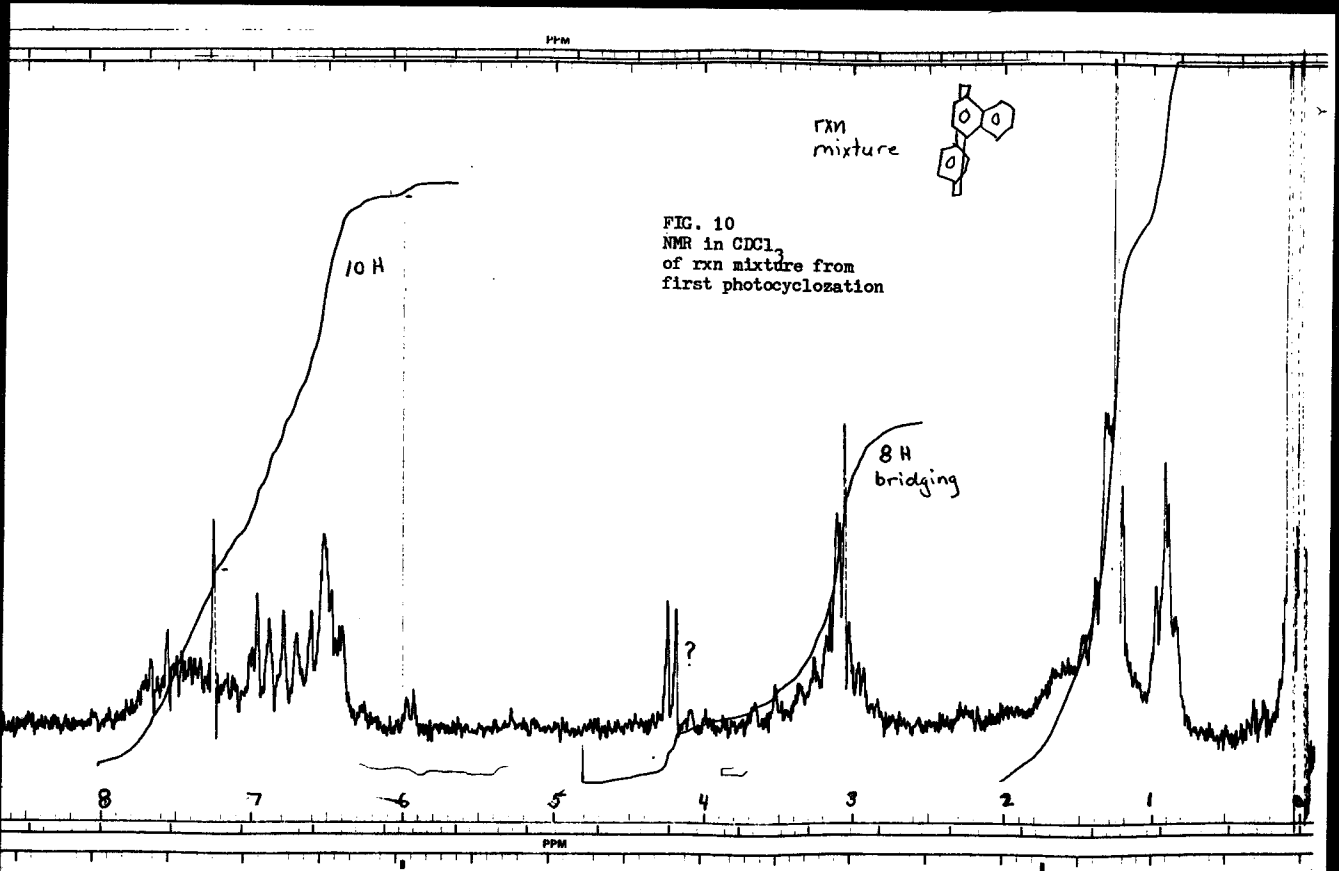
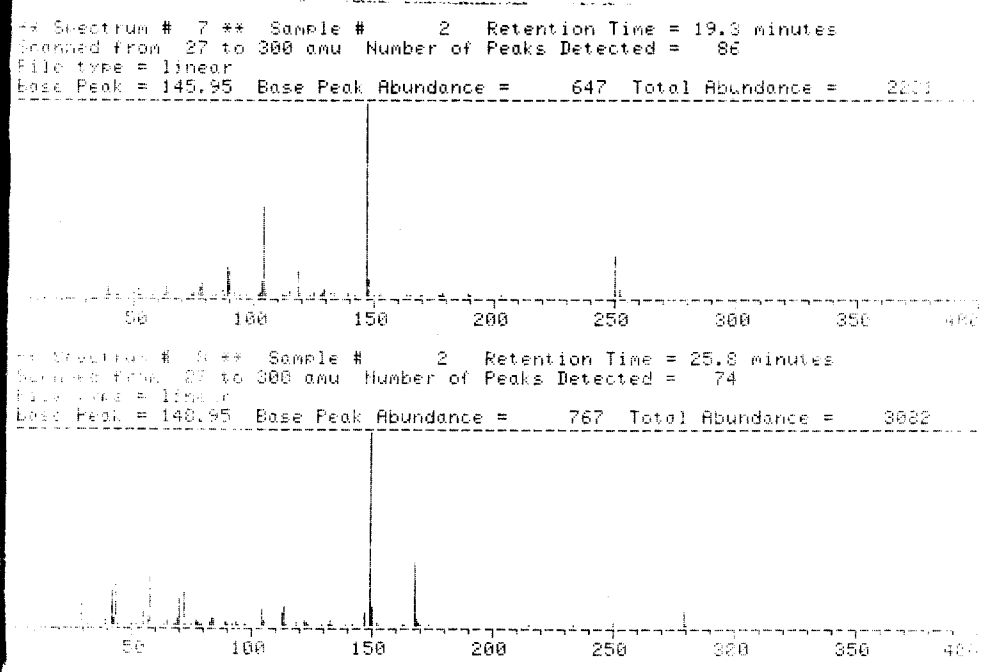


FIG. 10
NMR in $CDCl_3$
of rxn mixture from
first photocyclozation

FIG. 11
GC/mass spec
of rxn mixture of first
photocyclization



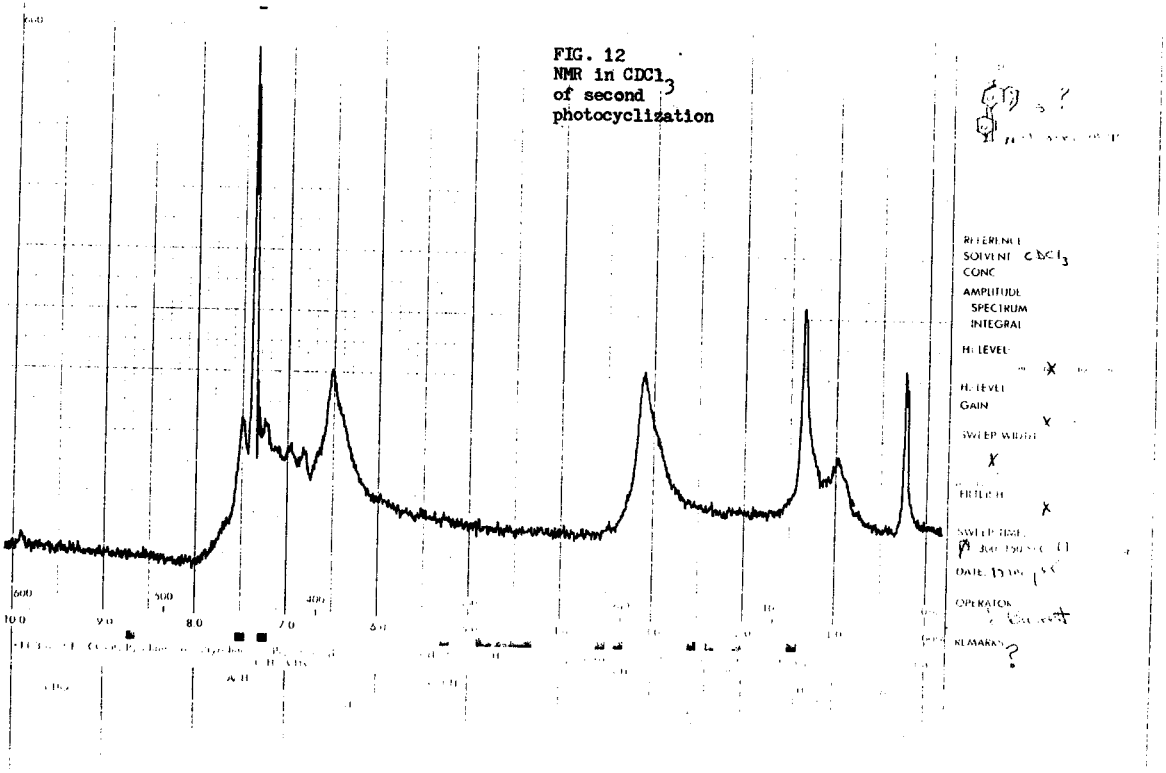


FIG. 12
NMR in $CDCl_3$
of second
photocyclization

FIG. 13
NMR in $CDCl_3$
of reaction mixture
of third photocyclization

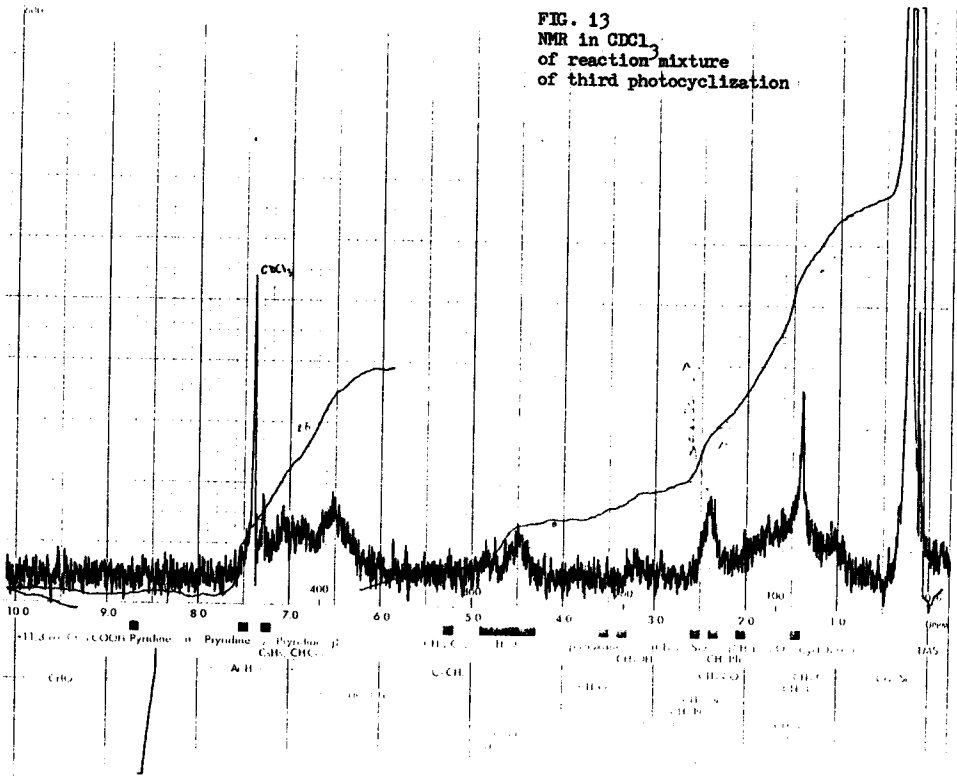


FIG. 14
UV-vis in benzene
of 3(1-buta-1,3-dienyl)(2.2)-paracyclophane(IX)

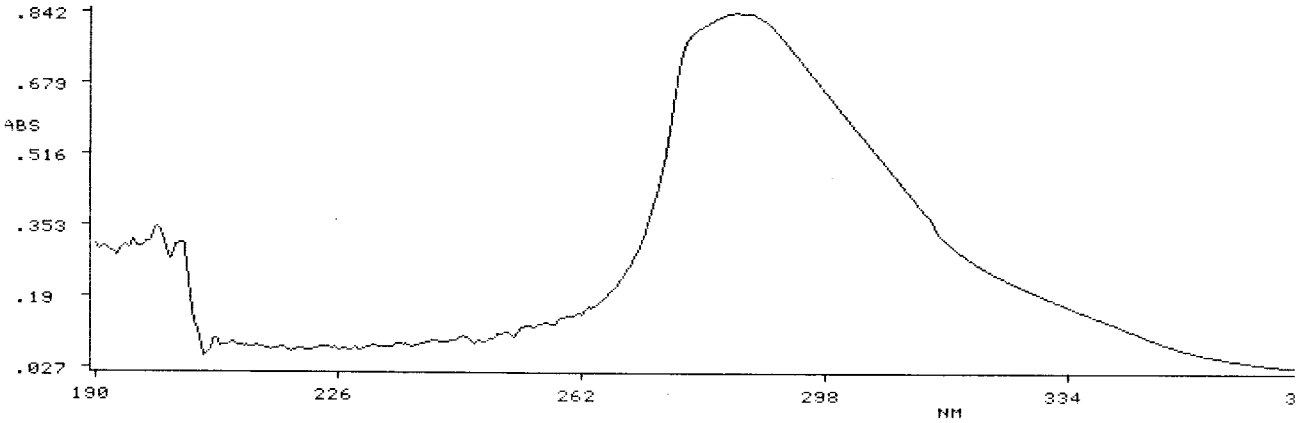
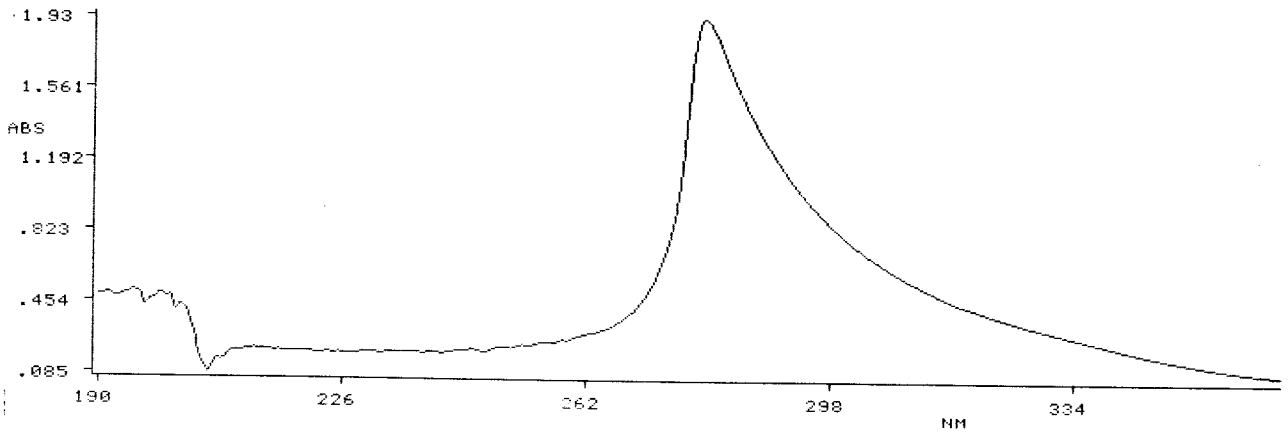


FIG. 15
UV-vis in benzene
of rxn mixture of
third photocyclization



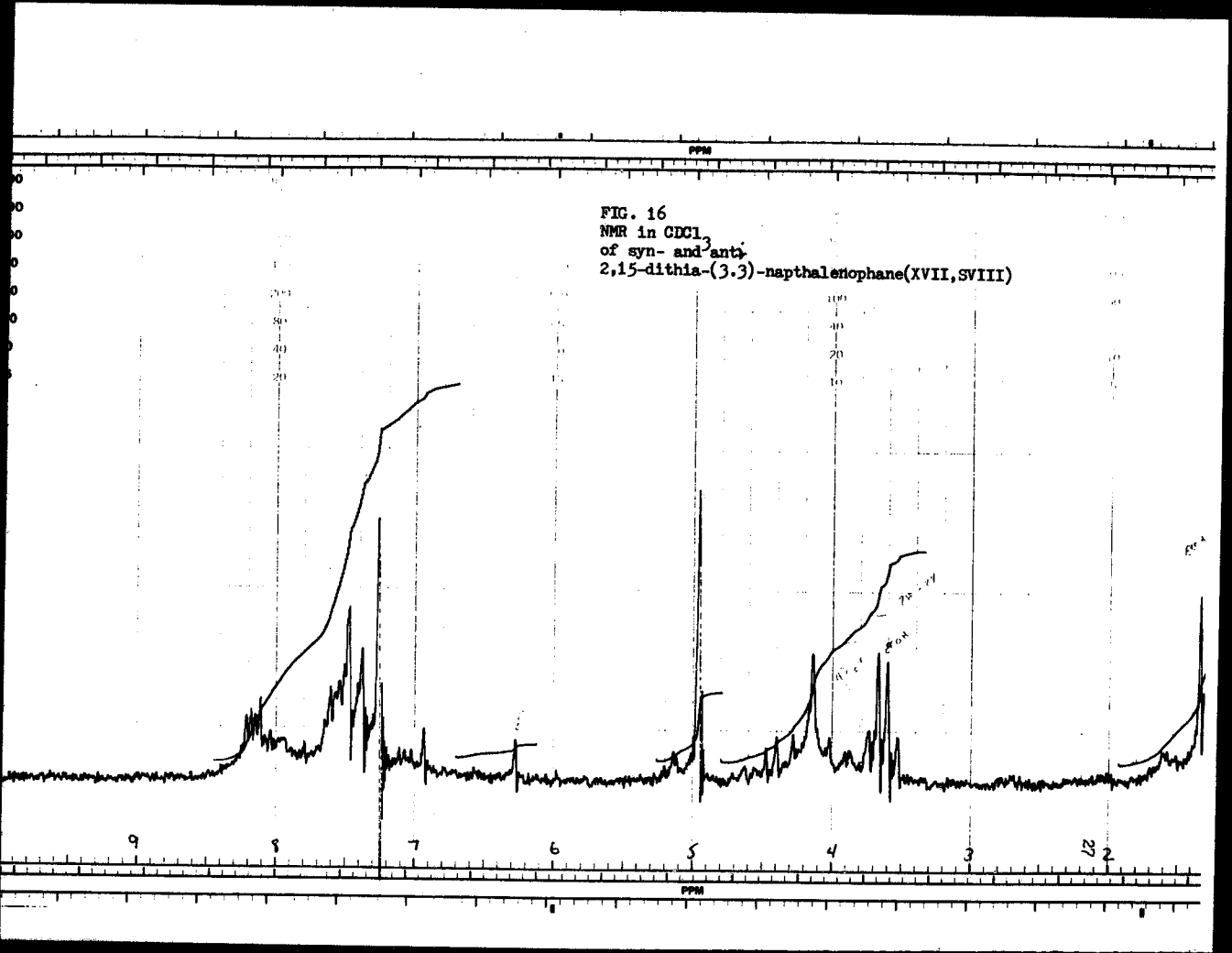


FIG. 16
NMR in $CDCl_3$
of syn- and anti-
2,15-dithia-(3.3)-napthalenophane(XVII,XVIII)

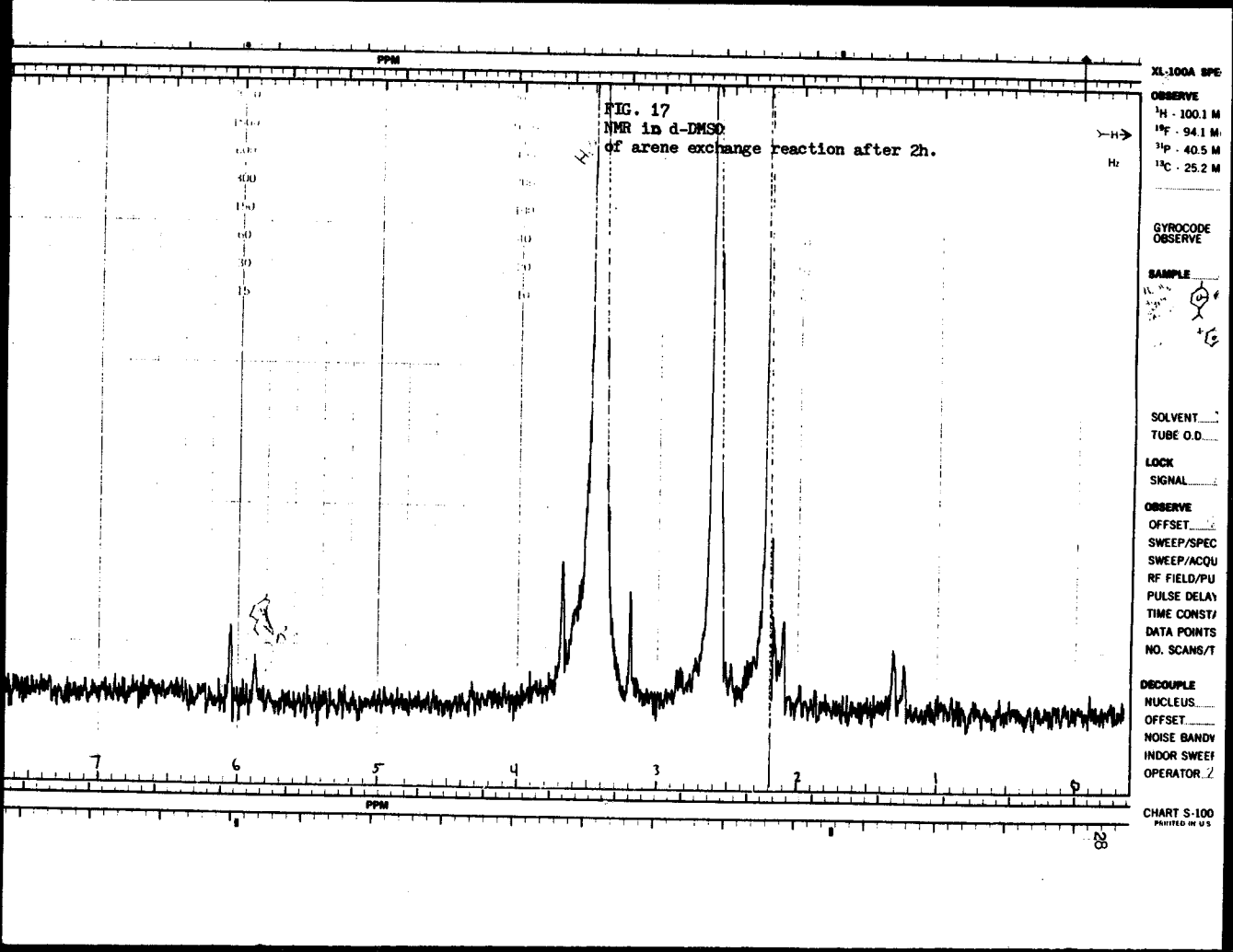


FIG. 17
NMR in d-DMSO
of arene exchange reaction after 2h.

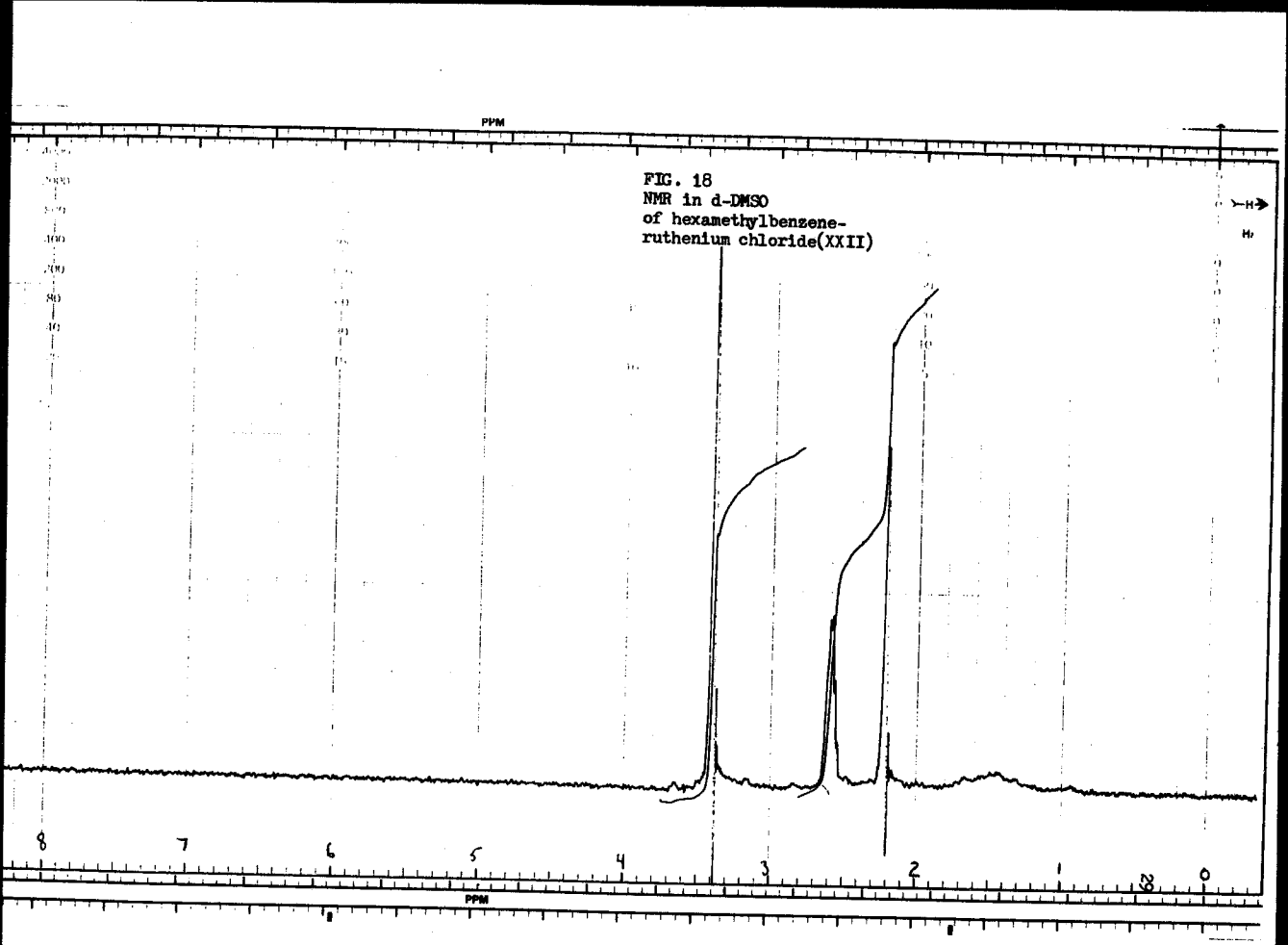
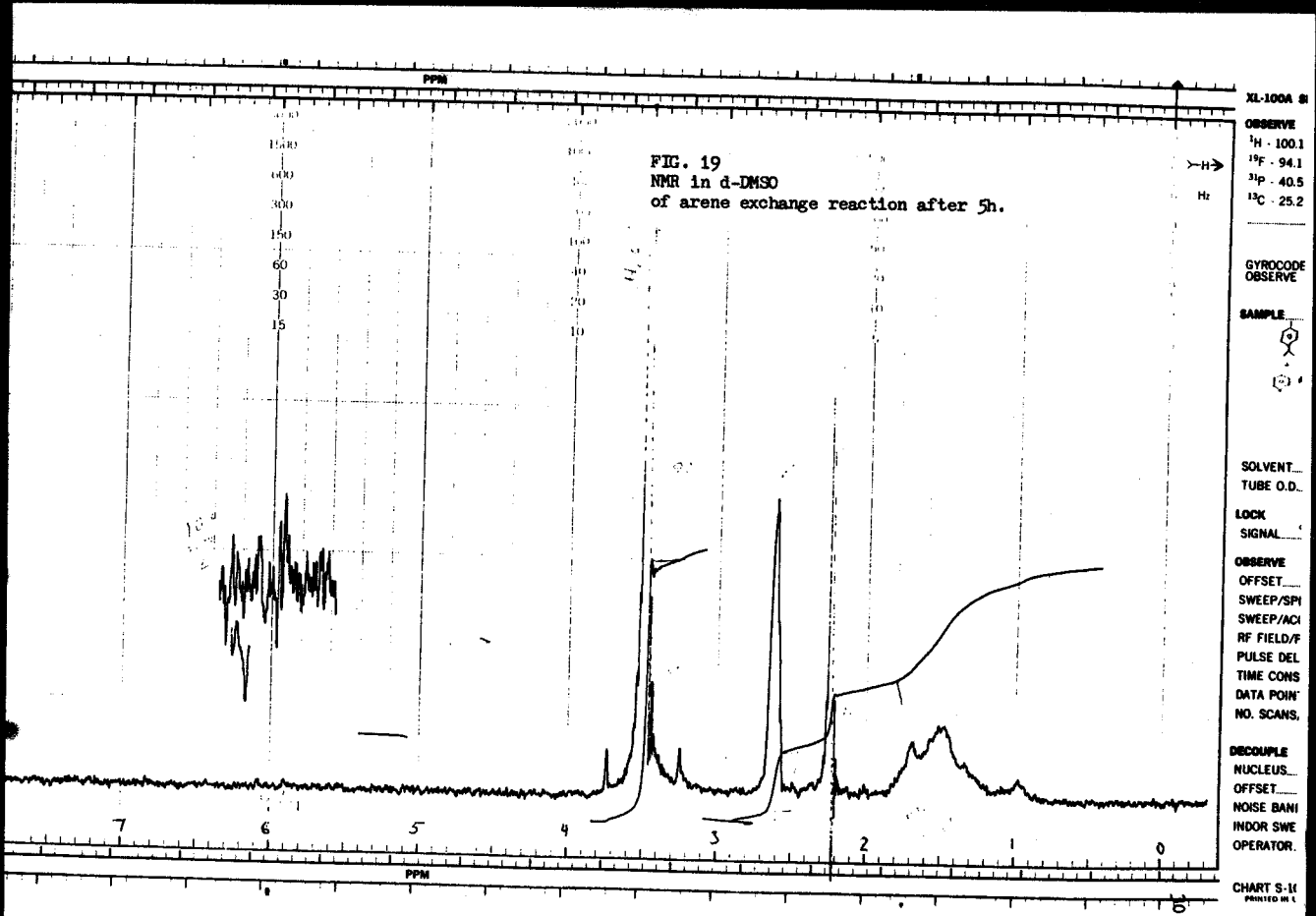


FIG. 18
NMR in d-DMSO
of hexamethylbenzene-
ruthenium chloride(XXII)


PPM
FIG. 19
NMR in d-DMSO
of arene exchange reaction after 5h.
Hz
PPM
XL-100A SI
OBSERVE
^{1}H - 100.1
^{19}F - 94.1
^{31}P - 40.5
^{13}C - 25.2
GYROCODE
OBSERVE
SAMPLE
SOLVENT
TUBE O.D.
LOCK
SIGNAL
OBSERVE
OFFSET
SWEEP/SPI
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RF FIELD/F
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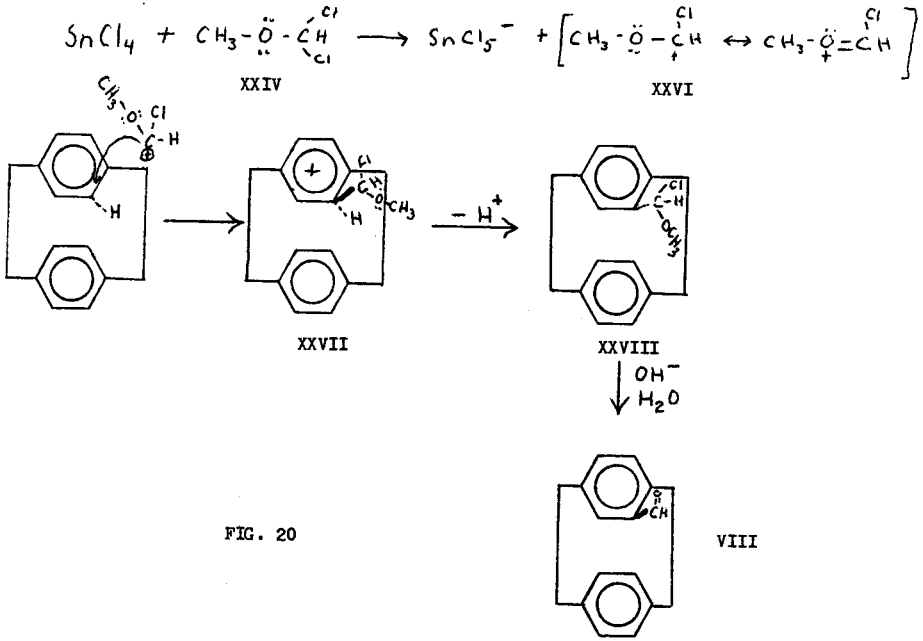
ANALYSIS

The Rieche formulation of (2.2)-paracyclophane proved to be a relatively simple reaction, giving excellent results. A proposed mechanism follows(Fig.20), in which tin(IV) chloride acts as a Lewis acid, removing a chlorine atom from the dichloromethyl methyl ether(XXIV). The resulting intermediate(XXVI) then attacks the aromatic ring of the cyclophane(I), producing a positively charged species(XXVII). This in turn loses a proton, forming the methoxy-containing species(XXVIII). In the presence of base and water, this is hydrolyzed to the aldehyde(VIII).



XXIV XXVI XXVII XXVIII VIII

FIG. 20

The NMR spectrum of the white powder remaining after workup verified the formation of 4-formyl-(2.2)-paracyclophane(see Fig.6). One aldehydic proton appeared at 9.9ppm. The eight bridging protons appeared at 3.16ppm, and 7 aromatic protons were seen, clearly split from each other in a region from 6.4 to 7.0ppm. The peaks were easily assigned to the appropriate protons by correlating the downfield shift to the position of the protons with respect to the deshielding aldehyde.

The Wittig reaction also proved to give good results. The reaction consists of two parts(19). In the first part, triphenylphosphine is reacted with an alkyl-, or in this case an allyl halide to produce a crystalline salt. The reaction proceeds by SN2 attack.

The second part of this reaction involves the removal of the allylic proton to the phophorous by a strong base, thus forming a neutral compound called an ylid(XXIX). This then rapidly reacts with the aldehyde or ketone, forming an intermediate called a betaine(XXX), which then transforms into an oxophosphetane(XXXI). This then decomposes to give the diene(IX) and triphenylphosphine oxide(XXXII). This addition proceeds via an SN2 attack(see Fig.21).

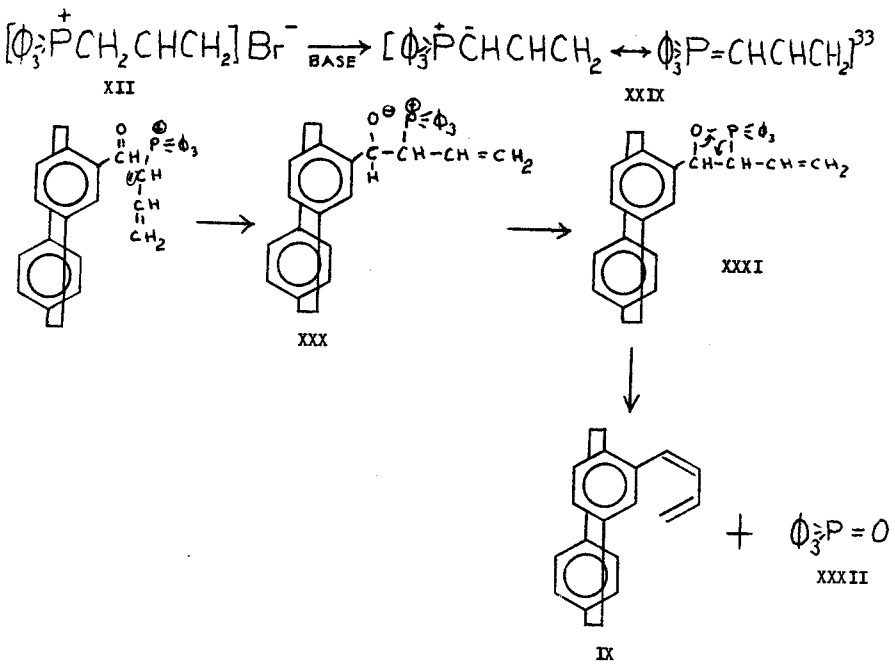


FIG. 21

Phosphines are excellent nucleophiles and weak bases. Therefore , nucleophilic attack is enhanced, while competing elimination reactions are greatly hindered, and have virtually no affect.

An NMR spectrum of allyl bromide was compared to that of the product of the allyl bromide/triphenylphosphine reaction in order to assign peaks. In the NMR of allyl bromide(Fig.7), there is a peak at 4.2ppm corresponding to the two protons nearest the bromine atom. There is a triplet

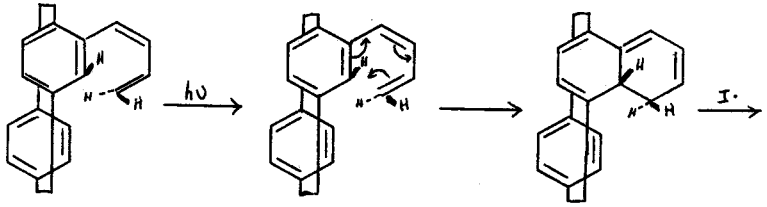
at 5.3ppm corresponding to the two protons furthest from the bromine, and a multiplet at 6.18ppm corresponding to the proton on the middle carbon.

An NMR spectrum of the allyltriphenylphosphonium bromide salt(XII)(Fig.8) showed 15 aromatic protons in a multiplet centered at 7.7ppm. The protons on the carbon that was originally bonded to the bromine are now shifted upfield to a doublet at 2.2ppm. The proton closest to the triphenyl substituent is represented by a peak at 6.6ppm. The other two allylic protons are buried under the aromatic peak.

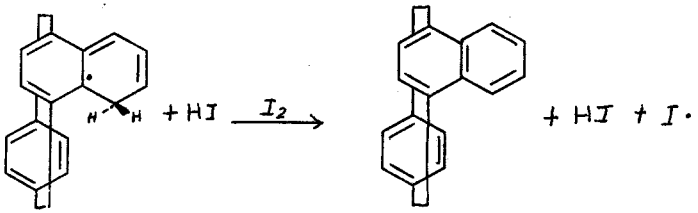
When this procedure was first applied, using lithium ethoxide, a suspect base due to the condition of the lithium metal from which it was made, no reaction occurred. However, when potassium t-butoxide was used, a brilliant red appeared, indicating the presence of an electron rich atom; in this case most likely the phosphorous. The NMR spectrum of the diene(IX)(Fig.9) showed ten protons in the aromatic region. They appeared as a multiplet centered around 6.5ppm. Two allylic protons were seen as a multiplet around 5.5ppm. The eight bridging appeared as a symmetrical multiplet centered around 3.2ppm.

The photocyclization step has not been successfully completed. The possibility exists that some product was obtained. However, attempts at purification were unsuccessful and are incomplete at this time. A proposed mechanism for this reaction is as shown below(Fig. 22). A concerted electron shift occurs when the molecule is struck

by light of the appropriate wavelenght. An hydrogen atom isthen lost, yielding most likely the tertiary radical(XXXIV), as shown. Iodine in the solution will pick up the hydrogen and propogate the reaction. A second hydrogen atom will leave the ring, producing the aromaticity.



IX



XXXIV XIV

An NMR spectrum of the crude product of the first attempt revealed a loss of allylic protons(Fig.10). There is a multiplet at 3.1ppm characterisric of bridging protons. A large multiplet between 6.4 and 7.0 indicates the presence of ten aromatic protons.However, a GC/ms showed no peak at 258amu(Fig.11). There was evidence for possible diels-alder and two plus two addition products in the GC/mass spec(Fig.11). However, there was no confirming evidence, and their presence, if real, does not mean they are major products, or that these reactions are major competitors with the ring-closing. The amounts that are possibly present are too small to indicate a major interference.

The second attempt yielded similar results to the first. An analysis of the NMR spectrum of the crude product also shows a loss of allylic protons and the presence of both bridging and napthalene-like protons(Fig.12).

The third attempt is a bit of a mystery. In order to eliminate reactions occurring due to the overly energetic emission of light allowed through the quartz filter, a pyrex filter was used. This, we thought, would better protect the bridges from irradiation by lower wavelenght light, which would cause rearrangement of the bridges. This would thus allow for a cleaner reaction. In fact, it would seem that quite the opposite occurred. An NMR spectrum(Fig.13) shows allylic protons between 4.0 and 5.0ppm, and no bridging protons. The aromatic section appears to contain some sort

of napthalene-like protons. Uv-vis spectra show a shift of 5.6nm toward the benzene absorption band(Fig.14,15). More work needs to be done in the analysis of this product to elucidate its structure and determine what happened.

The coupling of the 1,4-bis(bromomethyl)napthalene(XV) to the 1,4-bis(mercaptomethyl)napthalenophane(XVI) was carried out in dilute basic solution over a long period of time. This was done to hinder polymerization. In the presence of base, the mercaptan loses a proton and the resulting RS- substituent attacks the carbon to the halide by an SN2 mechanism. The other mercaptan group reacts in the same manner with the other alkyl halide. Depending on the geometry of the molecule when the final closing occurs, both the syn- and anti- isomers may form.

An analysis of the NMR spectrum(Fig.16) indicates 12 protons in the aromatic region, with a napthalene-like splitting into two groups. The bridging protons occur as a multiplet centered around 4.18ppm. This downfield shift from the normal bridging position in paracyclophanes is due to the presence of the sulfur.

The production of hexamethylbenzeneruthenium dichloride dimer also yielded excellent results. The time required for complete reaction is dependent upon the amount reacted. Therefore, because the reaction had never before been run on this scale it was difficult to judge exactly when to stop it.

The reaction produced some higher polymers of the compound, for example trimers due to the slightly longer than optimal reaction time. This was evidenced by the darker color of the product. Pure dimer is a bright orange. However this increased polymerization will not affect the performance of the capping agent. The only difficulty encountered because of this may be a slightly decreased solubility. In the future, reactions of this scale shoud be run no more than five hours.

As can be seen in figures 17, 18, and 19, the loss of aromatic protons indicates the completion of the reaction. The peak at 2.2ppm in figure 19 indicates the presence of six equivalent methyl groups on the aromatic ring.

Two mechanisms can be postulated for the arene exchange. In the first, a ruthenium-chlorine bond is broken to open up a coordination site for the hexamethylbenzene. This then bonds to the ruthenium, forming an unstable intermediate. This can then rearrange, losing either the benzene or the hexamethylbenzene. Due to the large excess of the latter, the equilibrium is driven to the right, and an arene exchange takes place. The second involves "slippage" of the benzene ring. In this case, the benzene-ruthenium bond can be thought to have localized on one "double" bond. This provides the necessary coordination site on the ruthenium for attack by the hexamethylbenzene. It then follows a similar route as described above(Fig.23). It should be noted here that hexamethylbenzene is a better ligand than benzene due to the

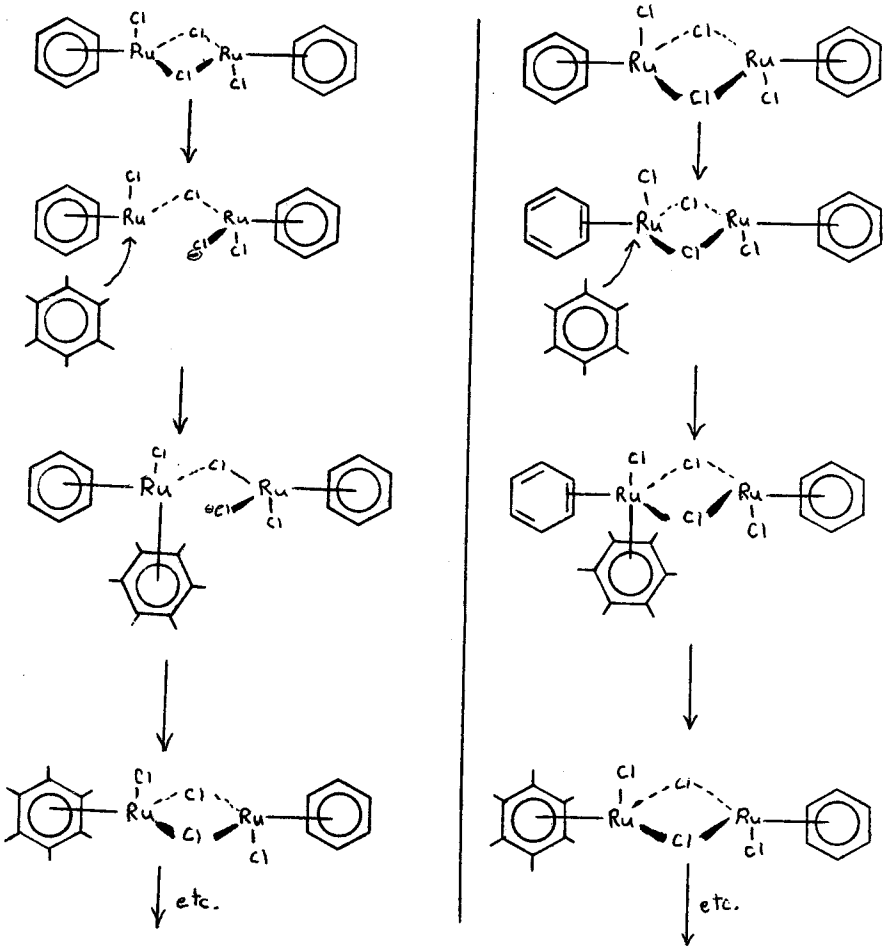


FIG. 23

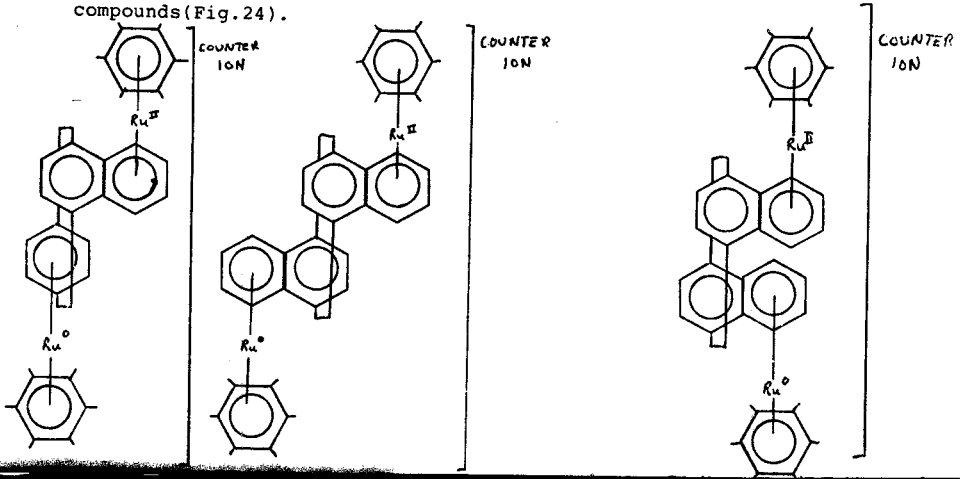
NOTE:
This is only 1 possible structure for the compound. Others containing an Ru-Ru bond may exist. However, this does not change the basic mechanism

CONCLUSION

The successful completion of the first two steps of a novel approach to the formation of benzo-(2.2)-paracyclophane was accomplished. The difficulty with the final and critical step has been limited to two possibilities. The first involves the use of benzene as the solvent. In attempts to remedy this situation, new solvents have been tried, and a new method of irradiation has been used in which the diene(IX) was irradiated through pyrex instead of quartz. The next possible step in attempting to solve this problem is to irradiate with this same set-up for a longer amount of time. However, a better alternative would be the use of either a pyrex cooling jacket or filter, allowing the higher intensity Hanovia mercury lamp to be used. Th second cause of difficulty is the purification of the crude product. NMR spectra show the probable existence of benzo-(2.2)-paracyclophane in the first two reactions. It is not felt that the diene(IX) underwent any form of rearrangement involving the bridging carbons, as no change is observed in the NMR spectra. However, no successful purification has been tried to date. One possibility suggested by Professor William B. Martin is the use of high pressure liquid chromotography(HPLC) to separate the components in the mixture. The fractions could then be

examined by GC/mass spec and the products identified. This would clarify the situation concerning side reactions and overirradiation. Another possible method of separation could be fractional sublimation. Benzo-(2.2)-paracyclophane melts at 115-116C(20), and might, like (2.2)-paracyclophane itself sublime undecomposed..

The syn- and anti- isomers of 2,15,dithia(3.3)(1,4)-napthalenophane have been successfully synthesized. Along with the production of the ruthenium capping agent, this allows for a continuation of the project. A photolytic desulfurization reaction will yield the napthalenophanes. The novel approach, or a coupling reaction followed by a desulfurization reaction will provide the benzo-(2.2)-paracyclophane. These may then be "capped" with the ruthenium capping agent, and their electrochemical properties studied. A very interesting study would concern the change in the barrier to electron transfer with respect to changes in the structures of these related compounds(Fig.24).



APPENDIX

Note- All necessary chemicals were purchased from Aldrich Chemical at reagent grade or spectral grade, unless otherwise noted.

ENDNOTES

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