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PREPARATION AND REACTIONS OF 1,5-BIS(*p*-SUBSTITUTED PHENYL) OCTAHYDRO-3,7-DISUBSTITUTED-1,5-DIAZOCINES

BY

ROY R. ODLE

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in Chemistry
South Dakota State University
1976

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PREPARATION AND REACTIONS OF 1,5-BIS(p-SUBSTITUTED PHENYL) OCTAHYDRO-3,7-DISUBSTITUTED-1,5-DIAZOCINES

This thesis is approved as a creditable and independent investigation by the candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

Head, Chemistry Department Date

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I would like to thank Dr. James J. Worman for his participation and encouragement in this work.

For my education and much moral support I would like to thank my parents.

My wife, Nancy, deserves a special thanks for much sacrifice and a lot of extra work while I was on this project.

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PURPOSE

The purpose of this research was to synthesize and study the reactions of 1,5-bis-(p-substituted phenyl)octahydro-3,7-disubstituted-1,5-diazocines. The compounds were to be used in attempts to prepare the diene(1) and also to help understand the mechanism of ring contractions to give substituted piperazines as shown in Figure 2.

INTRODUCTION

For many years, a small group of chemists have been interested in the reactions of 3,7-disubstituted-1,5-bis(para-substituted-phenyl)-octahydro-1,5-diazocines. These systems were first studied in an attempt to synthesize a model compound to approximate the expected site of activity of the calabash curarie alkaloids.[1] These kinds of alkaloids take part in photochemical reactions peculiar to nitrogen compounds of this type. To study the photochemical reactions, synthesis of a model similar to the circled portion of alkaloids, shown below (Figure 1), was attempted. This model would be 1,5-diphenyl-1,2,5,6-tetrahydro-1,5-diazocine(1).

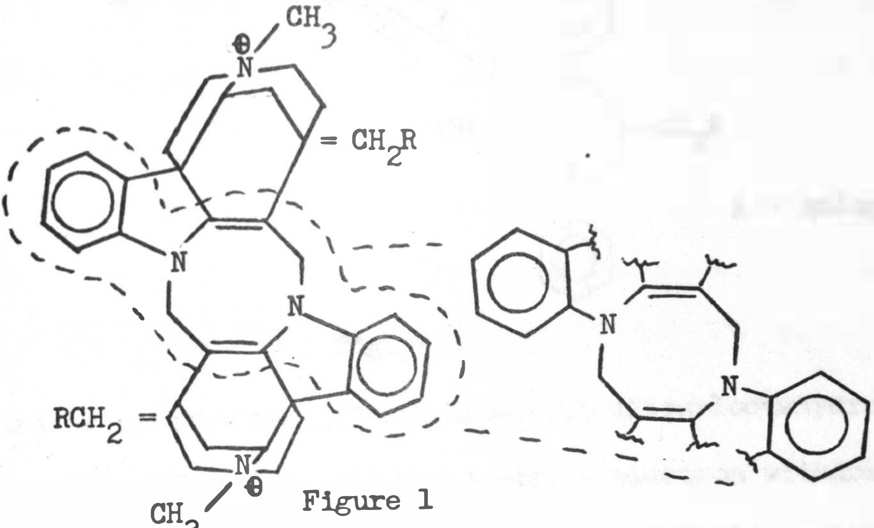


Figure 1

R=H dihydrotoxiferine
R=OH toxiferineI

To obtain the beginning eight membered skeleton, a synthesis described by Gaertner was used to give cis-3,7-dihydroxy-1,5-diphenyloctahydro-1,5-diazocine (2).[2,3] Dehydration reactions to give the diene 1 were unsuccessful and halogenation of the hydroxy groups to yield the dihalogenated species resulted in ring collapse leaving the dehydrohalogenation approach unsuitable for the synthesis of the diene 1.[1,4]

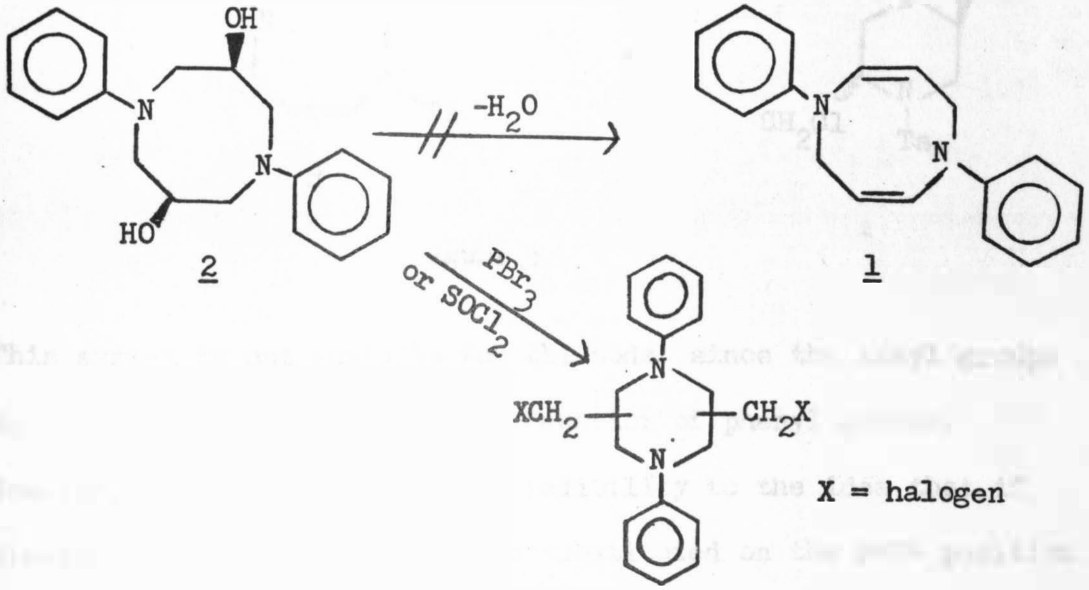


Figure 2

Paudler synthesized 3,7-dihydroxy-1,5-ditosyloctahydro-1,5-diazocine (3). This compound has a strong electron withdrawing group on the nitrogens which stabilizes the molecule toward ring collapse thus making halogenation and dehydrohalogenation to the diene 4 possible.[5]

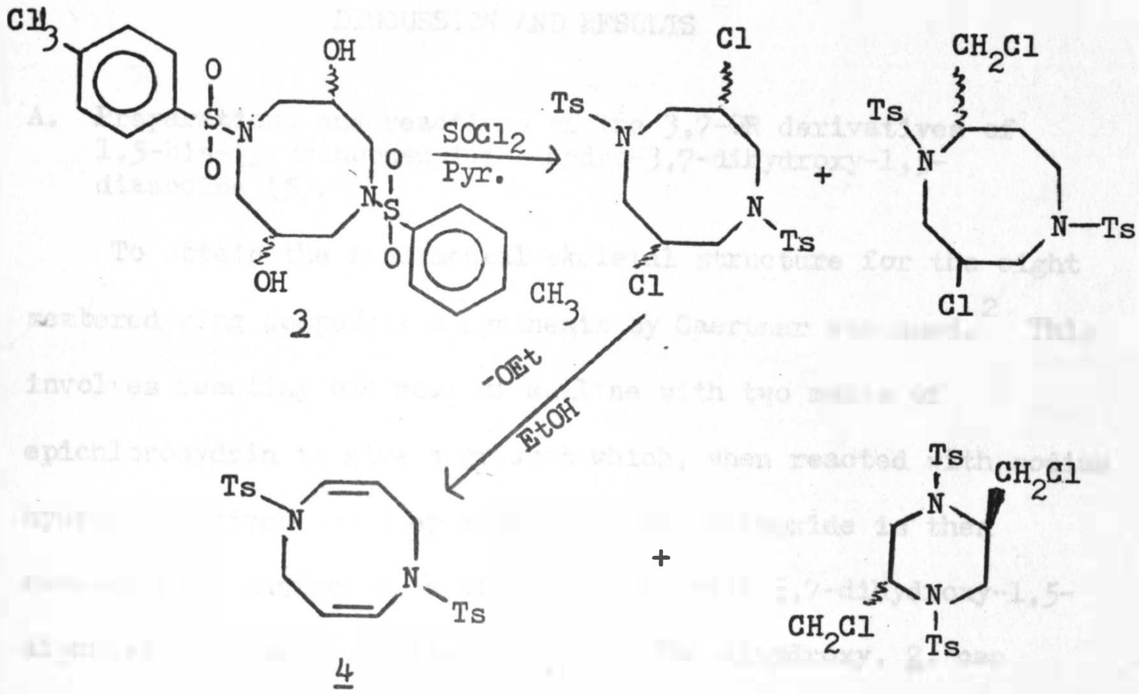


Figure 3

This system is not suitable for the model since the tosyl groups do not approximate the chemical behavior of phenyl groups. However, these results do give credibility to the idea that if electron withdrawing groups were substituted on the para position of the phenyl groups of 2, the ring might not collapse during halogenation. Nitration attempts resulted only in tars and polymers. A method of brominating the ring was discovered, which involves the reaction of DMSO with HBr. The resulting bromonium ions attack the phenyl rings exclusively at the para position. Using the product, 1,5-bis(p-bromophenyl)-3,7-dihydroxyoctahydro-1,5-diazocine (5), and other possible derivatives on the 3,7 positions one can devise many approaches to the preparation of the diene 1.

DISCUSSION AND RESULTS

A. Preparations and reactions of the 3,7-OR derivatives of 1,5-bis-(p-bromophenyl)octahydro-3,7-dihydroxy-1,5-diazocine (5).

To obtain the fundamental skeletal structure for the eight membered ring compounds a synthesis by Gaertner was used.[2] This involves reacting one mole of aniline with two moles of epichlorohydrin to give a product which, when reacted with sodium hydroxide, gives the diepoxide (9). The diepoxide is then reacted with another mole of aniline to give 3,7-dihydroxy-1,5-diphenyloctahydro-1,5-diazocine (2). The dihydroxy, 2, can easily be transformed into the 1,5-bis-(p-bromophenyl)-octahydro-3,7-dihydroxy-1,5-diazocine, 5, by reacting it with HBr in the presence of DMSO. This reaction involves HBr adding across the DMSO to give bromonium ions which substitute exclusively on the para positions of the phenyl groups.[6]

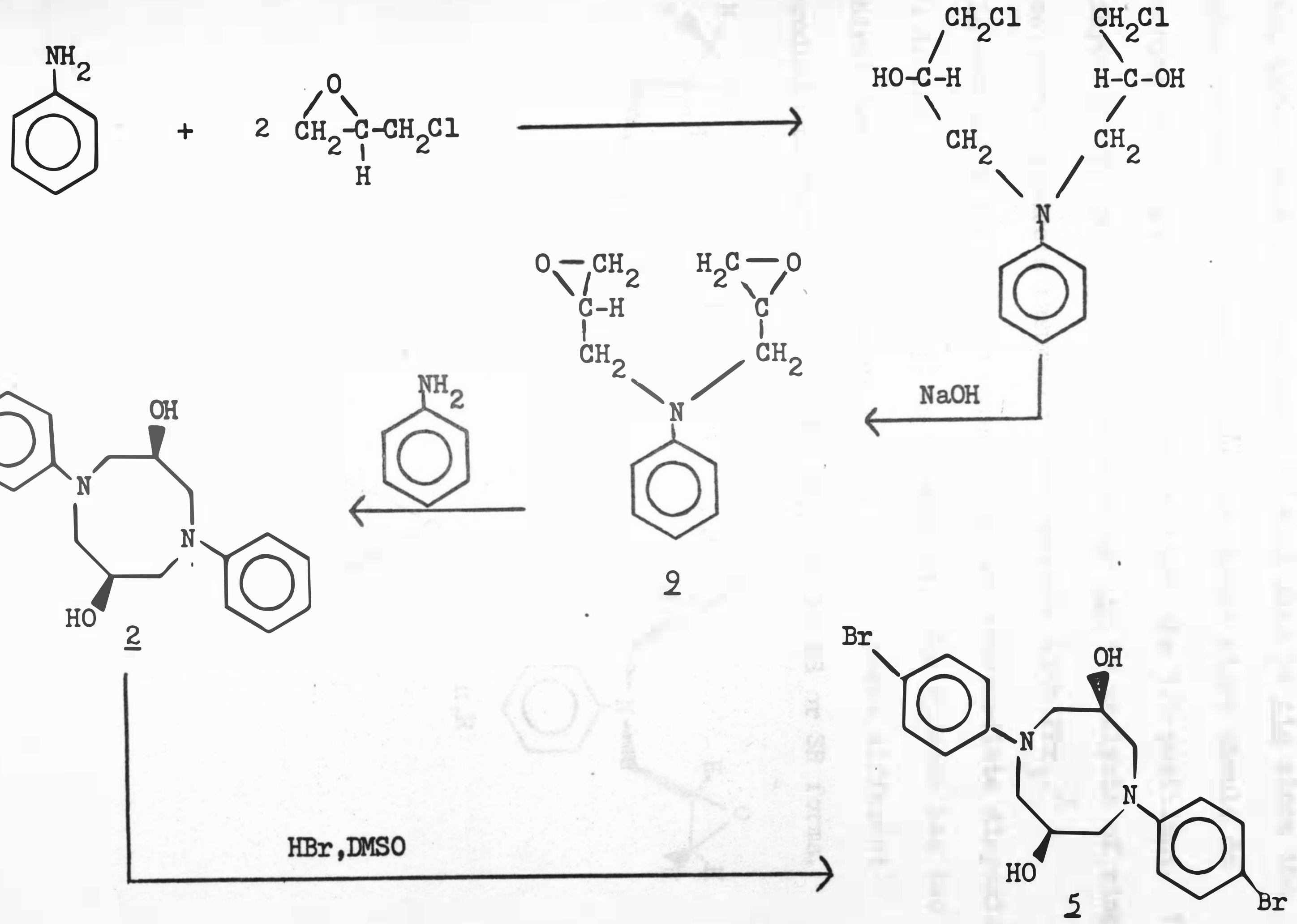
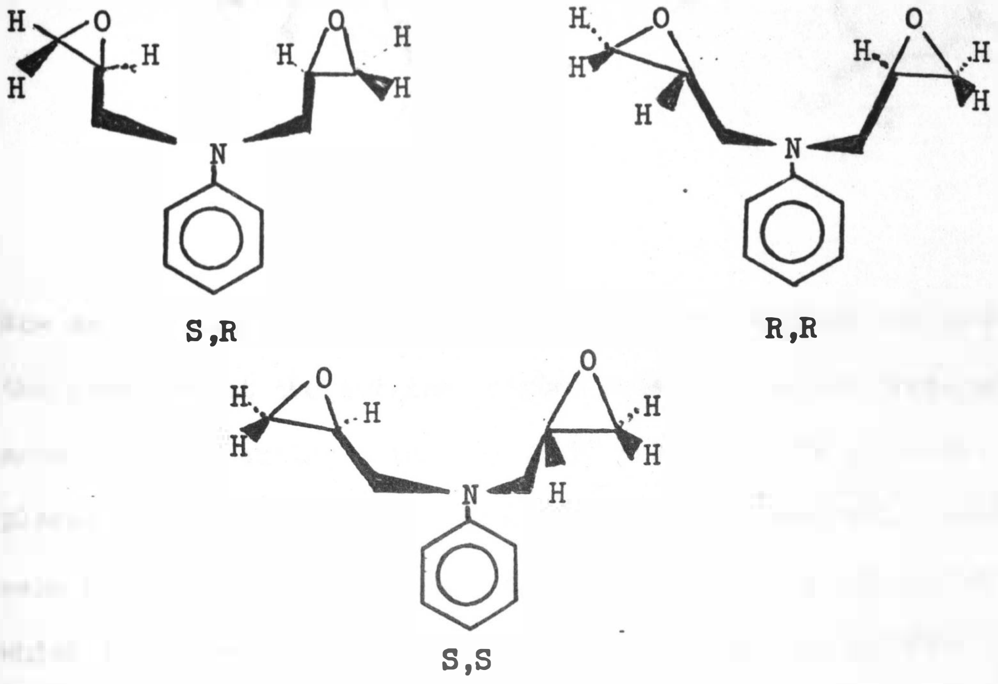


Figure 4

X-ray studies on the bis(*p*-bromophenyl)dihydroxy, 5, by Peters et al. have shown the hydroxyl groups on (5) to be *cis*.[3] This infers that the dihydroxy, 2, must also be *cis* since the substitution of the bromine onto the phenyl rings should do nothing to change the configuration about the 3,7-positions. The dihydroxy, 2, has also been shown to be *cis* by analysis of ring contracted products resulting from reaction with PBr_3.[1]
cis configuration is also expected if the intermediate diepoxide, 9, in the synthesis of (2) is considered. The epoxide has two chiral centers. This makes it possible for three different products to form. They are RR, SS, and the RS or SR forms.



S,R

R,R

S,S

Figure 5

To see how the cis product is favored in the synthesis, consider the intermediate after the aniline has added to one of the epoxide moieties.

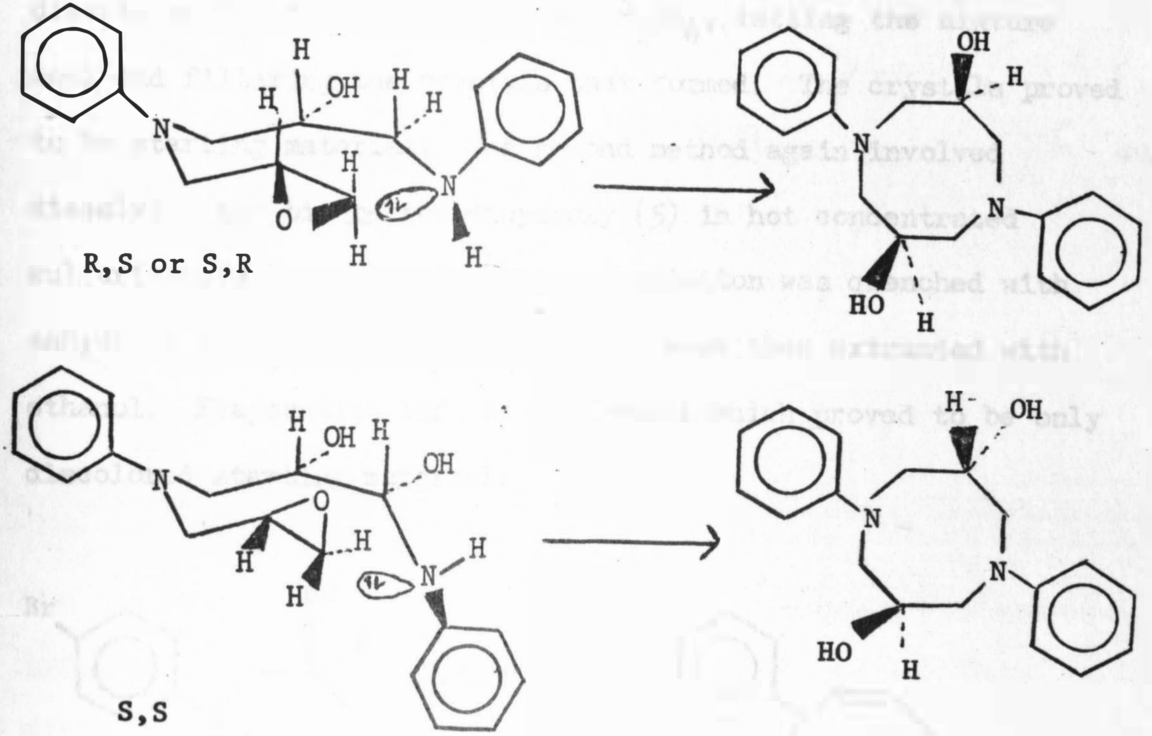
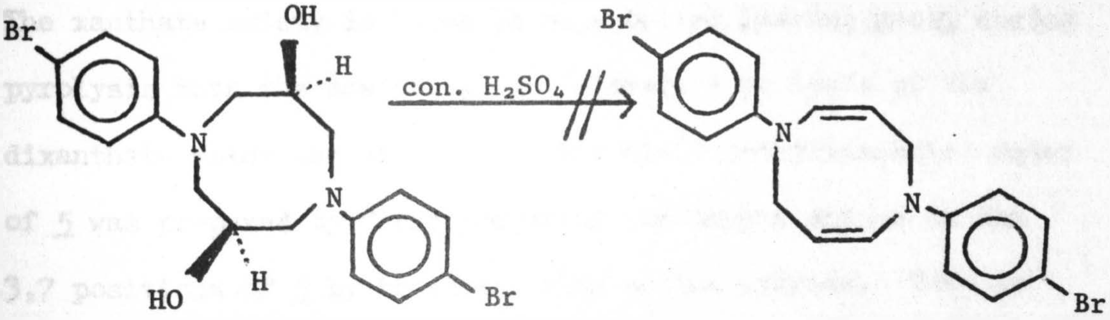


Figure 6

Now as the ring closes by attack of the non-bonding electrons on the nitrogen at the terminal carbon atom, we can see from molecular models that starting with a RR or SS molecule, the epoxide oxygen is placed in an unstable axial position. If the beginning molecule were either RS or SR then the epoxide molecule is equatorial which is preferred sterically. Since only the cis product is obtained from the conditions used, the conclusion that the steric effects in the transition state during the formation of the eight membered ring are great enough to exclude formation of the trans product can be made.

The most direct approach to a diene similar to 1 is simple dehydration. Two methods were tried. The first method involved dissolving (5) in hot concentrated H_2SO_4, letting the mixture cool and filtering the crystals that formed. The crystals proved to be starting material. The second method again involved dissolving the bis-p-bromodihydroxy (5) in hot concentrated sulfuric acid but this time the hot solution was quenched with anhydrous K_2CO_3. The resulting salts were then extracted with ethanol. Evaporation left blue crystals which proved to be only discolored starting material.



5

6

Figure 7

The diacetate ester of the bis-p-bromodihydroxy, 5, was easily prepared by treatment with acetic anhydride. Prolysis of this compound (7) was attempted in the GC/MS spectrometer but no molecular ion compatable with the expected diene, 6, was observed.

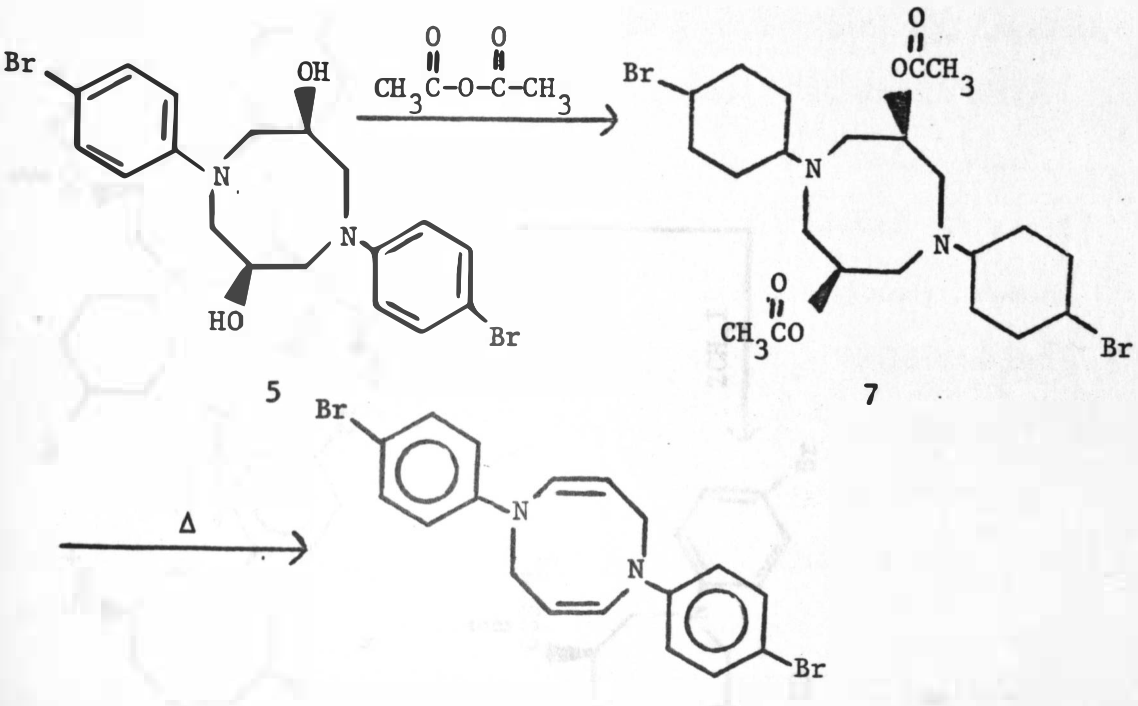


Figure 8

The xanthate moiety is known to be a better leaving group during pyrolysis than the acetate group; therefore prolysis of the dixanthate ester was attempted. The di-(S-methylxanthate) ester of 5 was prepared by first preparing the oxygen anions on the 3,7 positions of 5 by treatment with sodium hydride. This is followed by reaction with carbon disulfide and finally addition of methyl iodide. The oil resulting from work up is hard to crystallize but it can be accomplished by scratching the oil covered with a layer of hexane.

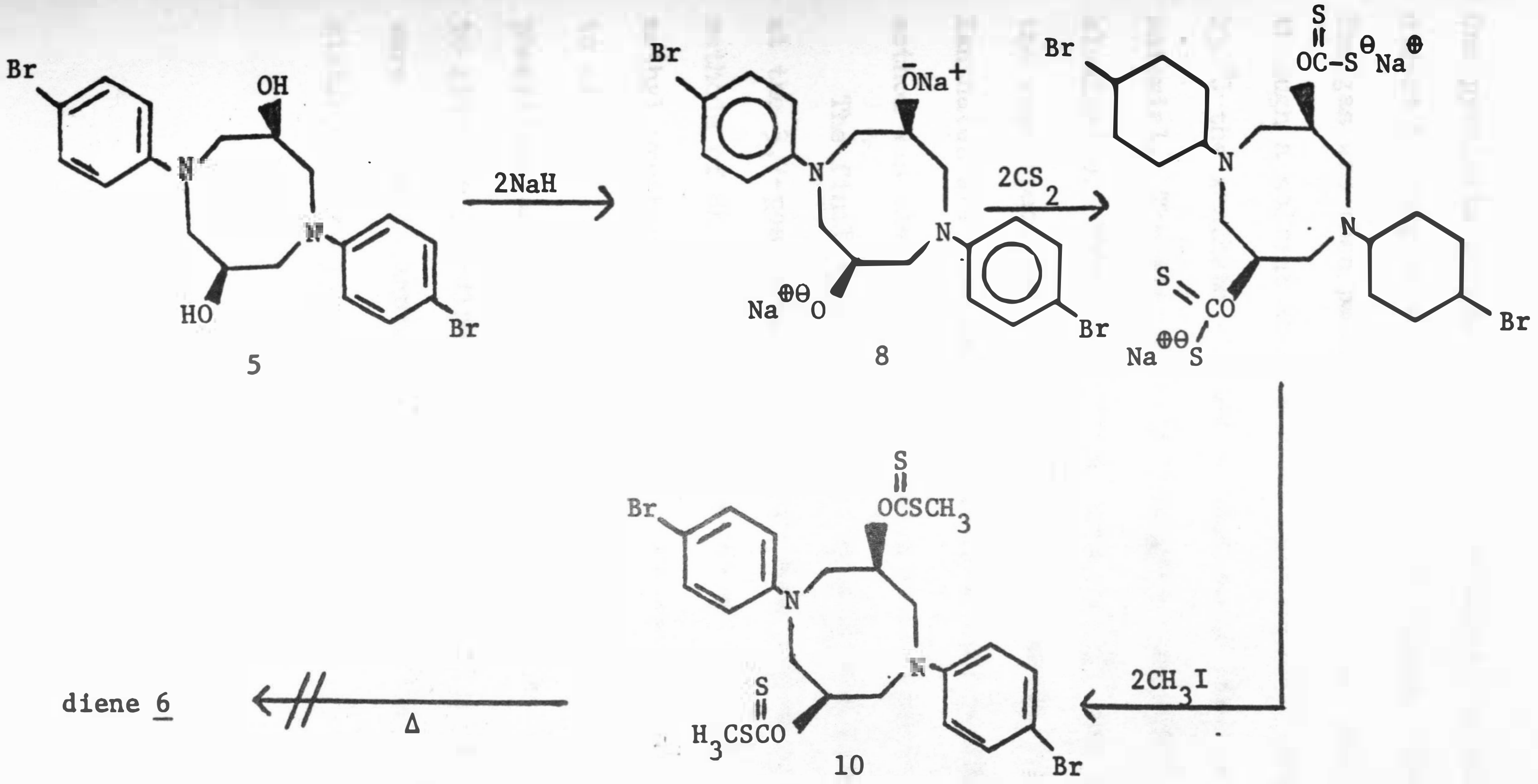


Figure 9

One pyrolysis attempt of the S-methylxanthate ester, 10, involved direct heating in a tube continually flushed with dry nitrogen. The gas was then passed through a cold trap and finally bubbled through a solvent such as chloroform or ethylacetate. At about 230°C the xanthate started to sublime to leave a glassy type of material. The structure of this glassy material could not be eludicated. Pyrolysis of the xanthate, 10, was also attempted in the mass spectrometer. There was no evidence of the diene, 6. Xanthates are also known to eliminate in hot phenyl ether.[7] This method was also tried but no reaction took place.

The final type of elimination attempted from-OR derivatives at the 3,7-positions was from urethane derivatives. Standard methods of Shriner and Fusion were used to obtain phenyl and methyl urethanes.[8] The methyl isocyanate only substituted once to give the 3-methyl urethane derivative, 11, of 5; while the phenylisocyanate substituted on both of the hydroxy groups on 5 to give the 3,7-diphenylurethane derivative, 12. These compounds were heated in hopes of elimination but they proved to be quite stable to pyrolysis.

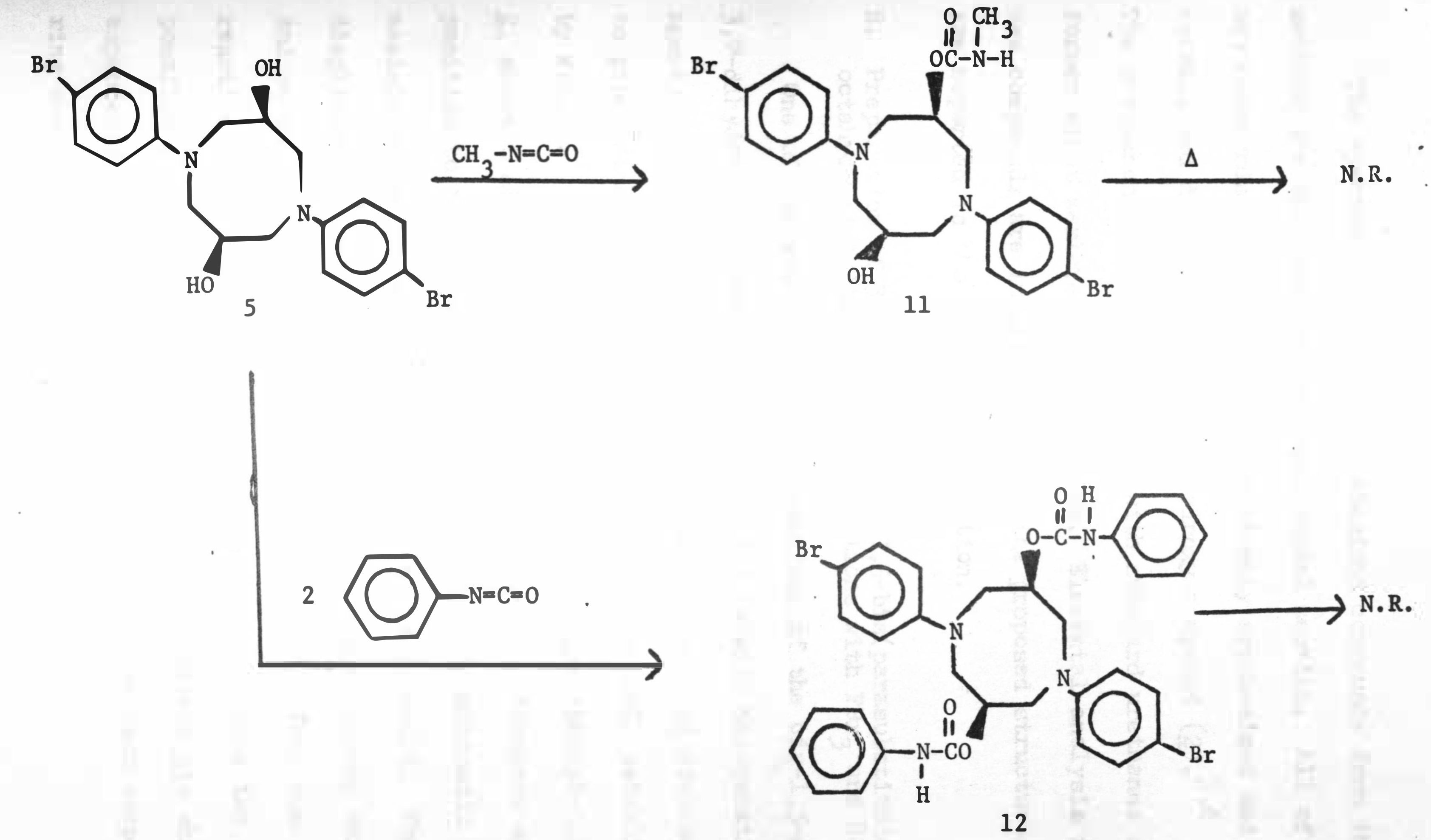

Br
OH
N
N
HO
Br
5
CH₃-N=C=O
O CH₃
OC-N-H
Br
N
N
OH
Br
11
Δ
N.R.
2
N=C=O
O H
O-C-N
Br
N
N
O
N-CO
H
Br
12
N.R.

Figure 10

The spectra of the newly synthesized compounds from this section are tabulated in the experimental section. All of the new compounds are comparable to previously synthesized and well established derivatives of the dihydroxy compound (2).[1,6] The urethanes are easily compared with standard urethanes and the former eight membered ring compounds. Elemental analysis for the new compounds are in agreement with the proposed structures and are reported in the experimental section.

B. Preparation of 3,7-disubstituted-1,5-bis(parasubstituted)-octahydro-1,5-diazocines and reactions with PBr_3 and $SOCl_2$.

One of the most interesting reactions of the cis-1,5-diphenyl-3,7-dihydroxyoctahydro-1,5-diazocine (2) is with halogenating agents, PBr_3 or $SOCl_2$. During these reactions ring contraction to piperazines occur. These contractions were well established by Worman.[1] Examination of models of the cis-diphenyl-dihydroxy, 2, shows that the non-bonding electrons on the nitrogens are in position to attack the 3,7-carbon atoms. This anchimeric assistance occurs after the ring has been halogenated. The displaced halogen then comes back to attack the primary carbon and opens the ring to a seven membered species. This same type of reaction can occur again with either nitrogen to give two possible piperazines. The products are exclusively cis which is expected for the two successive Sn2 reactions in each step of the ring contraction.[1]

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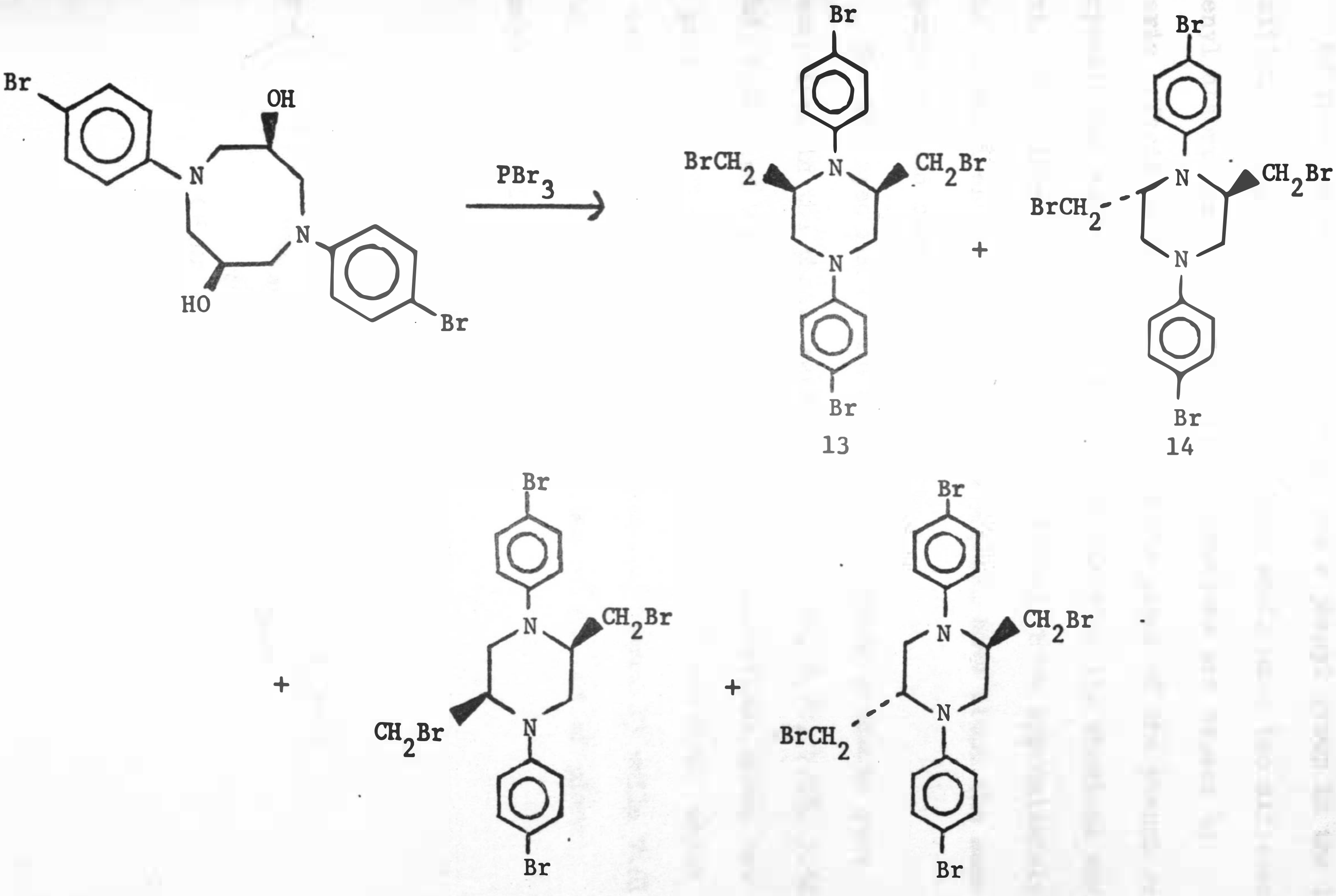
It was decided to try the same reactions on the bis-p-bromodihydroxy (5) to see if the negative inductive effect of the bromine would be sufficient to remove enough of the electron density from the nitrogen to prevent ankomeric assistance and in so doing stop ring contraction.

The ring contraction of these types of eight membered rings to the resulting piparizines can be followed, for the most part, by infrared spectroscopy. The eight membered rings have three characteristic absorptions in the 830-910 cm^{-1} region. The substituted piparazines that result from the ring collapse have one absorption at 900-950 cm^{-1}. This gives a very quick and easy method of determining that ring contraction has occurred.

The first reaction involved heating the bis-p-bromodihydroxy (5) with PBr_3 until the crystals just melted. The reaction mixture was then cooled, filtered, and the solid then recrystallized. The infrared spectra showed the absence of the OH absorption and disappearance of the three absorptions in the 830-910 cm^{-1} range and the appearance of an absorption at 950 cm^{-1} (see Appendix Spectrum No's. 3, 13). This evidence points to ring collapse and indeed the collapse is confirmed by NMR spectroscopy. The NMR spectrum shows an absence of the OH hydrogens and appearance of different methylene groups. The phenyl absorptions are changed (see Appendix Spectrum No. 14). The spectrum shows the presence of two phenyl groups with different chemical shifts. This is expected since ring collapse



13 14 15 16

Figure 12

can give four possible isomers.

Of these isomers only 13, which has a phenyl group in the 1 position and cis 2,6-bromomethyl groups, would have two different phenyl absorptions. The different absorptions are caused by steric effects of the CH_2Br's pushing the plane of the phenyl group perpendicular to the C-N-C plane, thus changing its chemical environment. The other isomers (14, 15, and 16) all have approximately the same chemical environment, hence the phenyls have about the same absorptions and chemical shift values.

The NMR spectrum of the mixture of reaction products gave absorptions in the phenyl region at 6.75, 6.90, 6.92, 7.08, 7.46, 7.48, 7.61, and 7.63 . Analysis of these absorptions shows two AB patterns. The first is at 7.63, 7.48, 7.08, and 6.92 which is caused by the unhindered phenyl group of isomer 13 while 7.61, 7.46, 6.90, and 6.75 are the absorptions of the out of plane phenyl group (Figure 13).

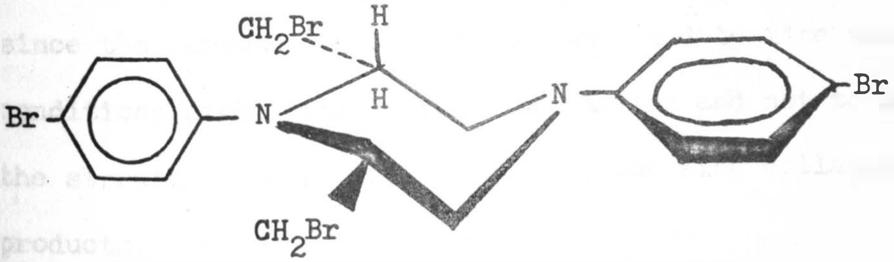


Figure 13

These absorptions are to be expected since reaction of dihydroxy, 2, with PBr_3 is known to yield mostly the cis 2,6 substituted piperazines.[1] Integration of the absorptions demands only this one isomer with the other isomers as impurities.

Using the afore mentioned infrared and NMR evidence, it is apparent that ring contraction did take place.

A second reaction was run with the bis-p-bromodihydroxy (5) and thionylchloride in an ether solution. The reaction mixture was refluxed and then quenched with water. The resulting layers were separated and the ether dried and evaporated to give crystals. The infrared spectrum of the resulting crystals again showed the disappearance of characteristic eight membered ring absorptions and the appearance of a single band at 900 cm^{-1}. The NMR spectrum also verified the ring collapse as before in the PBr_3 reaction except that now there is a very complex phenyl region indicative of more than one isomer of piperazine (See Appendix Spectrum No.'s 15, 16).

The products of the two previous reactions were not isolated since the purpose of this project was to determine what conditions might inhibit ring contraction and not to determine the structure and stereochemistry of the ring collapsed products.

Since the bromines on the p-position of the phenyl ring did not stop the ring contraction it was decided to place an even stronger electron withdrawing group on the para position of the phenyl groups.

The cis-diphenyl-dihydroxy ,2, was reacted with concentrated HNO_3 in concentrated H_2SO_4 in an attempt to nitrate the aromatic rings. The reaction mixture was hydrolyzed but no crystals were obtained; only tars which were unidentifable.

Another nitration attempt was made using an indirect nitration method. This involves first making the sulfonyl ester on the aromatic rings and then displacing them with HNO_3 to give the nitration product. This method did give green crystals but M.P. higher than 278°C and the compound was insoluble in all available solvents and could not be identified.

An alternate approach was an attempt to carboxylate the para positions of the bis-p-bromodihydroxy, (5), using the Grinard reaction. In order to use this approach the hydroxy groups in the 3,7-positions must be covered up lest they react with the Grinard reagent and give unwanted coupling reactions. The dihydroxy, 2, does react with NaH followed with CH_3I to give the diether moieties on the 3,7-positions.[4] In order to be a viable protecting group, the substituent must be subject to cleavage in order to return to the original hydroxy functional group. The methyl ether compound, 17, was subjected to cleavage with concentrated HI, HBr, and HCl but no cleavage products were obtained.

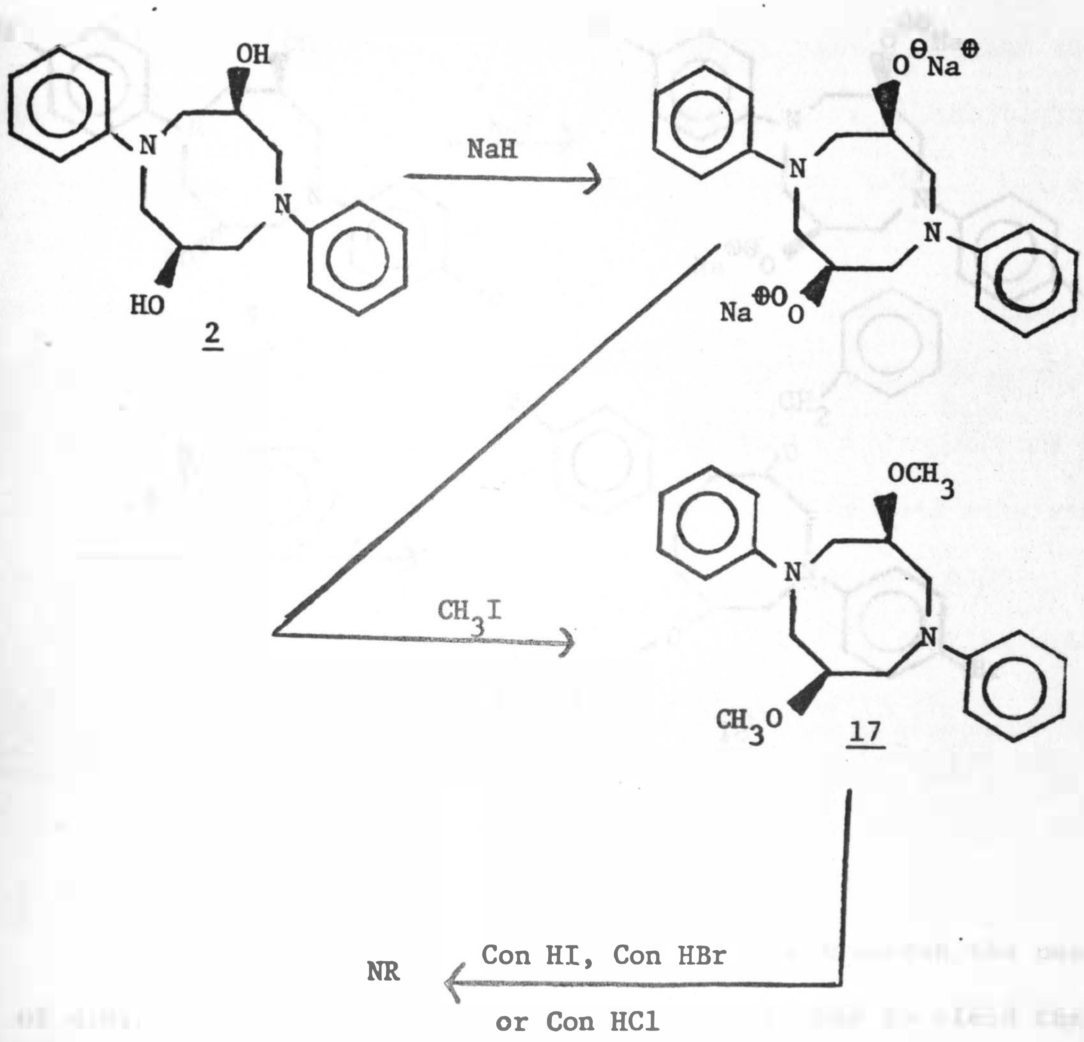


Figure 14

Ethers that can react to give stabilized carbonium ions are known to cleave with much greater ease. Hence an attempt to prepare the 2,7-bis(benzylether) derivative of the bis-p-bromodihydroxy, 5, was made. Compound, 5, was reacted with NaH followed by the addition of benzylchloride. Work up yielded only starting materials and no ether, 18.

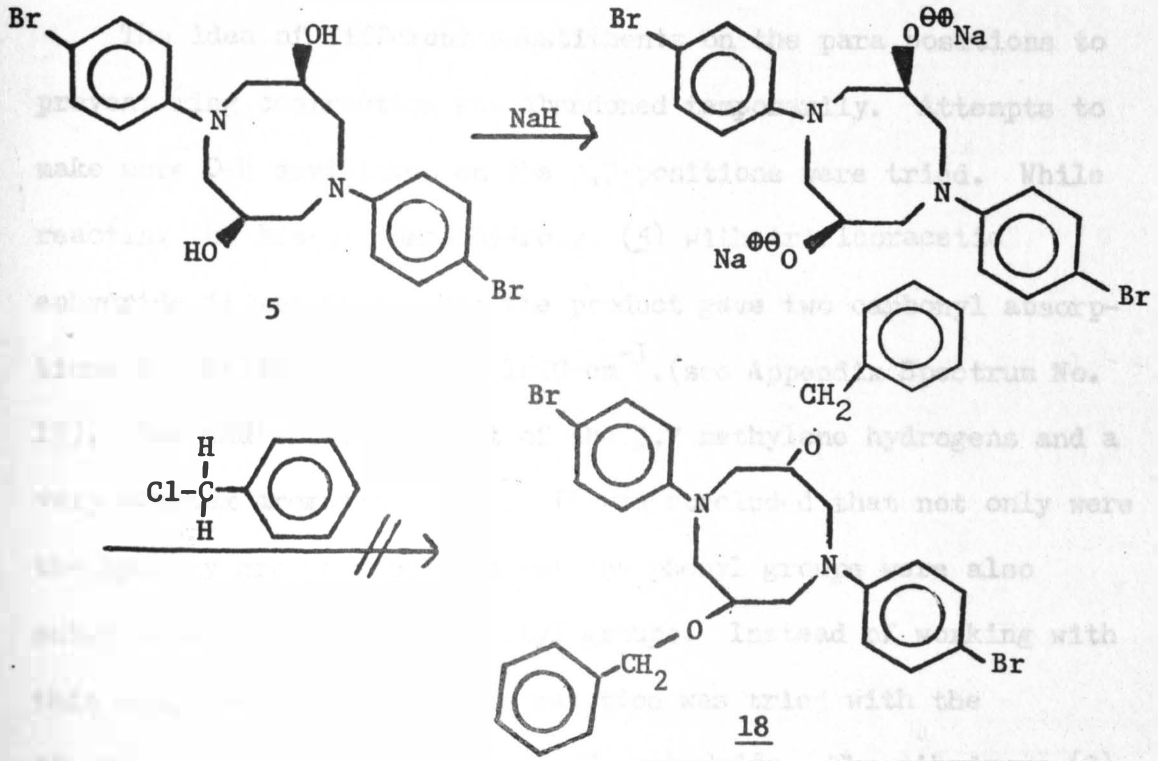


Figure 15

The last try to protect the hydroxy groups involved the use of dihydropyran. Compound, 5, was treated with DHP to yield the expected derivative, 19, but this derivative also proved stable to hydrolysis.

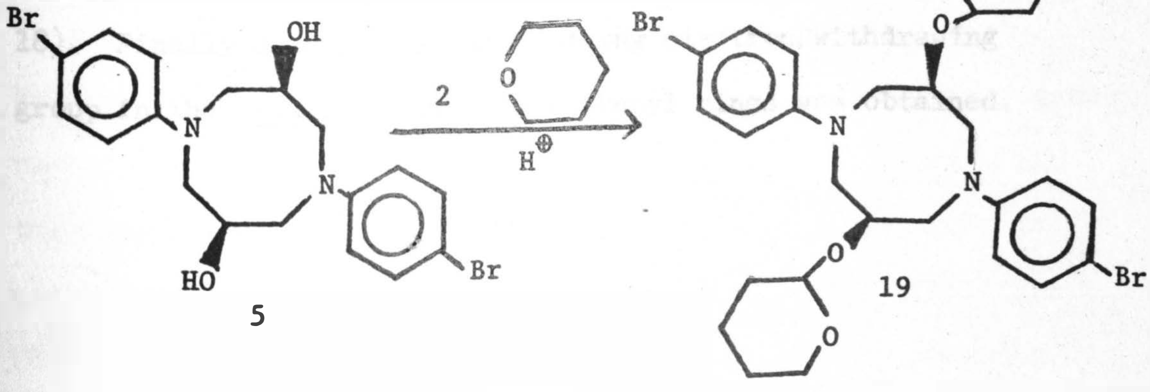


Figure 16

The idea of different substituents on the para positions to prevent ring contraction was abandoned temporarily. Attempts to make more O-R deviatives on the 3,7-positions were tried. While reacting the bis-p-bromodihydroxy, (5) with trifluoracetic anhydride it was found that the product gave two carbonyl absorptions in the IR at 1890 and 1690 cm^{-1}.(see Appendix Spectrum No. 17). The NMR showed a shift of the 3,7 methylene hydrogens and a very complex aromatic region. It was concluded that not only were the hydroxy groups accelated but the phenyl groups were also substituted with trifluoroacetyl groups. Instead of working with this compound the acetylation reaction was tried with the dihydroxy, (2), and trifluoroacetic anhydride. The dihydroxy (2) was added to trifluoroacetic anhydride, refluxed for an hour, poured into ice water, and the resulting crystals were analyzed. Recrystallization was difficult and is discussed in the experimental section. The trifluoroacetate ester derivative, 20, was very easily hydrolyzed with base to give 3,7-dihydroxy-1,5-bis(para-trifluoroacetylphenyl)octahydro-1,5-diazocine, 21, (Figure 18). Finally a compound with a strong electron withdrawing group in the para position of the phenyl rings was obtained.

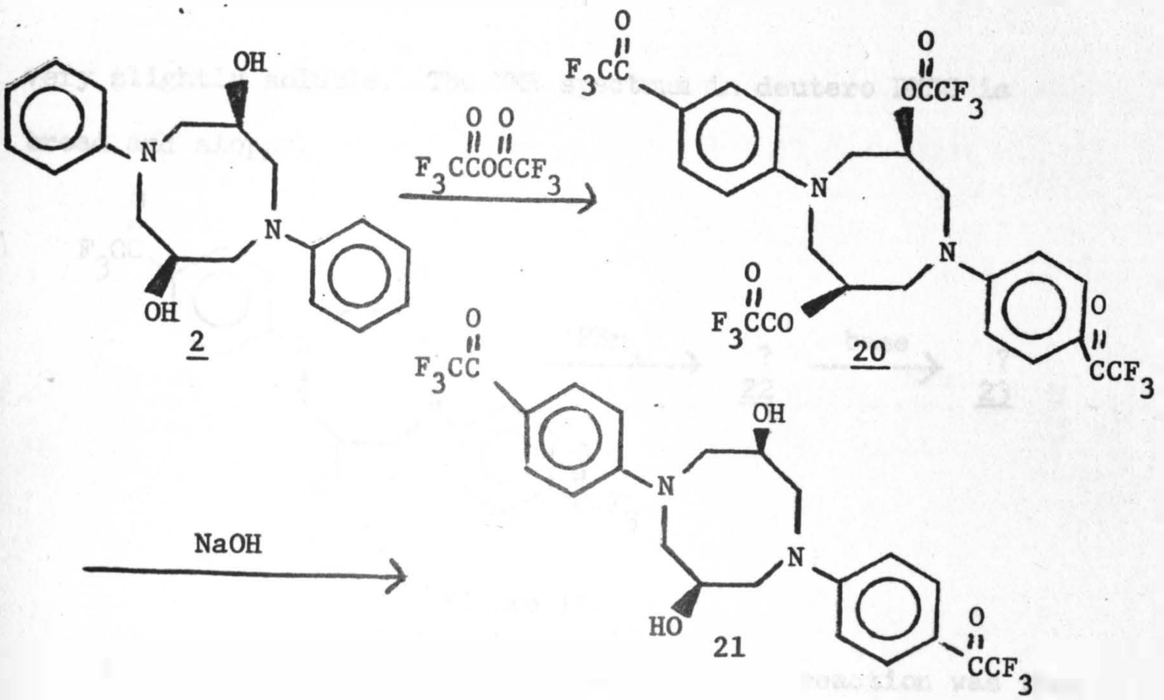
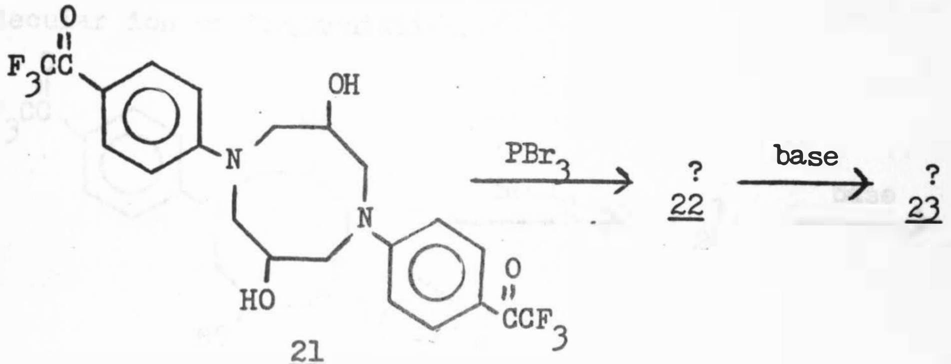


Figure 17

The IR and NMR spectra are in agreement with the expected structure of, 21, except for the infrared region where the characteristic bonds of the eight membered rings absorb. These absorptions are very weak (see Appendix Spectrum No. 18). However the NMR spectrum, elemental analysis, and mass spectrum do support the structure of 21.

The paratrifluoroacetyl-dihydroxy, 21, was reacted with PBr_3 in the same manner as the parabromo-dihydroxy, 5. Very high melting brownish crystals were obtained, 22. These crystals were washed with ethanol. The IR shows absence of OH absorption but the absence of peaks from 1100-900 cm^{-1} makes it impossible to use the previous IR behavior as criteria of ring collapse. The NMR does not prove to be much more enlightening. The compound is insoluble in all solvents tried except DMSO where it is only very slightly soluble. The NMR spectrum in deutero DMSO is broad and sloppy.



21

Figure 18

The resulting compound from the PBr_3 (22) reaction was then treated with base and a new product resulted, 23. This new product, 23, was very high melting and insoluble in every common solvent. The crystals were very hard to grind and did not mull satisfactorily for IR analysis. The physical properties made infrared and NMR analysis impossible. Compounds 22 and 23 were sent away for mass spectral analysis but they would not fragment even under the most stringent conditions.

The paratrifluoroacetyldihydroxy, (21) was then subjected to reaction with thionylchloride. The compound isolated, 24, was similar to the product of the PBr_3 reaction in that it is insoluble and high melting. The IR shows change in the OH region and in the fingerprint region also. Again the regions where we expect to find evidence of ring collapse, are weak to nill and the NMR spectrum is too broad and weak to interpret. Treatment of 24 with base leaves a very insoluble substance, 25, that will not mull to give a decent infrared spectrum or dissolve to give a NMR spectrum. The Mass Spectrometer again failed to give a molecular ion or fragmentation.

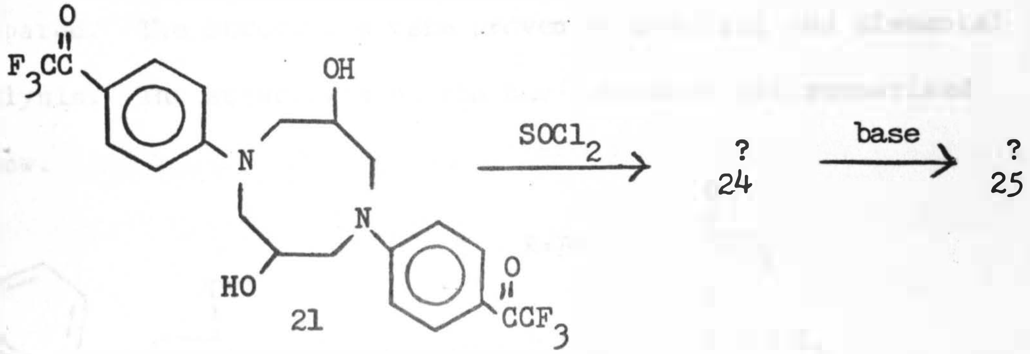
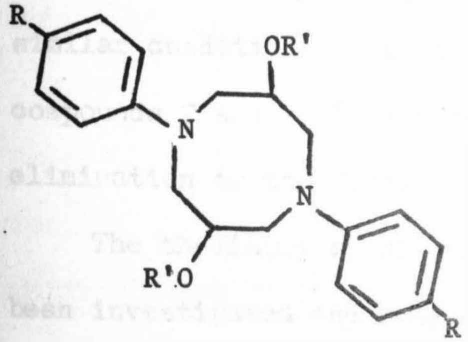


Figure 19

CONCLUSIONS

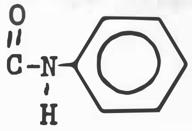
Several new substituted octahydro-1,5-diazocines were prepared. The structures were proven by spectral and elemental analysis. The structures of the new compounds are summarized below.

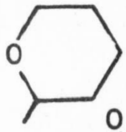


7 - R=Br, R' = $\overset{O}{\overset{\|}{C}}CH_3$

10 - R=Br, R' = $\overset{S}{\overset{\|}{C}}-S-CH_3$

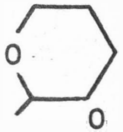
11 - R=Br, R' = H + R' = $\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH_3$

12 - R=Br, R' = 

19 - R=Br, R' = 

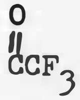
20 - R = $-\overset{O}{\overset{\|}{C}}CF_3$ R' = $-\overset{O}{\overset{\|}{C}}CF_3$

21 - R = $-\overset{O}{\overset{\|}{C}}CF_3$ R' = H

26 - R=H, R' = 

27 - R = $\overset{O}{\overset{\|}{C}}CF_3$, R' = $\overset{O}{\overset{\|}{C}}CH_3$

Compound 5 was reacted with PBr_3 and $SOCl_2$ to give ring contracted piperazines. Compound 21 reacted with PBr_3 and $SOCl_2$ to give compounds that gave no evidence as to whether ring contraction occurred or not. This means that the electron withdrawing $\overset{\overset{O}{\|}}{C}CF_3$ groups have definitely changed the reactivity of the eight membered ring.



Elimination reactions on compounds 5, 7, 10, and 12 in an attempt to prepare the unsaturated heterocyclic diene were unsuccessful. The dixanthate, 10, did decompose under pyrolysis conditions to give polymers while the acetate derivative under similar conditions gave no reactions. Attempts to pyrolyze compounds 7 and 10 in the mass spectrometer gave no evidence of elimination to the diene.

The chemistry of substituted octahydro-1,5-diazocines has been investigated and many chemical pathways to the diene have been eliminated.

EXPERIMENTAL

Preparation of 3,7-dihydroxy-1,5-diphenyloctahydro-1,5-diazocine(2).

To 100 ml of aniline in 150 ml of methanol was added 220 ml of epichlorohydrin and stirred for 12 hr in a 1 liter flask at room temperature. It was then stirred for another 15 hr at 55 deg. C. The excess epichlorohydrin was evaporated off under a vacuum at 80 deg. C until a heavy oil formed. The mixture was cooled and 100 g NaOH in 100 ml H_2O was added and then stirred for 12 hr more. Three 150 ml ether extracts were taken and dried over KOH for 1/2 hr. The mixture was filtered and evaporated *in Vacuo* until a thick heavy liquid was left. This oil was added to 100 ml aniline in 300 ml methanol. The mixture was transferred to a 1000 ml flask, a seed crystal added, and left to stand for a week. The crystals were then filtered and washed with cold methanol, mp 208-213 deg C. The infrared spectrum in nujol showed peaks at the following positions: (see Spectrum No. 1) 3300, 2970, 2870, 1610, 1580, 1515, 1480, 1460, 1380, 1365, 1350, 1279, 1262, 1220, 1180, 1105, 1099, 1060, 1040, 1020, 1000, 909, 890, 870, 820, 745, and 700 cm^{-1}. The NMR spectrum in deutero DMSO gave the following signals: (see Spectrum No. 2) 7.05 (4H), 6.5 (6H), and 3.1-4.3 (12H)δ. All data are consistent with that reported by Worman.[1]

Elemental Analysis: Calculated: 72.46% C; 7.38% H

Found: 72.41% C; 7.43% H

Yield = 20%

Preparation of 3,7-dihydroxy-1,5-bis(parabromophenyl)octahydro-1,5-diazocine (5).

To 1 g of the dihydroxy compound (2) in 50 ml of dimethyl sulfoxide was added 3.0 ml of 48% HBr. The reaction mixture was stirred at room temperature for 2 hr. The mixture was then added to 250 ml of water and 10% NaOH was added until the solution was basic. The solution was allowed to digest for 1 hr and the crystals were filtered. The product was then recrystallized from methanol, mp 176-178 deg. C. The infrared spectrum in nujol was as follows: (see Spectrum No. 3) 3300, 3950, 1599, 1580, 1505, 1490, 1470, 1390, 1361, 1339, 1270, 1220, 1201, 1160, 1150, 1100, 1070, 1060, 1040, 1030, 1000, 920, 899, 820, and 790 cm^{-1}. The NMR gave the following signals: (see Spectrum No. 4) 3.18, 3.25, 3.45, 3.64, 3.76, 4.00, 4.12, 4.19, 5.27, 6.45, 6.60, 7.11, 7.26δ. The spectra were run in deutero-DMSO and are similar to those reported by Worman.[6]

Yield = 90%

Preparation of 3,7-diacetoxy-1,5-bis(p-bromophenyl)octahydro 1,5-diazocine (7).

Three grams of the bis(p-bromophenyl)dihydroxy, (5), was mixed with 1.5 g of powdered sodium acetate and 15 ml of acetic anhydride. The mixture was refluxed overnight and then added to 100 ml of ice water. The crystals were filtered and recrystallized from methanol, mp over 235 deg. C. The infrared spectrum in nujol gave: (see Spectrum No. 5) 2900, 1740, 1720, 1590, 1500, 1460, 1380, 1340, 1300, 1280, 1260, 1240, 1200, 1175, 1070, 1040, 915, 860, 810, 780, and 710 cm^{-1}. The NMR spectrum in $DCCl_3$ gave the following signals: (see Spectrum No. 6) 7.15 (4H), 5.08 (4H), 5.0 (2H), 4.2-3.0 (8H), and 2.2 (6H)δ.

Elemental Analysis: Calculated: 48.91% C; 4.48% H

Found: 48.74% C; 4.5% H

Yield = 70%

Preparation of the di-S-methylxanthate of 3,7-dihydroxy-1,5-bis (p-bromophenyl)octahydro-1,5-diazocine, 10.

Into 25 ml of toluene was added 0.54 g bis(p-bromophenyl) dihydroxy, 5, 0.6 g NaH was added, and the mixture refluxed for 24 hr. To the mixture was added 0.2 g CS_2 and the mixture refluxed for 4 hr more. To the mixture was added excess CH_3I (10 ml) and the mixture was left at room temperature. The excess NaH was hydrolyzed carefully with cold water, the layers were separated, the organic layer was dried over $CaCl_2$, and the solvent was evaporated in vacuo. A mixture of brown and yellow oils resulted. The oils were washed with petroleum ether and brownish crystals remained. The melting point was 206 deg. C as decomposition took place. The infrared spectrum showed the following absorptions in nujol: (see Spectrum No. 7) 2900, 1590, 1500, 1460, 1380, 1330, 1265, 1200, 1075, 1060, 965, 950, 910, 870, 803, and 720 cm^{-1}. The NMR spectrum gave the following signals in deutero-DMSO: (see Spectrum No. 8) 7.15 (4H), 6.7 (4H), 5.8 (2H), 4.03-3.6 (8H), 2.6 (6H)δ.

Yield = 9%

Preparation of the mono-methylurethane of 1,5-bis(p-bromophenyl) octahydro-3,7-dihydroxy-1,5-diazocine, 11.

To 0.5 g of bis(p-bromo)dihydroxy, 5, was added 2 ml of methylisocyanate and 1 drop of pyridine. The mixture was heated gently for 3 hr. The resulting crystals were then recrystallized from $CHCl_3$. Melting point was 204-206°C. The nujol mull gives absorptions at: (see Spectrum No. 9) 3430, 3350, 2950, 2860, 1720, 1600, 1500, 1460, 1380, 1340, 1310, 1260, 1220, 1140, 1070, 1020, 950, 920, 880, 810, and 780 cm^{-1}. The NMR gave absorptions in deutero-DMSO: (see Spectrum No. 10) 2.48, 2.55, 2.65, 3.25, 3.48, 3.70, 3.92, 4.60, 5.16, 6.51, 6.68, 6.80, 7.12, and 7.27δ.

Elemental Analysis:		
	Calculated:	46.8% C; 4.52% H
	Found:	46.7% C; 4.39% H

Yield = 60%

Preparation of the phenyl urethan derivative of 3,7-dihydroxy-1,5-bis(p-bromophenyl)octahydro-1,5-diazocine, 12.

To 1.0 g of the bis (p-bromophenyl)dihydroxy, 5, was added 10 ml of phenyl isocyanate. The reaction was catalyzed with one drop of anhydrous pyridine and warmed for 1 1/2 hr. The mixture was filtered and recrystallized first from CCl_4 and then from methanol. The crystals were then subjected to sublimination conditions of 250 deg. C and 0.5 Torr. Diphenyl urea sublimed off leaving the desired derivative whose mp was greater then 250 deg. C. The infrared spectrum showed absorptions at: (see Spectrum No. 11) 3400, 2900, 1740, 1600, 1520, 1500, 1465, 1445, 1385, 1330, 1320, 1270, 1220, 1075, 1050, 1035, 1000, 920, 803, 760, 740, and 700 cm^{-1}. The NMR spectrum gave the following signals in deutero DMSO: (see Spectrum No. 12) 9.9 (2H), 7.3-6.5 (18H), 4.6-4.9 (2H), and 4.2-3.5 (8H)δ.

Yield = 76%

Reaction of 3,7-dihydroxy-1,5-bis(p-bromophenyl)octahydro-1,5-diazocine, 5, with PBr$_3$.

To 2 g of the bis(p-bromophenyl)-dihydroxy, 5, was added 10 ml of PBr$_3$. The heat was raised slowly until the crystals of 5 just melted and were floating around as a liquid on top of the PBr$_3$. The reaction was then allowed to come to room temperature and then cooled in an ice bath. The mixture was then carefully hydrolyzed with cold H_2). The resulting crystals were suction filtered and recrystallized from either ethanol or chloroform, melting point 139-142°C. The nujol mull infrared spectrum yielded absorptions at: (see Spectrum No. 13) 2950, 2860, 1590, 1500, 1460, 1380, 1345, 1290, 1265, 1215, 1165, 1100, 1080, 1075, 1045, 1000, 950, 860, 830, 820, 760, 690, and 670 cm^{-1}. The NMR spectrum in $DCCl_3$ yielded absorptions at: (see Spectrum No. 14) 133, 2.98, 3.12, 3.19, 3.34, 3.38, 3.54, 3.70, 3.90, 4.12, 6.76, 6.90, 7.03, 7.08, 7.46, 7.61, and 7.63δ.

Yield = 10%

Reaction of 3,7-dihydroxy-1,5-bis(p-bromophenyl)octahydro-1,5-diazocine, 5, with $SOCl_2$.

To 0.1 g of, 5, in 60 ml of ether was added 2 ml of thionyl chloride. The reaction was refluxed for one day. The mixture was washed 3 times with 20 ml portions of water, 2 times with 20 ml portions of 6N NH_4OH, and again 3 times with 20 ml portions of water. The ether layer was then dried over anhydrous $MgSO_4$, filtered and evaporated in Vacuo to yield a brown-gray oil. The infrared spectrum of this product (neat) gave absorptions at: (see Spectrum No. 15) 2930, 2860, 1670, 1600, 1500, 1465, 1400, 1370, 1340, 1300, 1270, 1250, 1210, 1180, 1100, 1080, 1020, 980, 960, 910, 810, and 740 cm^{-1}. A suitable solvent to recrystallize this brown oil was not found. NMR analysis in $DCCl_3$ yielded absorptions at: (see Spectrum No. 16) 2.95, 3.09, 3.17, 3.40, 3.55, 3.65, 3.78, 3.98, 4.15, 4.36, 6.41, 6.45, 6.52, 6.56, 6.67, 6.85, 6.98, 7.00, 7.22, 7.36, 7.40, and 7.57δ.

Yield = 5%

Another chlorination involved adding 0.2 g of, 5, to 2 ml of pyridine and 5 ml of thionyl chloride. The mixture was warmed for 3 hr, filtered, and the resulting crystals washed with H_2O, ethanol, and then methanol. The resulting crystals were high melting and gave the following infrared spectrum in nujol: (see Spectrum No. 20) 2930, 2860, 1590, 1500, 1470, 1390, 1330, 1270, 1210, 1080, 1050, 1020, 930, 890, 810, 780, and 730 cm^{-1}. The NMR spectrum in deutro DMSO yielded the following broad absorptions: (see Spectrum No. 21) 3.80, 4.70, 6.75, 7.25, and 7.35δ.

Yield = 5%

Indirect nitration attempt on cis-3,7-dihydroxy-1,5-diphenyl-octahydro-1,5-diazocine, 2.

To 1.76 g of dihydroxy, 2, was added 5 ml of concentrated

H_2SO_4 and the mixture heated with swirling on a steam bath for 5 minutes. The solution was then cooled in an ice bath and 12 ml of H_2O was added. The mixture was again cooled in the ice bath to 15°C.

To 3 ml of concentrated HNO_3 was added 3 ml of H_2O. The acid was then added dropwise with stirring to the reaction mixture keeping the temperature at 15°C. The mixture was then warmed to 50°C for 1 minute more on the steam bath. To the brown gray reaction is added 60 ml of H_2O. The mixture is cooled, stirred, and then suction filtered. The blackish gray residue is recrystallized from hot ethanol which washes the brown color away and leaves green crystals, <u>28</u>, with a melting point greater than 280°C. Infrared spectrum in nujol (see Spectrum No. 22) gave absorptions at: 3360, 2920, 2840, 1600, 1520, 1500, 1460, 1400, 1375, 1335, 1200, 1140, 1060, 1003, 980, 830, 818, 770, 740, and 715 cm^{-1}.

The green crystals were then treated with NH_4OH and then filtered and air dried. This left brown crystals, <u>29</u>, with melting point greater than 280°C. Infrared nujol (see Spectrum No. 23) gave absorptions at: 3250, 2920, 2850, 1600, 1500, 1460, 1390, 1340, 1200, 1105, 955, 825, 805, 740, and 720 cm^{-1}.

NMR analysis was not done since a suitable solvent could not be found to dissolve either the green or brown compound.

In an attempt to make the product more soluble the indirect nitration product was reacted with acetic anhydrode. To 0.41 g of the green crystals isolated from the indirect nitration of the dihydroxy, 2, was added 10 mls of acetic anhydride. The mixture was warmed for about 5 minutes to aid dissolution. The mixture was allowed to cool and then quenched in approximately 70 ml of ice water. The brown crude product was then suction filtered, $NaHCO_3$ washed, and then air dried. The product was then heated in 20 ml of ethanol, but it did not dissolve, consequently it was again suction filtered to dryness, 30.

Yield = 0.53%

The melting point was very broad 230-280°C but no solvent could be found to recrystallize the product. The infrared spectrum, nujol mull, gave the following absorptions: (see Spectrum No. 24) 3360, 2930, 2870, 1740, 1610, 1510, 1470, 1380, 1350, 1240, 1150, 1140, 1090, 1040, 1080, 835, 825, 750, and 725 cm^{-1}. No suitable solvent was found to do a NMR analysis.

Preparation of 1,5-diphenyl-3,7-bis(2-oxacyclohexyloxy)octahydro-1,5-diazocine, 26.

To 0.4 g of diphenyldiphdroxy, 2, was added 10 mls of dihydropyran and 4 drops of concentrated HCl. The reaction mixture was warmed until the crystals were all in solution. The reaction mixture was allowed to cool and 10 ml of 10% naOH was added and the mixture stirred. The resulting crystals were filtered and then heated in ether and suction filtered again. The melting point was 176-177°C. The infrared spectrum from a nujol mull gave absorptions at: (see Spectrum No. 25) 2940, 2860, 1600, 1570, 1510, 1460, 1380, 1358, 1330, 1280, 1230, 1218, 1160, 1135, 1085, 1060, 1045, 1030, 1010, 980, 940, 910, 860, 820, 745, and 700 cm^{-1}.

Elemental Analysis: Calculated: 72.31% C; 7.85% H

Found: 71.12% C; 8.05% H

Yield = 60%

No NMR spectrum was obtained since the instrument broke down. The pyranyl ether was heated in boiling 6N HCl but no cleavage of the ether resulted.

Preparation of 1,5-bis(p-bromophenyl)-3,7-bis(2-oxacyclohexyloxy)-oxctahydro-1,5-diazocine, 19.

To 0.2 g of the bis (p-bromophenyl)dihydroxy, 5, was added 10 ml of dihydropyran and 2 drops of HCl. After all of the crystals had dissolved, 10 ml of 10% NaOH was added and the reaction stirred. Twenty ml of ether was then added and layers separated. The ether was evaporated in Vacuo to yield a yellow oil. To this oil was added 5 ml of ether and crystals formed. The crystals were isolated by suction filtration. Their melting point is 168-170°C. The infrared spectrum in nujol is as follows: (see Spectrum No. 26) 2940, 2860, 1600, 1500, 1480, 1380, 1340, 1280, 1220, 1200, 1165, 1140, 1120, 1080, 1060, 1035, 1000, 980, 910, 870, and 810 cm^{-1}. No NMR was taken since the instrument was broke down.

Yield = 60%

The ether was reacted with boiling 6N HCl in an attempt to cleave the ether but no reaction occurred.

Reaction of 1,5-bis(p-bromophenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 5, with trifluoroacetic anhydride.

To 0.5 g of 5 was added 15 ml of trifluoroacetic anhydride and the mixture was refluxed for 2 hr. The mixture was then poured into 300 ml of ice water. The resulting blue crystals, 31, were suction filtered. The melting point was 129-132°C. A suitable solvent for recrystallization was not found. The infrared spectrum of the nujol mull (see Spectrum No. 17) yielded the following absorptions: 3300, 2930, 3850, 1770, 1670, 1580, 1540, 1490, 1450, 1365, 1150, 1050, 1000, 980, 950, 900, 860, 800, 760, 740, 720, and 710 cm^{-1}. The NMR spectrum in deutero DMSO was weak and broad and could not be used to confirm the structure.

Preparation of 3,7-bis(trifluoroacetoxy-1,5-bis(p-trifluoroacetyl) octahydro-1,5-diazocine, 20.

To 0.5 g of dihydroxy, 2, was added 15 ml of trifluoroacetic anhydride and the mixture refluxed for 2 hr. The mixture was then poured into 350 ml of ice water and the resulting green crystals suction filtered. The crystals were then recrystallized from an ethanol water mixture to give yellow crystals with a melting point 180-183°C. The infrared spectrum run as a nujol mull, gave the following absorptions: (see Spectrum No. 18) 3400, 2940, 2850, 1780, 1680, 1590, 1540, 1520, 1500, 1460, 1390, 1370, 1280, 1220, 1160, 1060, 1040, 1000, 960, 940, 910, 840, 830, 765, 745, 730, and 690 cm^{-1}.

Yield = 40%

The NMR spectrum in duetero DMSO gave the following absorptions (see Spectrum No. 19) 3.25, 3.60, 3.80, 4.08, 6.55, 6.72, 7.61, and 7.78 δ.

Elemental Analysis: Calculated: 45.75% C; 2.65% H

Found: 47.09% C; 2.94% H

Preparation of 1,5-bis(p-trifluoroacetyl-3,7-dihydroxyoctahydro-1,5-diazocine, 21.

To 0.3 g of compound, 20, was added 40 ml of 10% NaOH. The mixture was heated on the hotplate just to boiling and was then filtered while hot. The filtrate was then titrated with concentrated HCl until green crystals formed (the solution was neutral). The mixture was cooled and filtered. No solvent was found for recrystallization. The melting point of the air dried crystals was greater than 270°C. The infrared spectrum of the nujol mull gave the following absorptions: (see Spectrum No. 31) 3300, 3950, 3870, 1680, 1600, 1580, 1520, 1500, 1460, 1380, 1320, 1260, 1190, 1120, 1060, 990, 940, 900, 880, 830, 770, 740, and 690 cm^{-1}.

Yield = 80%

The NMR spectrum in deutero DMSO gave (see Spectrum No. 32): 3.15, 3.37, 3.61, 3.81, 4.06, 4.68, 6.63, 6.79, 7.68, and 7.81δ.

Elemental Analysis: Calculated 50.53% C; 3.36% H

Found: 49.28% C; 3.45% H

Preparation of 3,7-diacetoxy-1,5-bis(p-trifluoroacetylphenyl) octahydro-1,5-diazocine, 27.

To 0.3 g of the 3,7-dihydroxy-1,5-bis(p-trifluoroacetylphenyloctahydro-1,5-diazocine was added 10 ml of acetic anhydride and refluxed for 1 hr. The mixture was then hydrolyzed with 50 ml ice water. Then a layer of ethyl acetate was added and solid NaCl, to make crystals form at the solvent interface. They ethyl acetate was decanted and the crystals were filtered, washed with H_2O, and air dried. The melting point was 286-290°C. The infrared spectrum in nujol mull yield absorptions at: (see Spectrum No. 27) 2940, 2870, 1960, 1940, 1700, 1605, 1560, 1525, 1470, 1460, 1425, 1400, 1360, 1340, 1280, 1240, 1200, 1260, 1080, 1060, 1010, 1090, 950, 920, 860, 840, 790, 780, 740, and 720 cm^{-1}.

The NMR spectrum gave the following signals in trifluoroacetic acid (see Spectrum No. 28) 1.86, 2.73, 2.95, 3.20, 3.38, 3.85, 4.20, 5.05, 6.58, 6.62, 7.50, and 7.68δ.

Elemental Analysis: Calculated: 54.36% C; 4.18% H

Found: 54.31% C; 4.30% H

Yield = 80%

Reaction of 1,5-bis(p-trifluoroacetylphenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 21, with PBr_3.

To 0.2 g of the bis(triflurotacetylphenyl dihydroxy, was added 10 ml of PBr_3 and the mixture heated until the PBr_3 began to change color. The mixture was cooled and the crystals collected on sintered glass funnel and washed with CCl_4 and H_2O. The melting point was greater than 280°C. The infrared spectrum gave the following absorptions: (see Spectrum No. 29) 3250, 3960, 2860, 1690, 1610, 1520, 1490, 1470, 1390, 1270, 1190, 1110, 950, 840, 760, 720, and 690 cm^{-1}.

The compound was too insoluble to do a NMR analysis.

Reaction of 1,5-bis(p-trifluoroacetylphenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 21, with $SOCl_2$.

To 0.2 g of the bis(trifluoroacetyl dihydroxy was added 10 ml of $SOCl_2$ and 2 drops of pyridine. The mixture was cooled and the crystals collected on a sintered glass funnel and washed with CCl_4 and H_2O. The melting point was greater than 280°C. The infrared spectrum in nujol gave absorptions at: (see Spectrum No. 30) 2820, 2870, 1670, 1600, 1550, 1510, 1490, 1460, 1370, 1290, 1250, 1190, 1110, 1050, 1010, 950, 830, 800, 770, 720, and 690 cm^{-1}.

The compound was too insoluble to do a NMR analysis.

APPENDIX

The NMR spectra in this thesis were run on a Varian A-60A 60MHz NMR Specttophotometer. TMS was used as an external standard and all absorptions are reported in delta units.

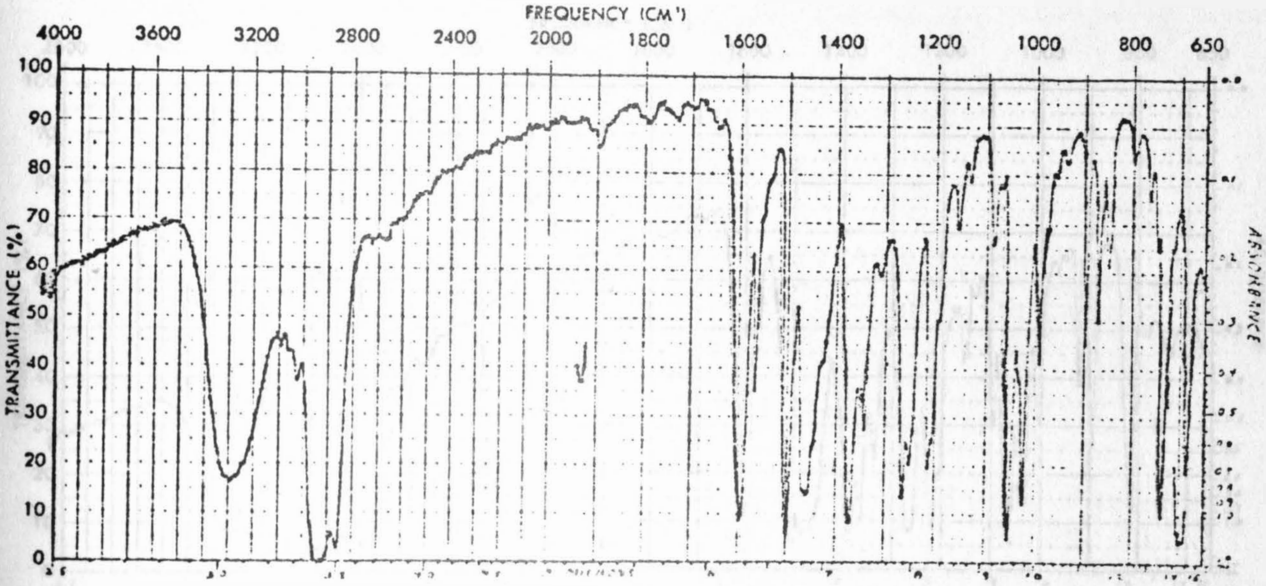
The infrared spectra were run as nujol mulls on NaCl plates. The instrument used was a Perkin-Elmer model 700 infrared spectrophotometer.

The Mass Spectrometer work was sent to the University of Wyoming and was done by Dr. D. Nelson.

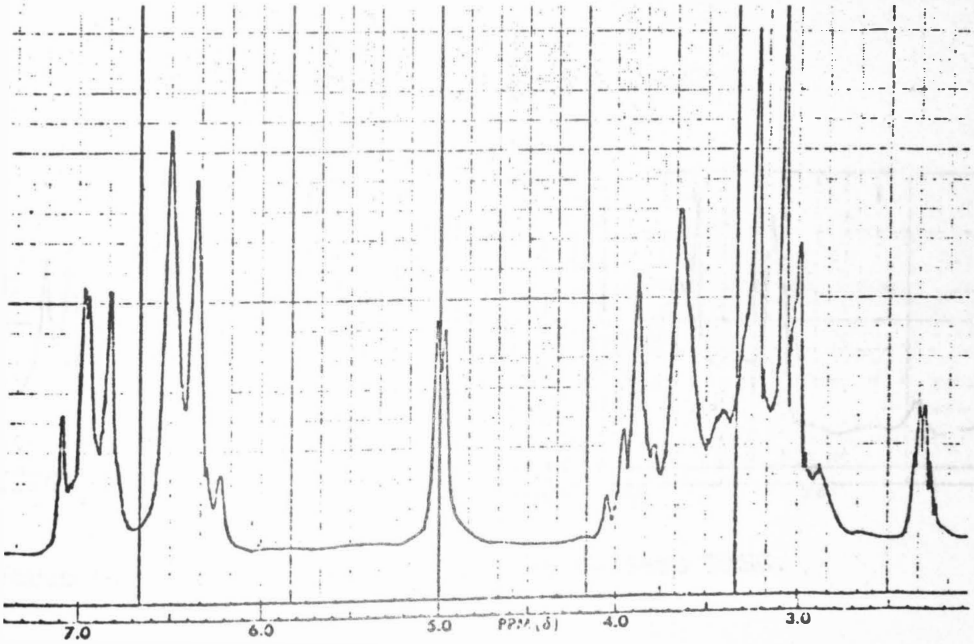
The compounds were sent to Galbraith Laboratories, Inc., Knoxville, Tennessee for elemental analysis.

Melting points are uncorrected and were run on a Fisher-Johns melting point apparatus.

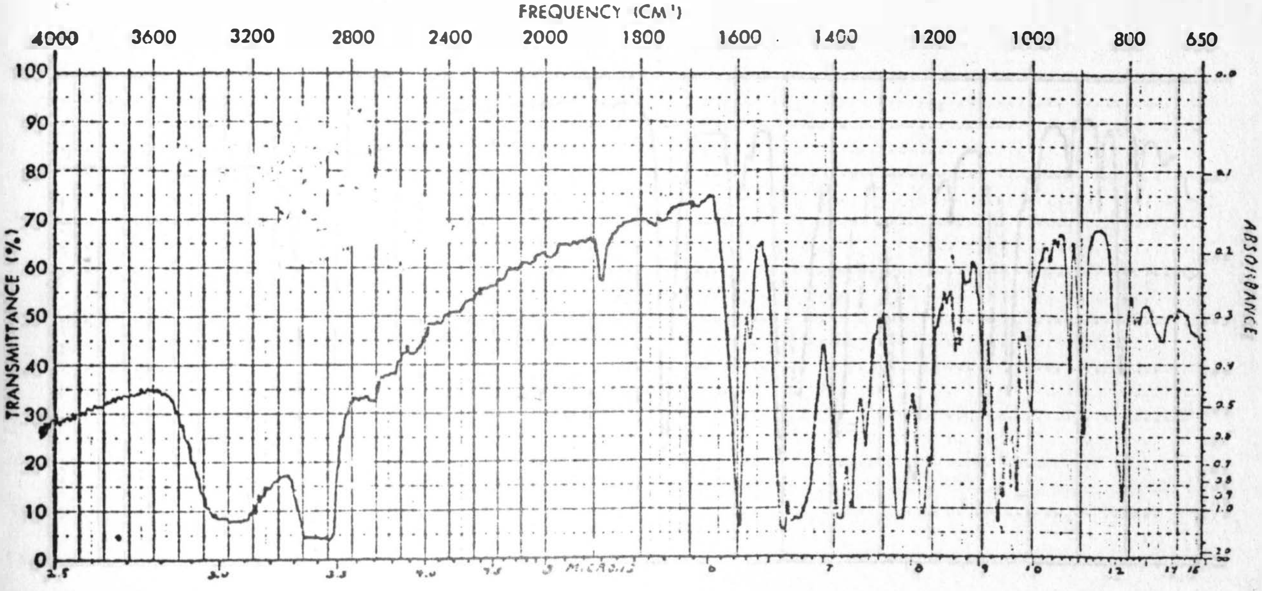
When it is stated that a compound is insoluble in solvents tried, the following are the solvent systems which were tried: methanol, ethanol, acetone, benzene, ethyl acetate, ether, THF, toluene, chloroform, carbon tetrachloride, water, concentrated H_2SO_4, concentrated NH_4OH, trifluoroacetic acid, hexane, methylcellusolve, DMSO, toluene, pyridine, and methylen chloride.



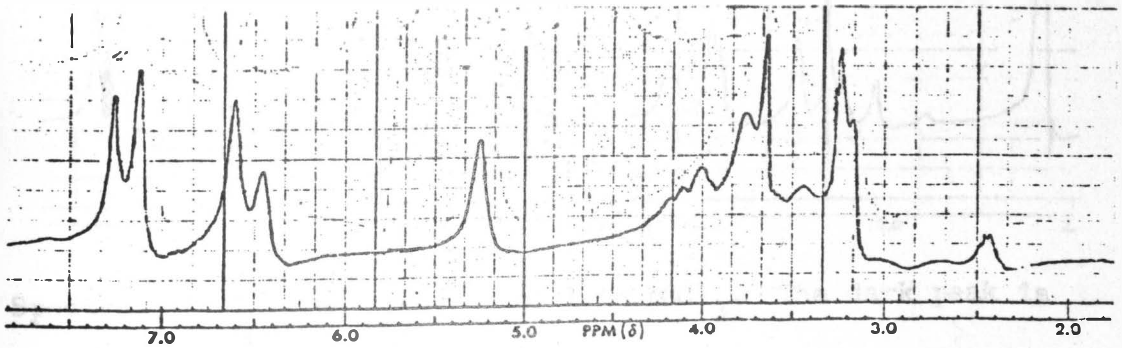
Spectrum 1: The infrared spectrum of 3,7-dihydroxy-1,5-diphenyloctahydro-1,5-diazocine, 2.



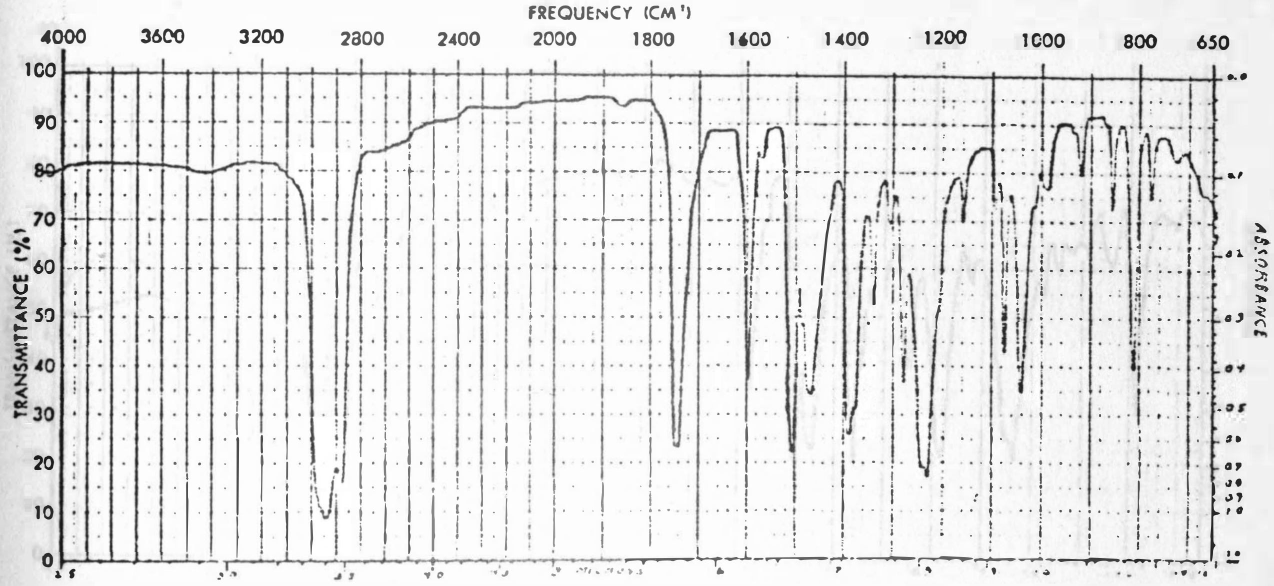
Spectrum 2: The NMR spectrum of 2 in deutro DMSO.



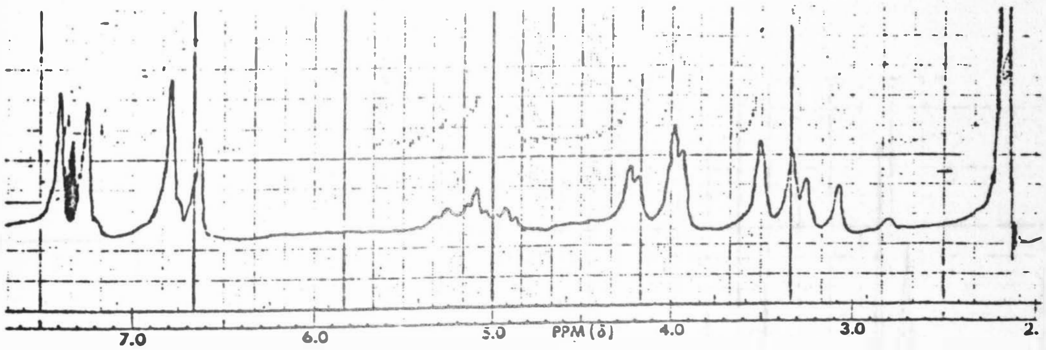
Spectrum 3: The infrared spectrum of 1,5-bis(p-bromophenyl)-3,7-dihydroxyoctahydro-1,5-diazocine 5.



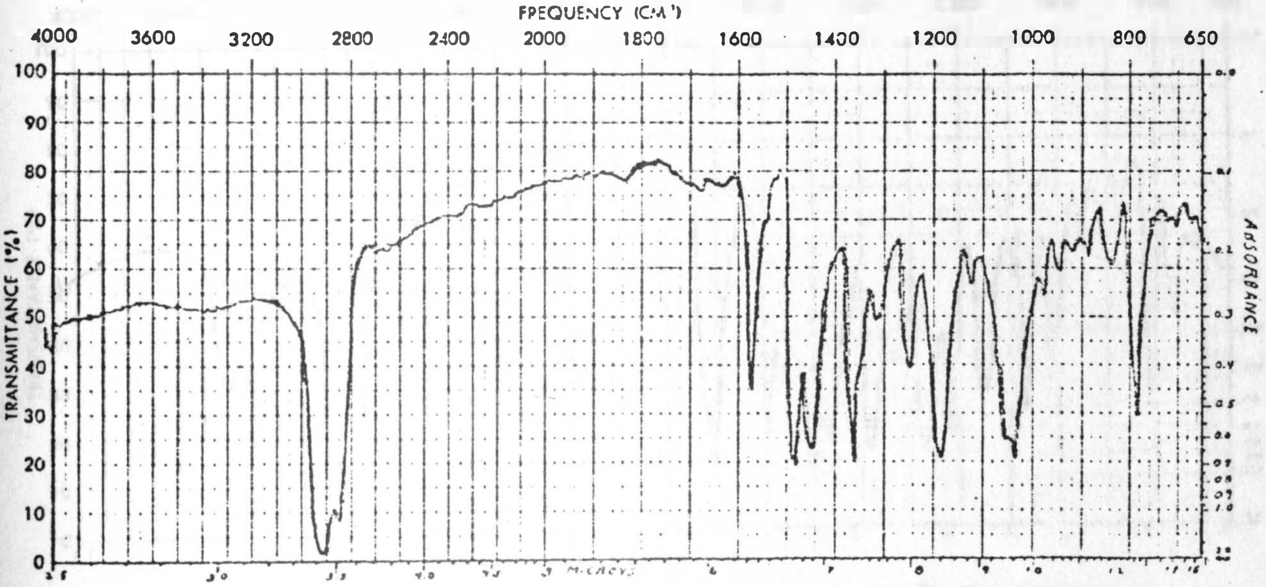
Spectrum 4: The NMR spectrum of 5 in deutero DMSO.



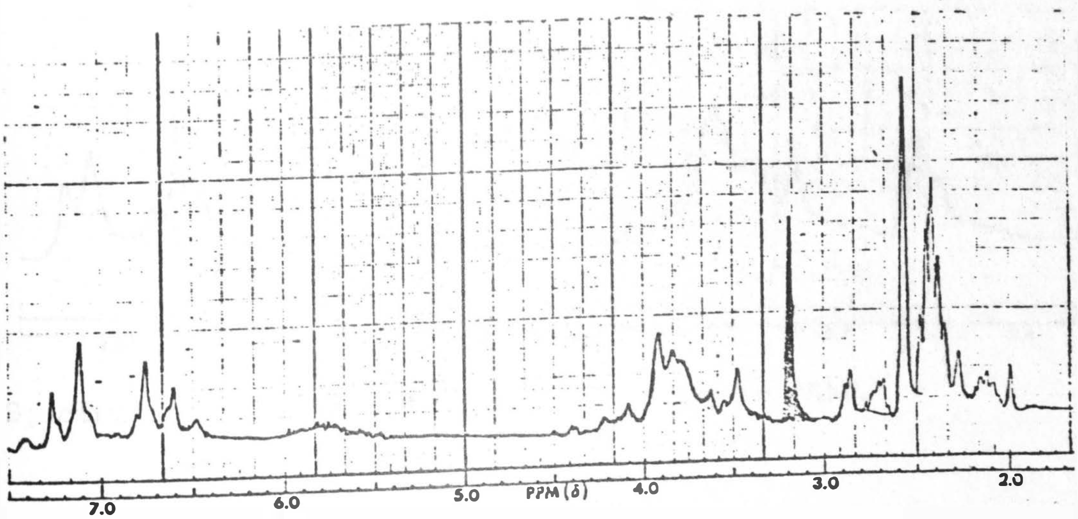
Spectrum 5: The infrared spectrum of 3,7-diaectoxy-1,5-bis(p-bromophenyl)octahydro-1,5-diazocine, 7.



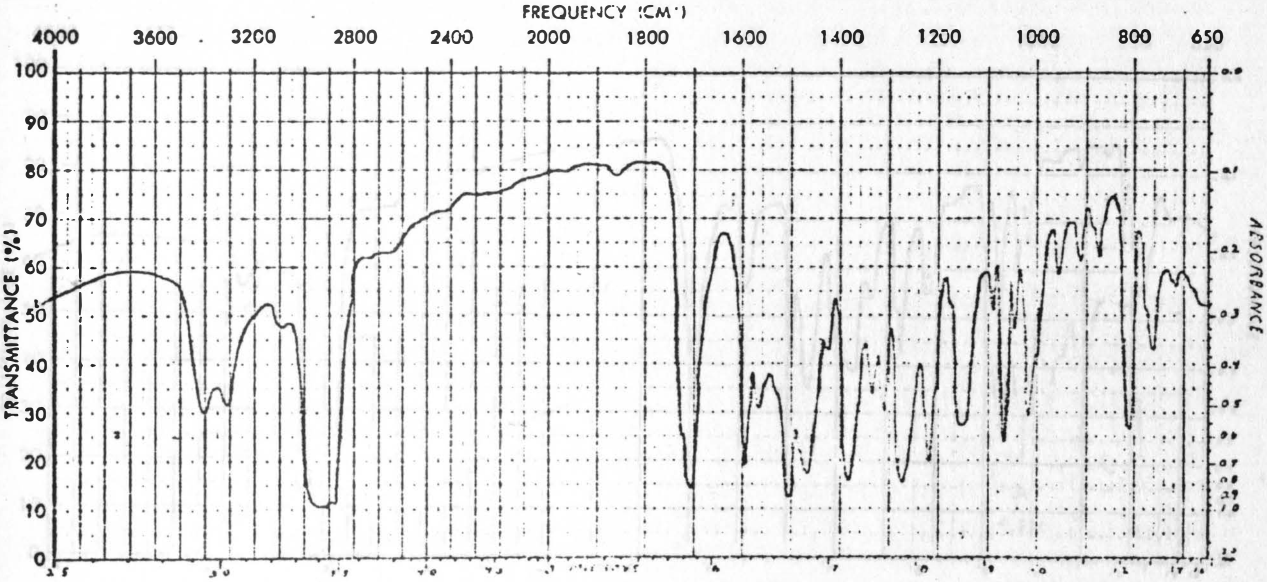
Spectrum 6: The NMR spectrum of 1 in $DCCl_3$. The dark peak is $HCCl_3$ absorption.



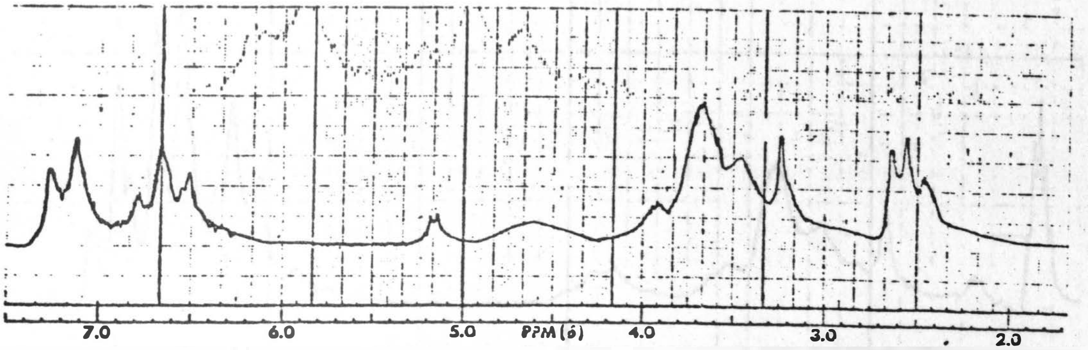
Spectrum 7: The infrared spectrum of the S-methylxanthate ester of 1,5-(p-bromophenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 10.



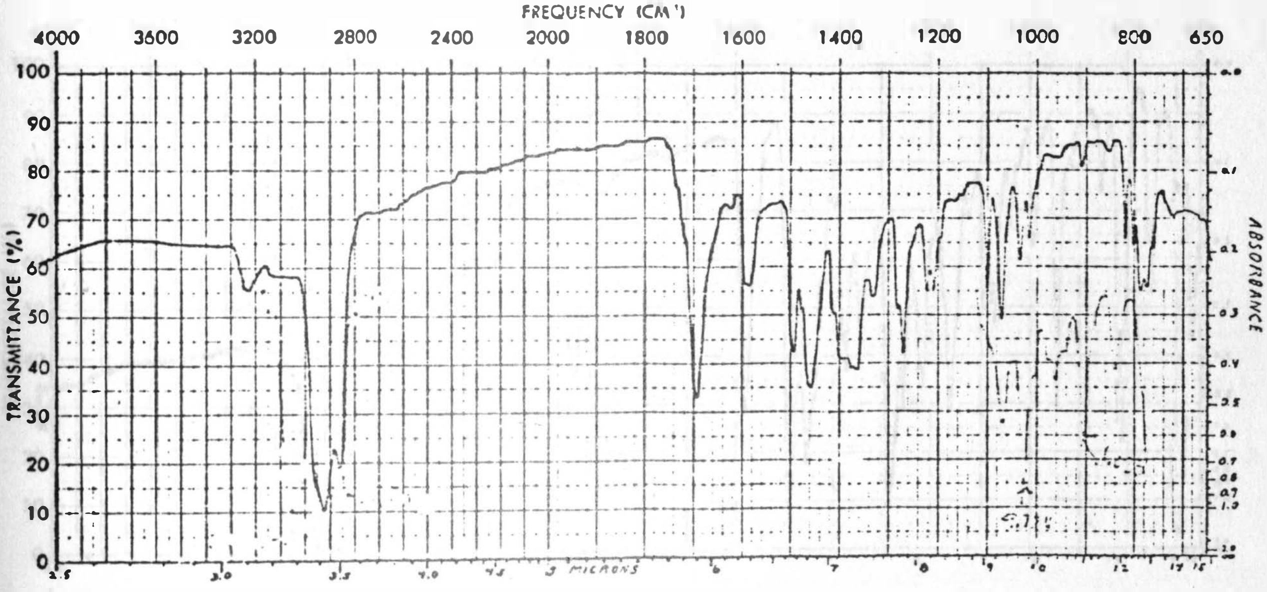
Spectrum 8: The NMR spectrum of 10 in deutero-DMSO. The dark peak is H_2O absorption.



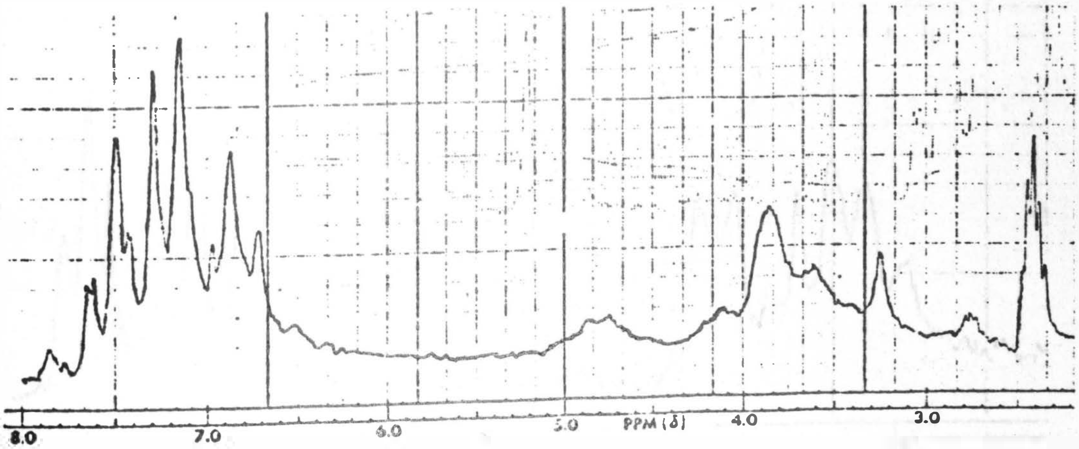
Spectrum 9: The infrared spectrum of the mono-methylurethane derivative of 1,5-bis(*p*-bromophenyl)-3,7-dihydroxy-octahydro-1,5-diazocine, 11.



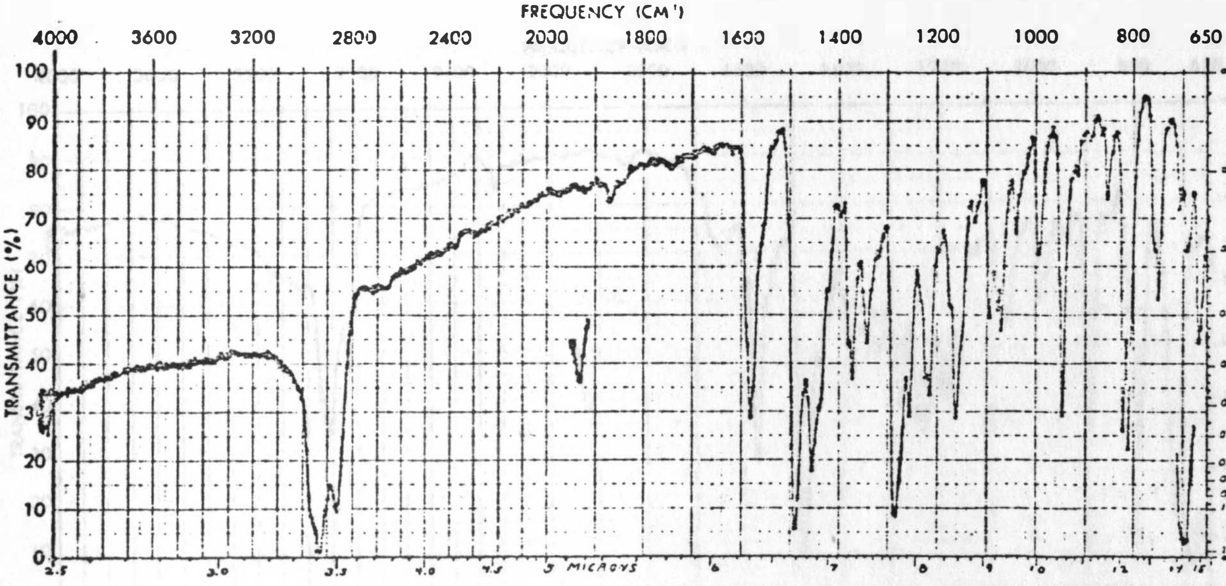
Spectrum 10: The NMR spectrum of 11 in deutro DMSO.



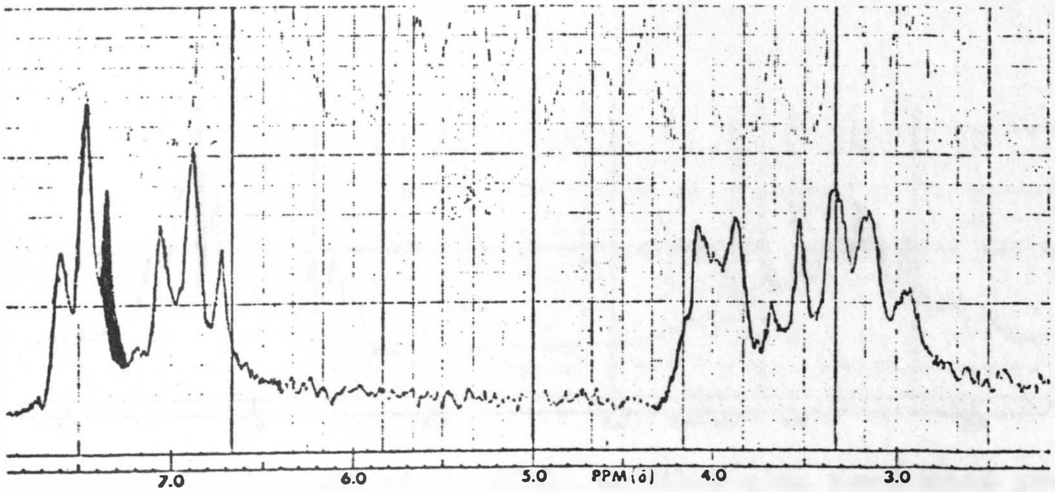
Spectrum 11: The infrared spectrum of the phenylurethane derivative of 1,5-bis(p-bromophenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 12.



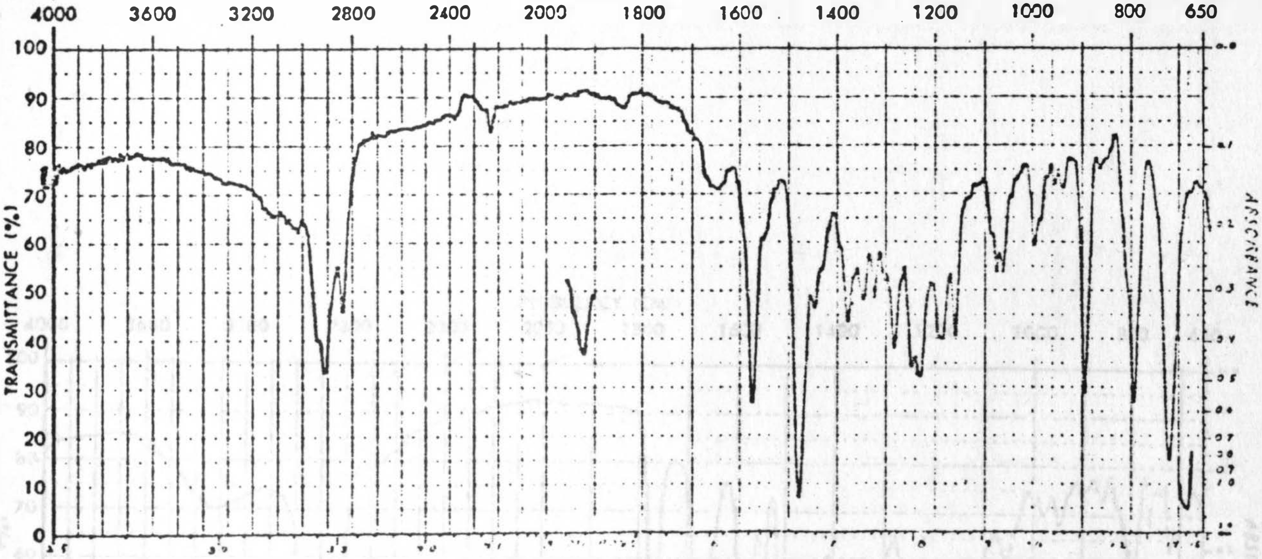
Spectrum 12: The NMR spectrum of 12 in deutro DMSO.



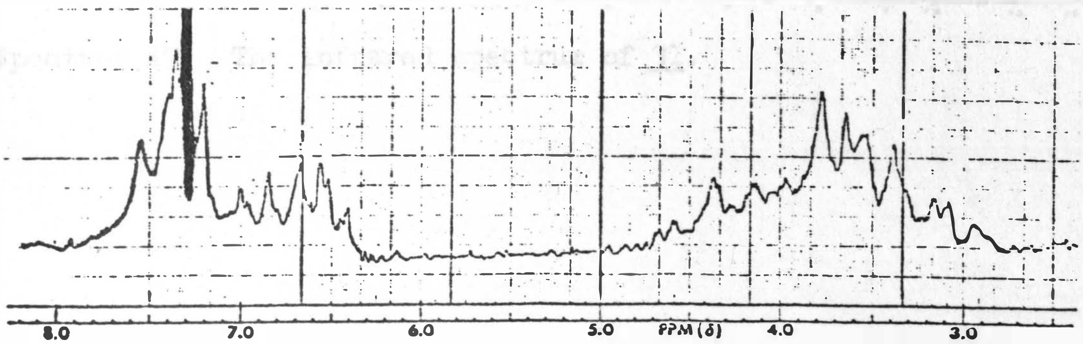
Spectrum 13: The infrared spectrum of the PBr_3 ring contracted products 13, 14, 15, and 16.



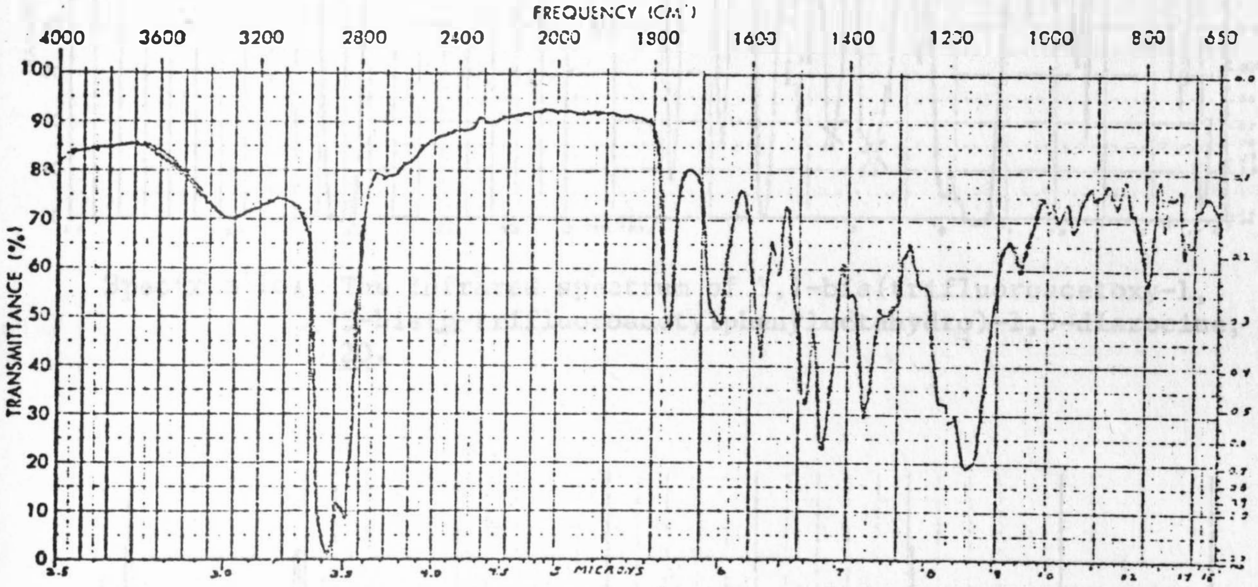
Spectrum 14: The NMR spectrum of ring contracted products in $DCCl_3$. The dark peak in $HCCl_3$ absorption.



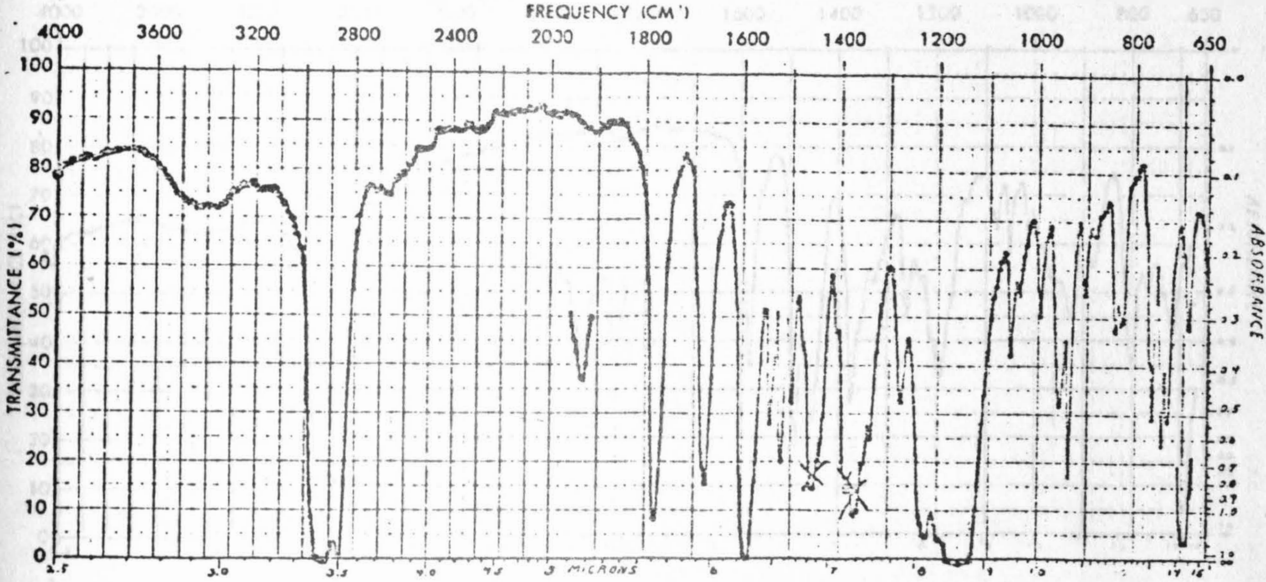
Spectrum 15: The infrared spectrum of the $SOCl_2$ in ether ring contracted products.



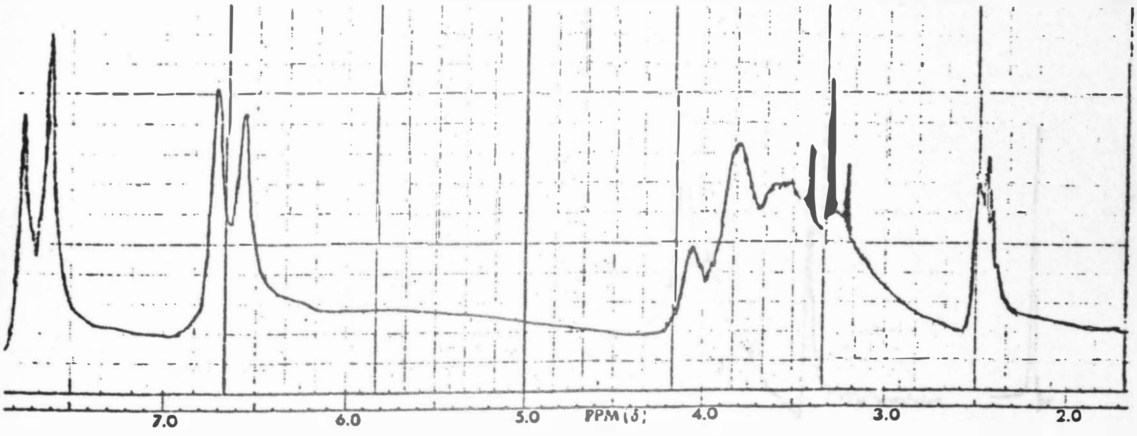
Spectrum 16: The NMR of the $SOCl_2$ in ether ring contracted products in $DCCl_3$. The dark peak is $HCCl_3$ absorption.



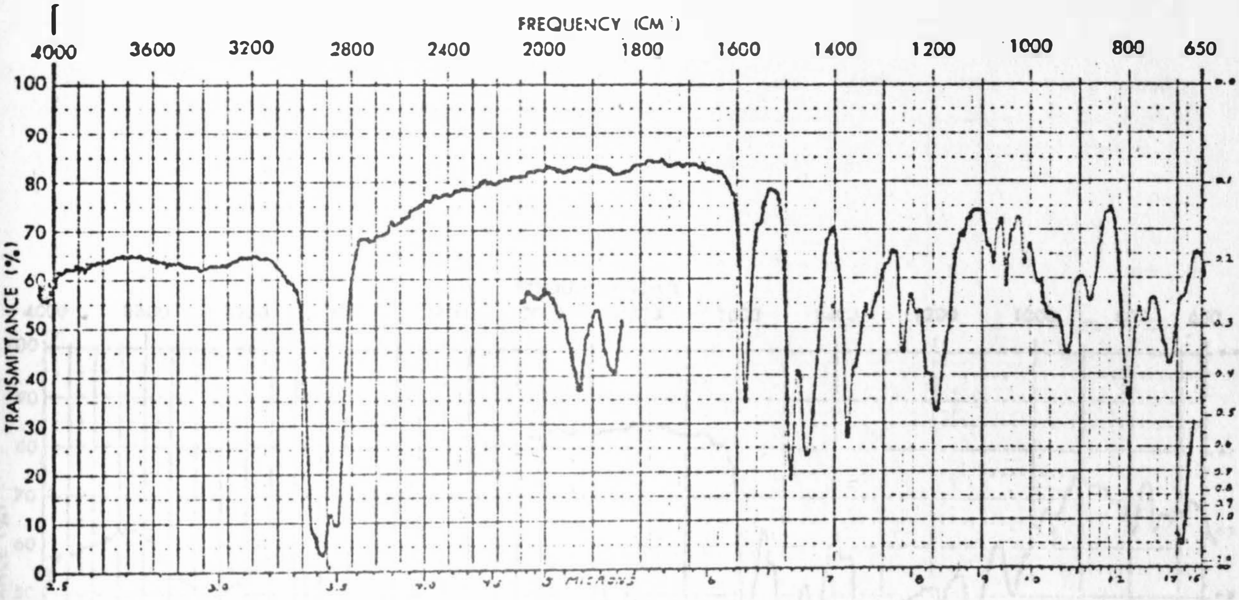
Spectrum 17: The infrared spectrum of 31.



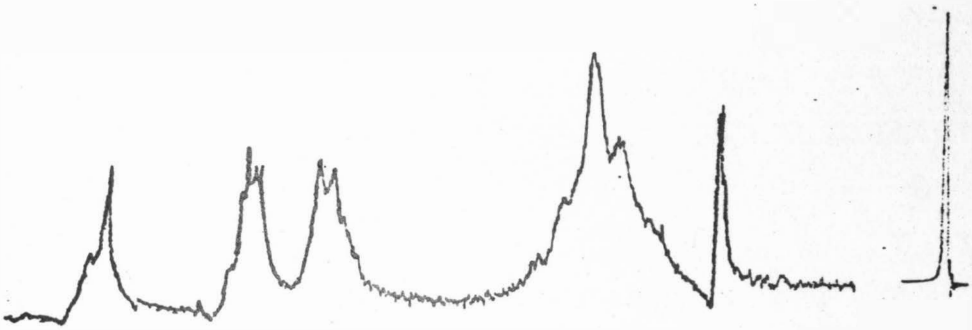
Spectrum 18: The infrared spectrum of 3,7-bis(trifluoroacetoxy-1, 5-bis(p-trifluoroacetylphenyloctahydro)-1,5-diazocine, 20.



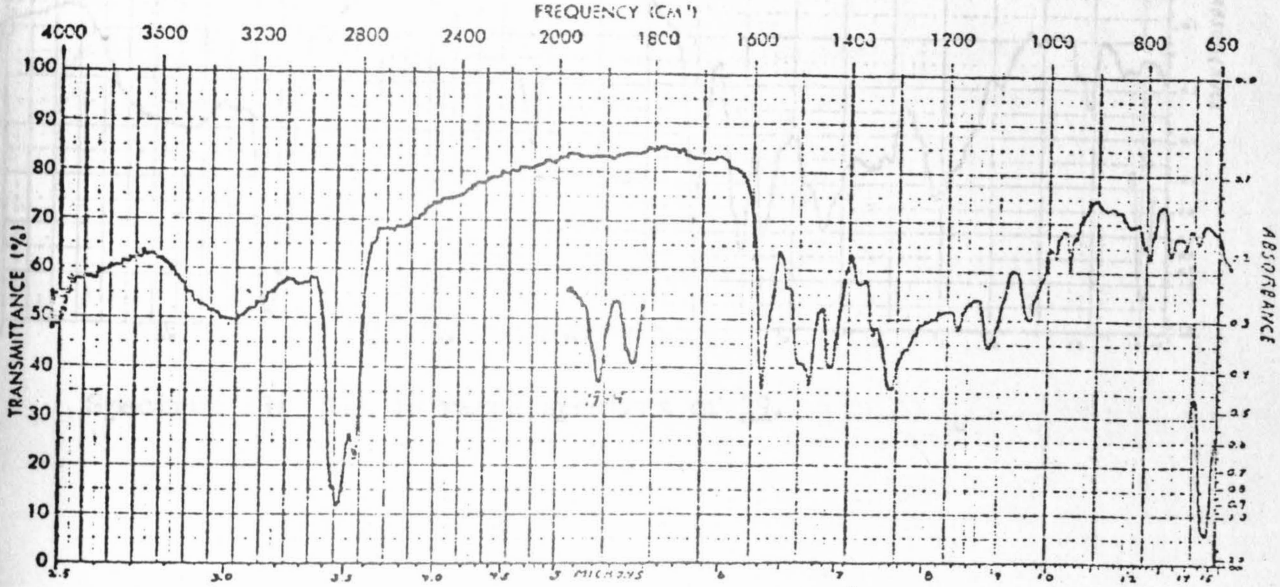
Spectrum 19: The NMR spectrum of 20 in deutero DMSO. The dark peaks are an impurity.



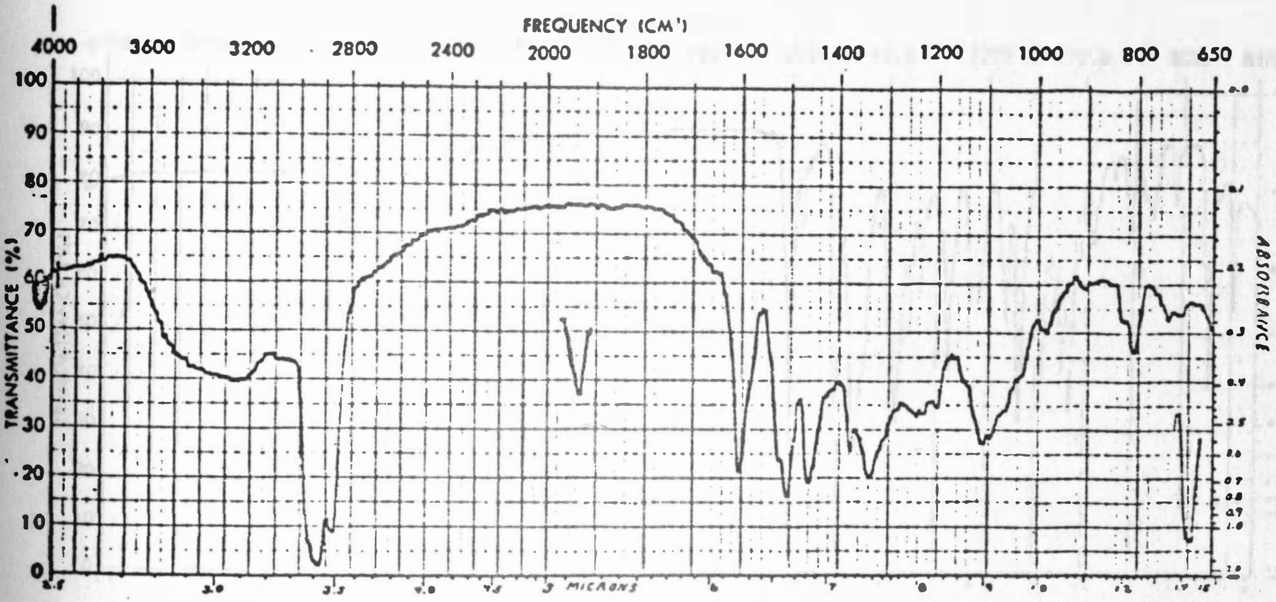
Spectrum 20: The infrared spectrum of $SOCl_2$ ring collapse products.



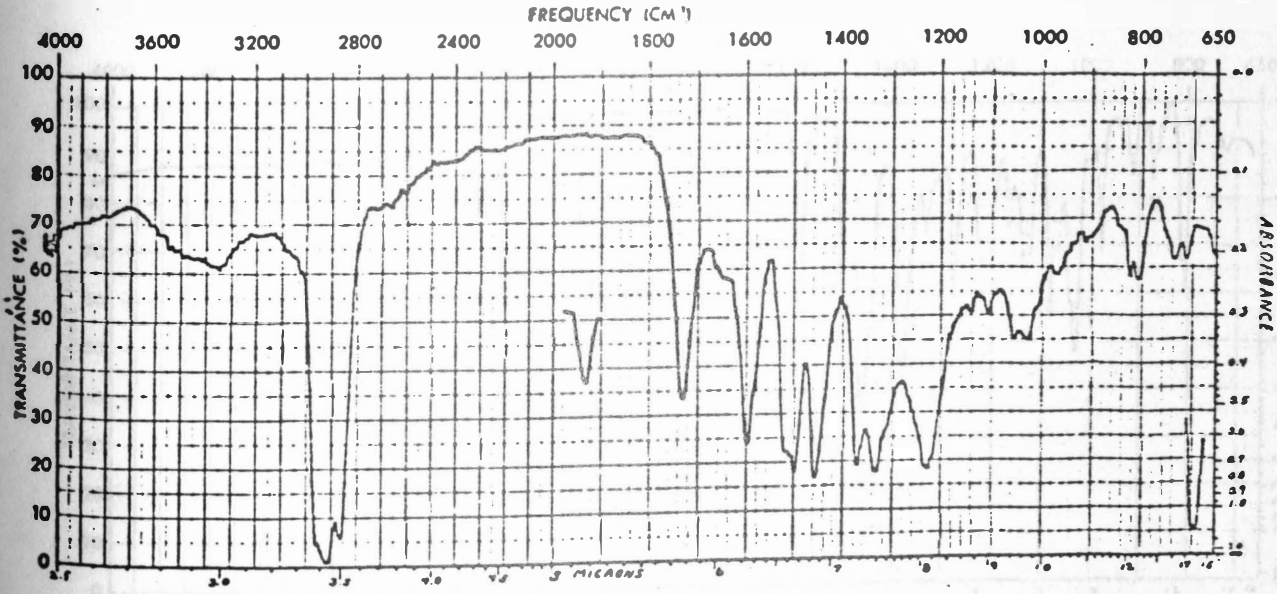
Spectrum 21: The NMR spectrum of $SOCl_2$ ring collapse products in deutero DMSO.



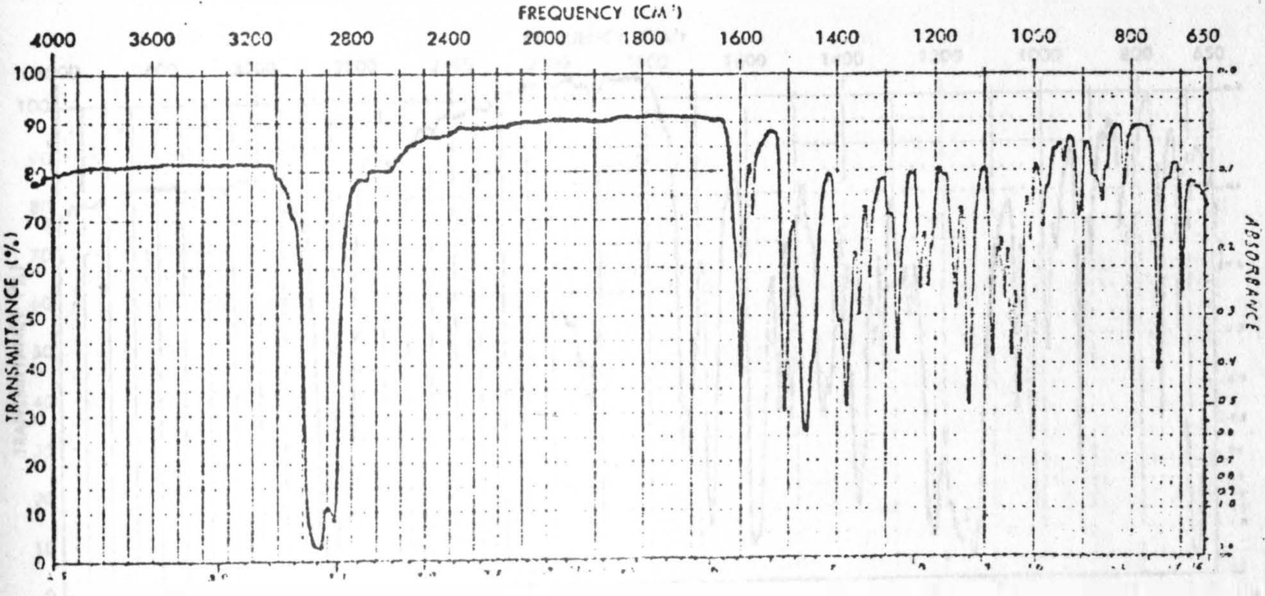
Spectrum 22: The infrared spectrum of <u>28</u>.



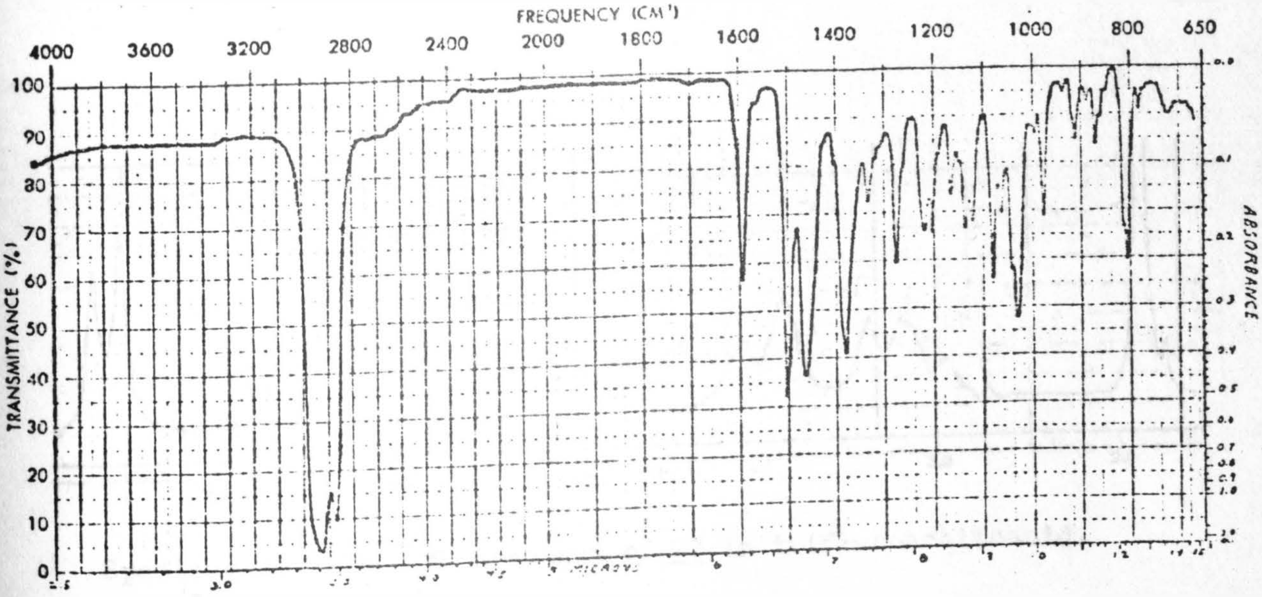
Spectrum 23: The infrared spectrum of 29.



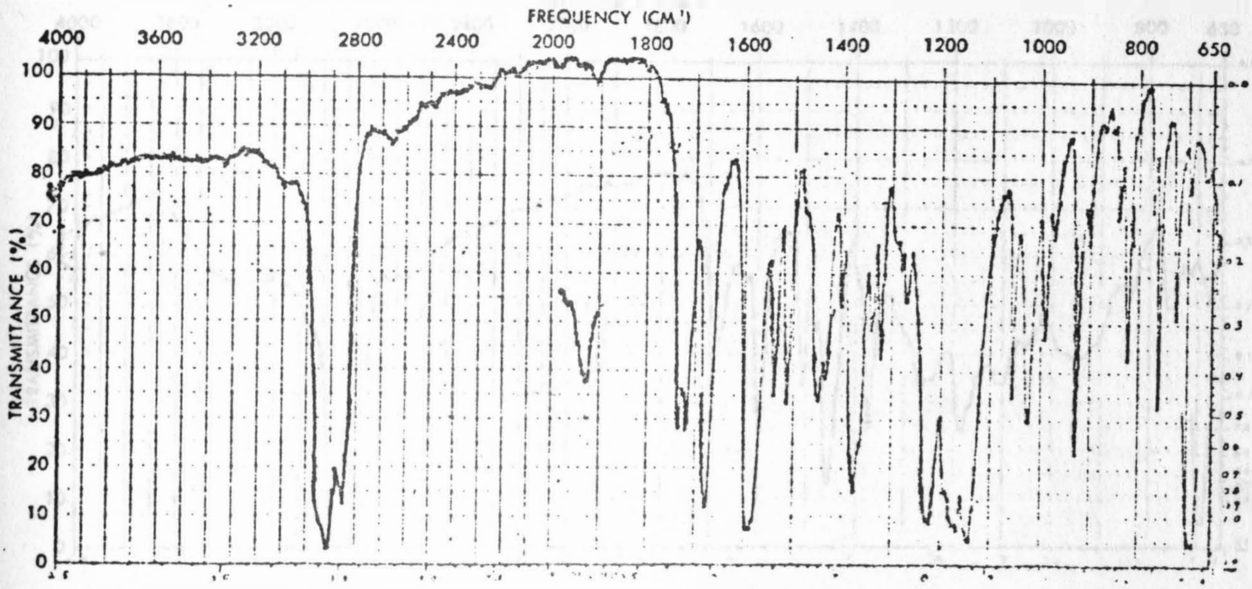
Spectrum 24: The infrared spectrum of 30.



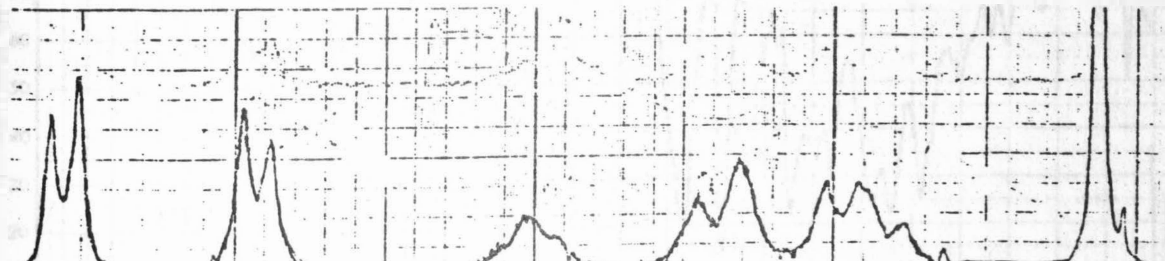
Spectrum 25: The infrared spectrum of 1,5-diphenyl-3,7-bis(2-oxacyclohexyloxy)octahydro-1,5-diazocine, 26.



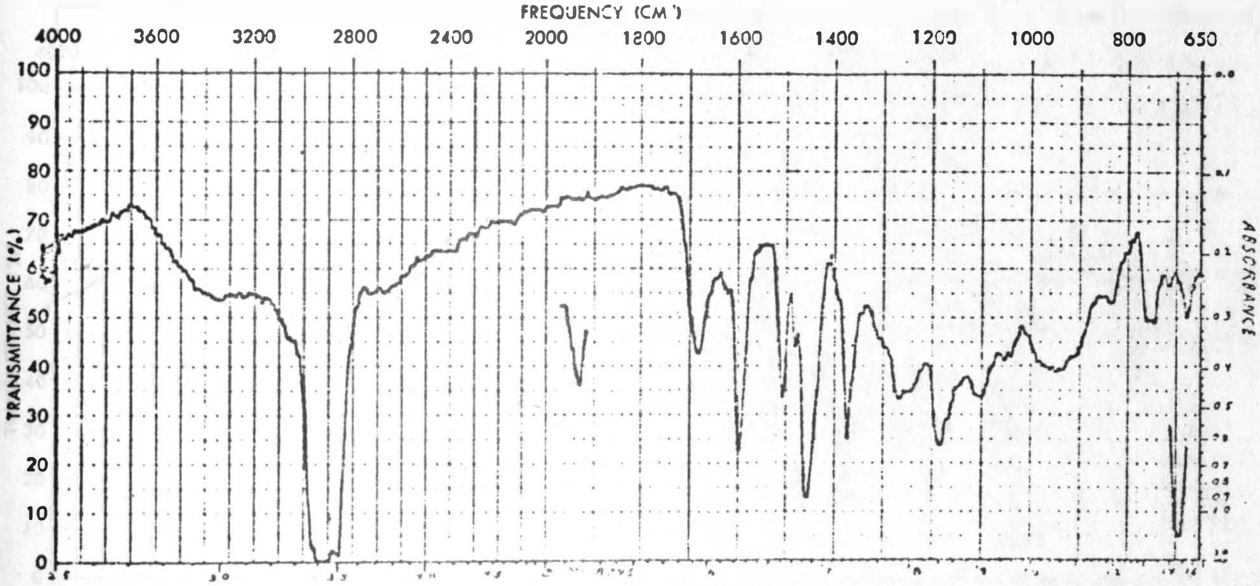
Spectrum 26: The infrared spectrum of 1,5-bis(p-bromophenyl)-3,7-bis(2-oxacyclohexyloxy)octahydro-1,5-diazocine, 19.



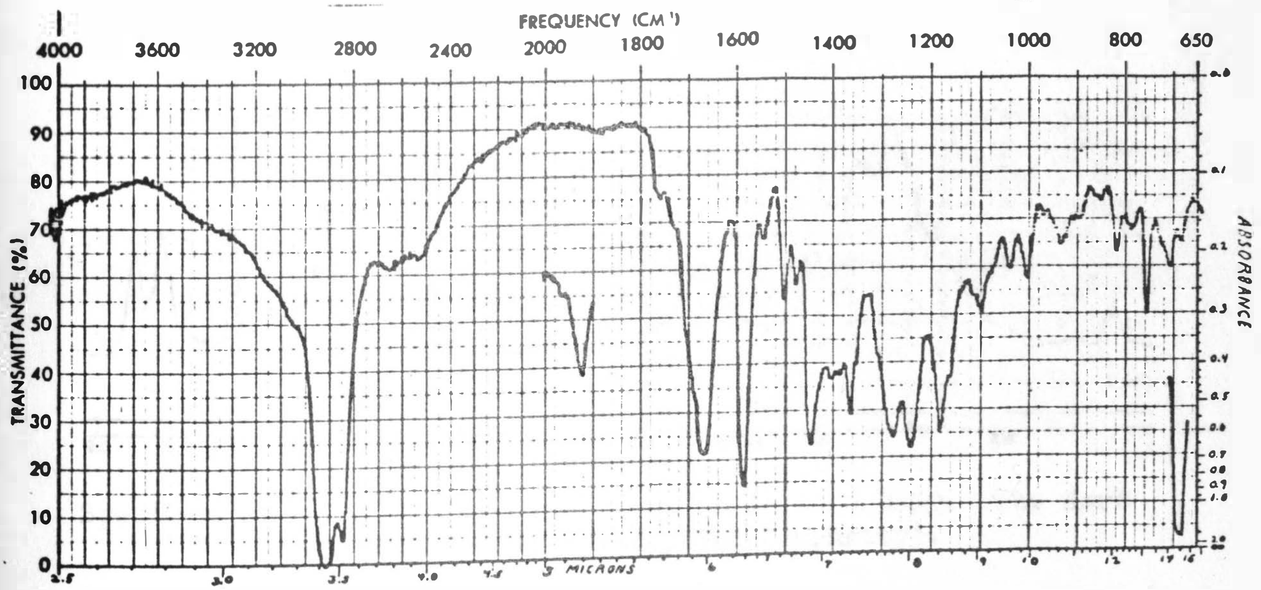
Spectrum 27: The infrared spectrum of 3,7-diacetoxy-1,5-bis(p-trifluroacetylphenyl)octahydro-1,5-diazocine, <u>27</u>.



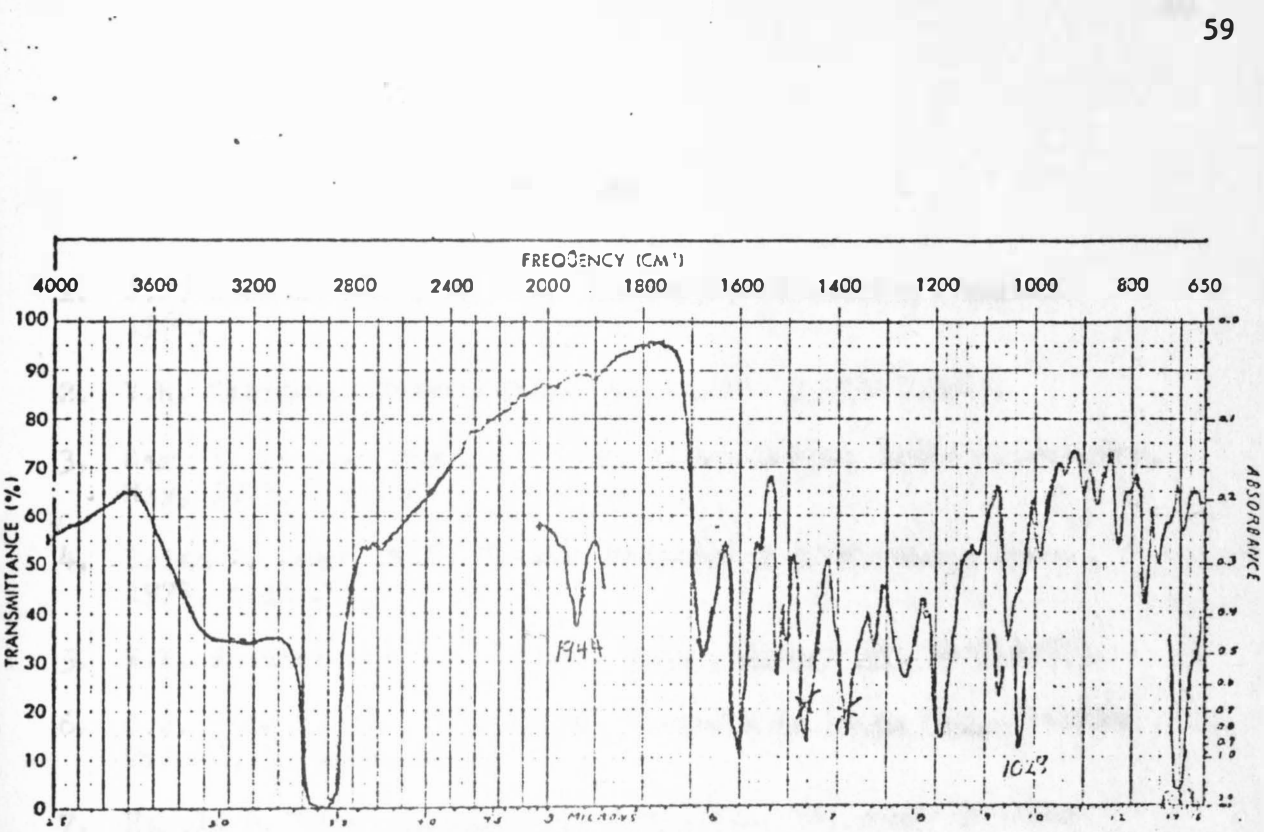
Spectrum 28: The NMR spectrum of <u>27</u> in trifluroaceticacid.



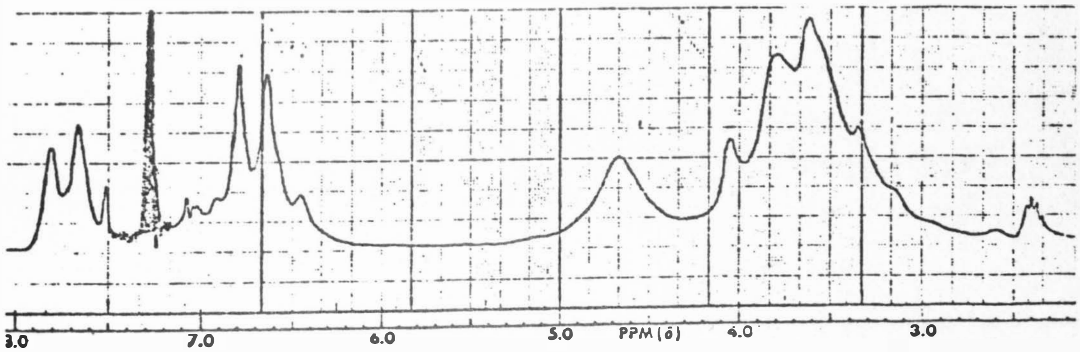
Spectrum 29: The infrared spectrum of 22.



Spectrum 30: The infrared spectrum of 24.



Spectrum 31: The infrared spectrum of 1,5-bis(p-trifluroacetylphenyl)-3,7-dihydroxyoctahydro-1,5-diazocine, 21.



Spectrum 32: The NMR spectrum of 21 in deutero DMSO. The dark peak is benzene absorption (impurity).

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