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Abstract

In an attempt to further substantiate the findings of Stiles and Salisbury on the rearrangement of aryl disubstituted dibenzo [a,e] cyclooctatetraenes a new pair of derivatives were synthesized. The 5,6 and 5,11 dideuteriodibenzo [a,e] cyclooctatetraenes were prepared. The 5,6 derivative was prepared starting with dibenzo [a,e] cyclooctene-5,6-dione. The 5,11 derivative was prepared starting with o-tolualdehyde. In the case of the 5,6 derivative the deuterium was introduced by a LiAlD_4 reduction of the dibenzo [a,e] cyclooctene-5,6-dione. The 5,11 derivative had been labeled with deuterium in the final step during the Wittig reaction. The use of methanol- d_1 as the solvent in place of methanol facilitated the exchange. These compounds can be distinguished by proton nuclear magnetic resonance spectroscopy. The 5,6 derivative had a n.m.r. spectrum with a sharp singlet in the olefinic region. The 5,11 derivative had a n.m.r. spectrum with an unresolved triplet in the olefinic region. The corresponding 5,6 aryl disubstituted dibenzo [a,e] cyclooctatetraenes were shown by Stiles and Salisbury to rearrange to the 5,11 isomer. Supporting evidence for a diradical intermediate was developed by use of benzenethiol in trapping experiments. Our thermolysis studies revealed no rearrangement with the deuterium labeled species. The temperature at which our experiments were conducted exceeds other published experimental data with aryl substituents which underwent high yield

rearrangements. Therefore the lack of stabilization by the deuterium as opposed to the phenyl substituents in this rearrangement lends credence to the diradical intermediates.

Thermal Rearrangement Studies of Deuterium Labeled
Dibenzo [a,e] cyclooctatetraenes

by
Charles W. Wenger

A Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial ful-
fillment of the requirements for the degree of Master of
Science in Chemical Engineering, May 1982

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APPROVAL SHEET

Thermal Rearrangement Studies of Deuterium Labeled
Dibenzo [a,e] cyclooctatetraenes

Charles W. Wenger
Master of Science in
Chemical Engineering, 1982

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Vita

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To my family

Acknowledgment

My deepest appreciation to Doctor Howard D. Perlmutter for his steadfast guidance, infinite perseverance and wholehearted cooperation in the achievement of this work.

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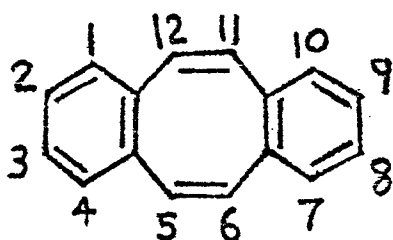
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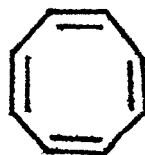
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I. Introduction

The hydrocarbon of interest in this thesis is dibenzo-**[a,e]** cyclooctatetraene (I). For brevity the compound name dibenzo **[a,e]** cyclooctatetraene may be abbreviated DBCOT. The events leading up to the present day concern with this molecule started with Willstätter in 1911 (1,2). Willstätter had prepared cyclooctatetraene (II) by the degradation of pseudo-plalletierine. For brevity the compound name cyclooctatetraene will be abbreviated COT. The COT molecule is the parent hydrocarbon of the DBCOT molecule.



I



II

COT was the next highest fully conjugated homolog after that of benzene. Willstätter found that addition of bromine and oxidation by permanganate occurred readily on COT. Both are characteristic reactions of olefins rather than an aromatic compound such as benzene.

COT is nonaromatic as defined by the Hückel Theory. The rule for electronic stability is the " $4n+2$ " rule, stated as follows: " Those monocyclic coplanar systems of trigonally hybridized atoms which contain $4n+2$ π electrons (where "n"

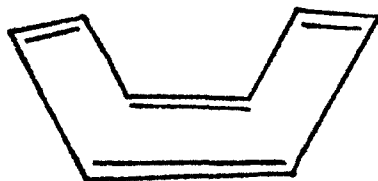
is zero or an interger) will possess relative electronic stability." (2,3)

The COT molecule was found to be nonplanar. The stable conformation of the COT molecule is the tub which has D_{2d} symmetry (Fig. 1). The carbon-carbon bond distances alternate between long and short around the ring.

Electron diffraction has established the D_{2d} conformation for COT and its simple mono- and disubstituted derivatives, as well as its benzo analogs (4). Such molecules are capable of two dynamic processes, ring inversion and bond shifting (5). In the case where benzene is fused to the COT ring, bond shifting becomes less possible as the number of fused benzene rings increases thereby decreasing the number of π electron clouds.

Figure 1.

Conformation of Cyclooctatetraene, D_{2d} symmetry



A high degree of stabilization due to conjugation of the π electron clouds was found to be absent in the COT molecule (6). An aromatic behavior exists in the cyclooctatetra-

enyl anions (7,8,9). A planar 10 π system is evident here. The DBCOT and benzocyclooctatetraene molecules do not form planar diradicals, although these two systems do approach planarity and increased conjugation is noted. The annelation of benzene is suggested as the reason for these two compounds not generating dianion species (4,5). The lack of conjugation and planarity in the DBCOT molecule has been verified extensively (4-13).

The chemistry of COT in the ground state can tell us nothing about the properties of a "Hückel" 8 π planar system. For example, whereas the lack of conjugation in COT is due in part to its nonplanarity, a planar COT should be even less stable due to angle strain. This is so because any conjugation is prohibited by the Hückel rule.

The two methods of interest used to investigate the relative stabilities of nonplanar and planar COT have been;

a) racemization studies of optically active COT's

b) nmr studies of inversion of properly substituted COT's.

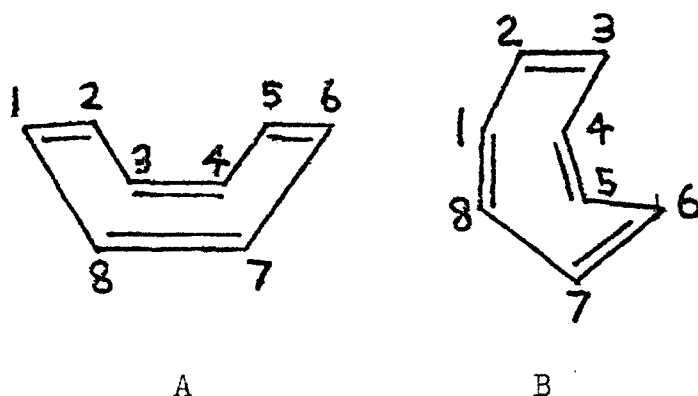
In both of these methods the assumption is made that the transition state to inversion is planar.

In the absence of labeling, structure A (Fig. 2) is equivalent to structure B (Fig. 2) (10). The bond shift from A to B is believed to involve a planar intermediate which would be electronically unstable as defined by the Hückel Theory. With the entropy of activation assumed to be

zero, the energy barrier is about 13.7 kcal/mole for the difference in planar and tub form energies as calculated by nmr studies (10). The earlier failure of Cope and Kinter (14) to resolve the monosubstituted COT would have been expected since the barrier to ring inversion is so small (10).

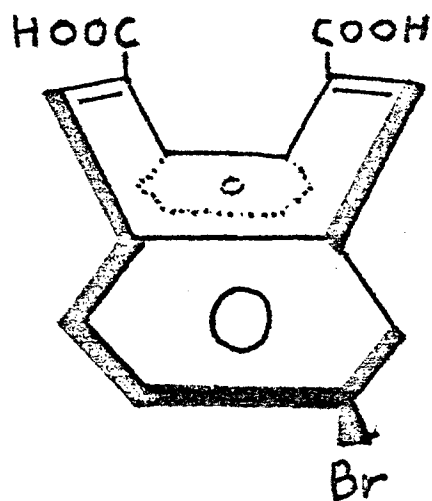
Figure 2

Bond Shifting of the Cyclooctatetraene Molecule



The resolution of an optically active derivative of DBCOT was first accomplished by Mislow and Perlmutter (2,15). The liberated acid of compound III was stable to inversion in solution for eight weeks at room temperature without loss of optical activity. At temperatures of 120^o-140^o the racemization occurred with 27 kcal/mole estimated for the barrier to ring inversion.

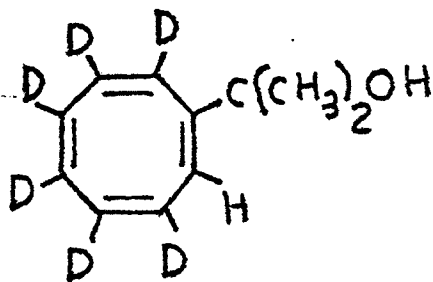
Later work by Mislow (16) using nmr confirmed that the value of 27 kcal/mole for the racemization barrier was high. This was due to "non-bonded interaction of carboxyl groups



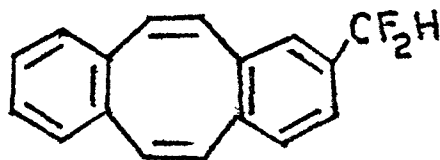
III

and benzene hydrogens in the transition state which is likely to contribute significantly to the destabilization of the transition state". Indeed, when CH_2OH and CH_3 are substituted for CO_2H in III the E_{act} is reduced to 23 and 21 kcal/mole respectively. (38)

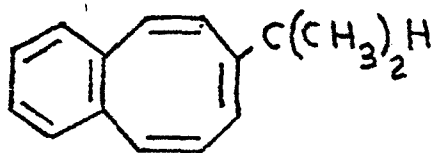
By comparison compound IV had a barrier to ring inversion of 12.3 kcal/mole. Compound V had a value of 14.7 kcal/mole and compound VI, the benzocyclooctatetraene, a value of 13.4 kcal/mole. The inversion barrier of the tetrabenzocyclooctatetraene derivative (VII) was found to be 21 kcal/mole which represents a lower limit (16,17).



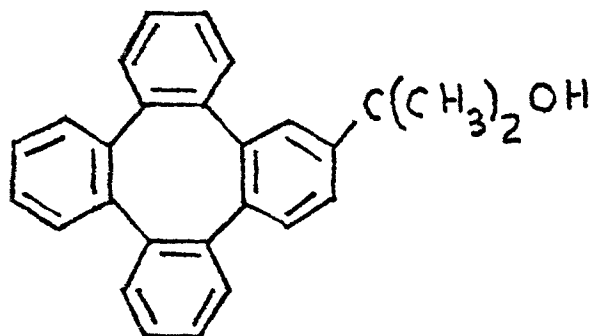
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V



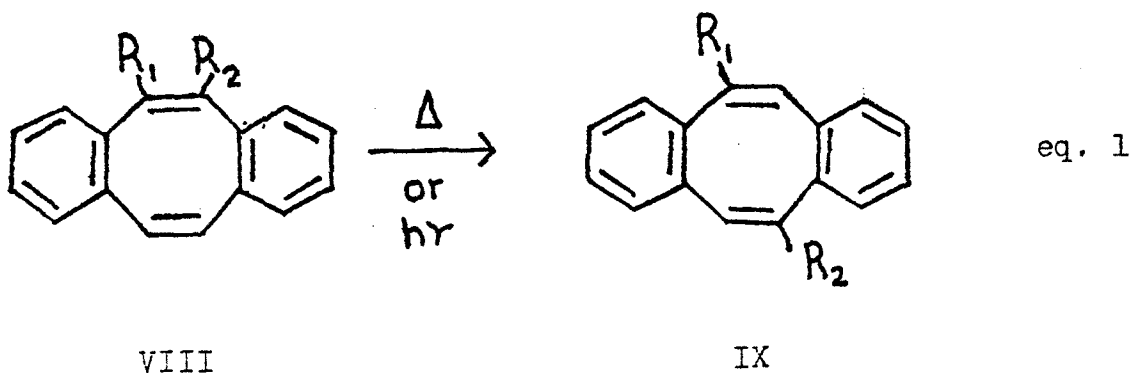
VI



VII

Where no substitution is present that can form nonbonded interactions, the effect of benzene fusion on the conformational stability of the COT molecule is really very minor.

Stiles and Burckhardt found that 5,6 disubstituted DBCOTs (VIII) underwent rearrangement to the 5,11 disubstituted isomers (IX). This occurred by photolysis or by thermolysis of the compound in solution or as the pure melt, eq. 1 (18). The hydrocarbon was heated at temperatures in the range of 140°-200° for the melt or solution.



VIII

IX

Table 1 summarizes the derivatives used and the subsequent results.

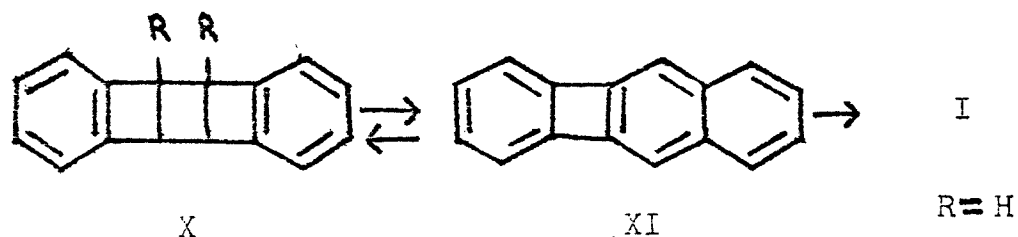
Table 1.

Compd. VIII	% Rearr.	Solvent, (temp., C°)	Rate, 10 ⁵ k, sec. ⁻¹	E _a , kcal.
a) R ₁ :C ₆ H ₅ R ₂ :C ₆ H ₅	96	Decalin, 164.5	4.8	28.9
a') R ₁ :C ₆ H ₄ -p-CH ₃ R ₂ :C ₆ H ₄ -p-CH ₃	93	Triglyme, 164.0	4.6	29.1
b) R ₁ :C ₆ H ₄ -p-Br R ₂ :C ₆ H ₄ -p-Br	87	Decalin, 164.9	7.1	29.1
c) R ₁ :C ₆ H ₅ R ₂ :C ₆ H ₄ -p-Br	95	Decalin, 164.8	5.3	31.7
d) R ₁ :CO ₂ ⁻ CH ₃ R ₂ :CO ₂ ⁻ CH ₃	75	Decalin, 164.8	4.9	30.1

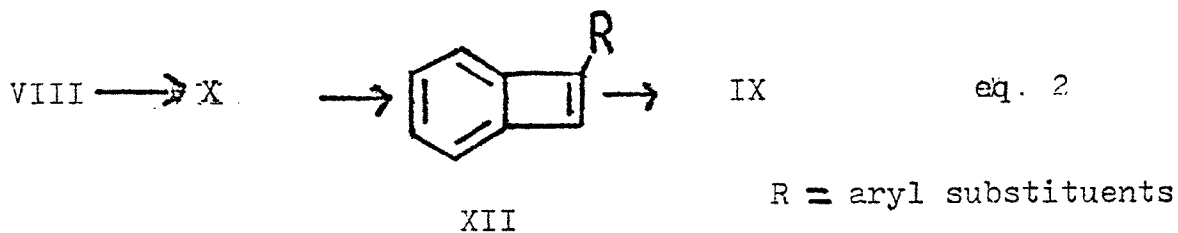
The activation parameters for the thermal rearrangement of compounds VIIIA-d are close to that found by Mislow and Perlmutter for the racemization of 2-Bromodibenzo[a, e] cyclooctatetraene-6,11-dicarboxylic acid (III) at 120°-140°, where the energy of activation was given as 27 kcal/mole.

Photolysis of VIIIA in methylcyclohexane produced IXa with no detectable levels of other isomers. The remainder was starting material.

The compound (3:4,7:8)-dibenzotricyclo [4.2.0.0^{2,5}] octa-3,7-diene (X), which would be the 2+2 transannular cycloaddition product of DBCOT, is readily converted to DBCOT (I) as found by Avram and Nenitzescu (19).



A dissociation-recombination mechanism as shown in equation 2 was ruled out as a possible mechanism. This type of mechanism was tested by heating an equimolar mixture of VIIIa and VIIIc in triglyme at 195°. The reaction yielded a 99% mixture of IXa and IXc which are the pure rearranged products. No contamination by IXb was detected. The rearrangement of VIIIId yielded only IXd with no detectable levels of IXa or IXc.



A 1,2 diaryl dibenzotricyclo[3.3.0.0.^{2,6}]octane (XIIa) was postulated as a possible intermediate in the rearrangement of VIII to IX. There exists a wealth of reported thermal and photochemical reactions of COFs. Interrelated are structures similar to COF such as XIII.

The photolysis of cis,cis-1,5-cyclooctadiene (XIII) yielded the tricyclo[4.2.0.0.^{2,6}]octane (XIV) as reported by Srinivisan (20). The starting material is predominately in the cis,cis configuration whereas the tricyclooctane is derived from the trans,trans configuration (Fig. 3).

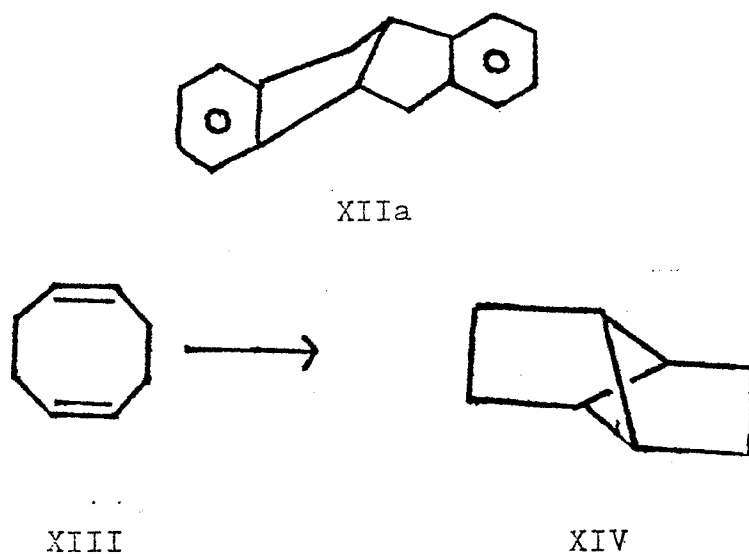
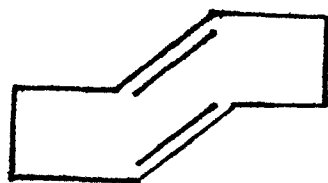


Figure 3

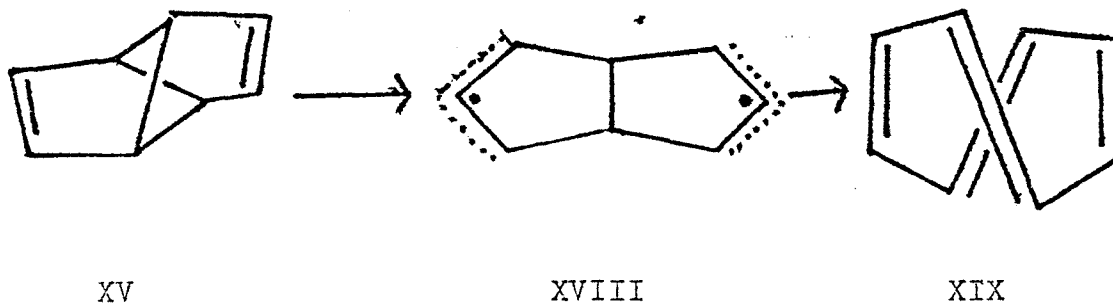
trans,trans Configuration of 1,5-Cyclooctadiene



Zimmerman and Iwanura (21) have prepared semibullvalene by sensitized photolysis of cyclooctatetraene. Two routes were proposed for this type of reaction as can be seen in Chart 1 and Chart 2.

The highly strained tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (XV), a valence isomer of COT, undergoes thermal rearrangement to semibullvalene (XVI) (Chart 3). Photochemical conversion yields XVI as well as COT (Chart 3) (22,23). Control experiments validated the formation of COT directly from the tricyclo compound and not from the semibullvalene.

A proposed route to rearrangement is given by way of the doubly allylic diradical intermediate (22,24). This is the pathway of the thermal rearrangement (Chart 3).

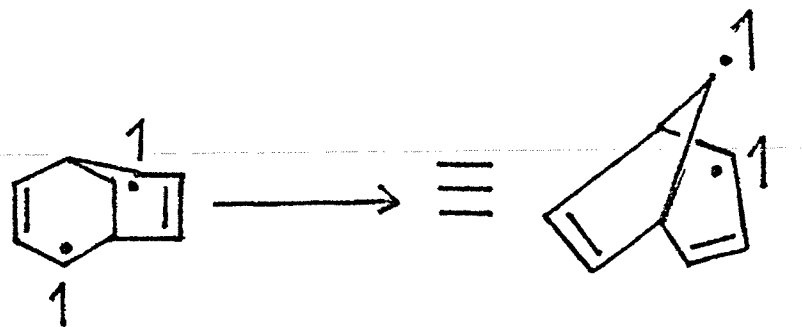
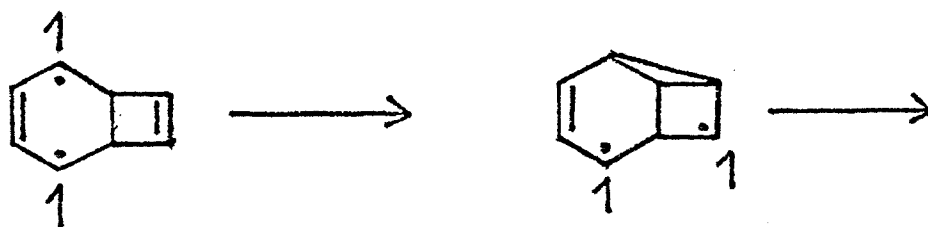
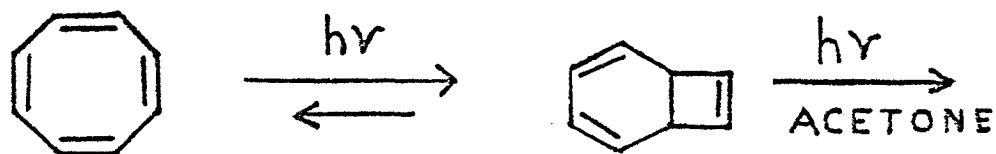


Three interpretations are given for the photochemical rearrangement of compound XV (Chart 3).

- (i) initial formation of diradical XVIII
 - (a) formation of XVII by radical recombination
 - (b) further bond cleavage to form II
- (ii) formation of XVII by way of XVIII and independently a retro (2,2) reaction yielding cis,trans,cis,trans II (XIX).

Chart 1.

Di π Methane Route for Cyclooctatetraene to Semibullvalene



INTERSYSTEM
CROSSING



AND
BONDING



Chart 2.

Direct Route for Cyclooctatetraene to Semibullvalene

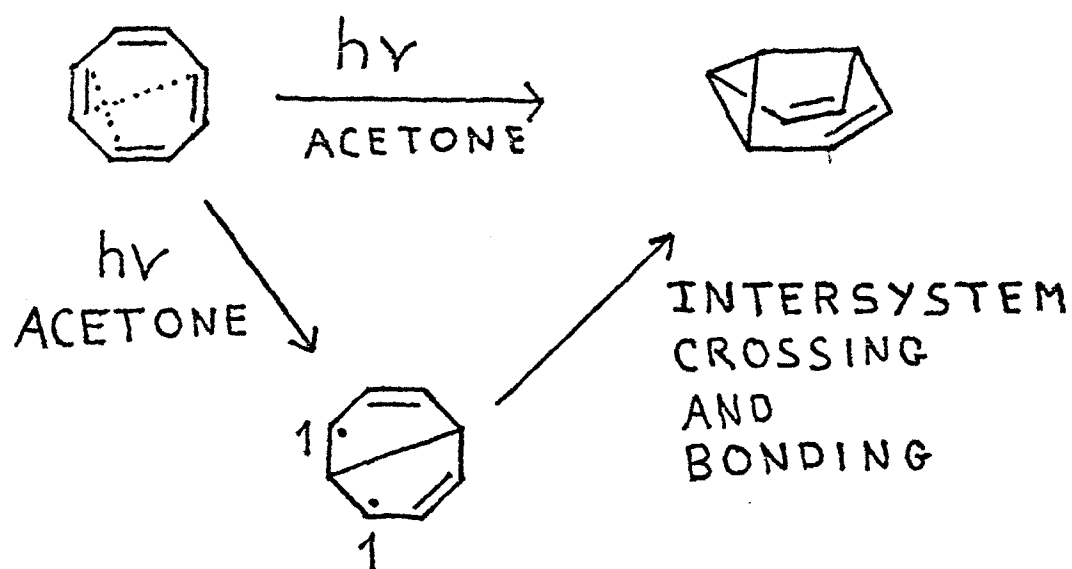
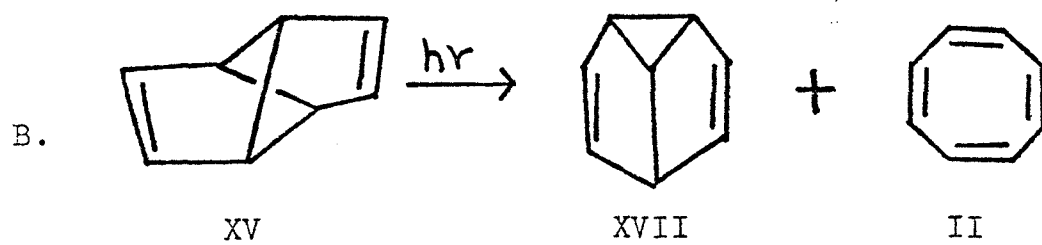
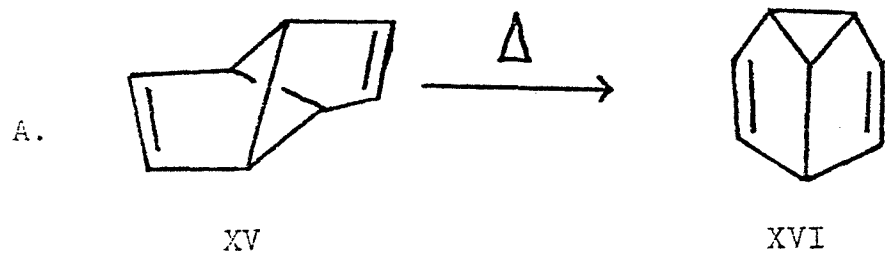


Chart 3.

Thermal and Photolytic Reactions of Tricyclo [3.3.0.0^{2,6}]
octa-3,7-diene (XV)



(iii) compound XVII from XV by a concerted suprafacial [1,3] sigmatropic shift and compound II by (i) or (ii) above.

More recent and much more relevant work on substituted DBCOTs has been done. It was proposed by Stiles that the racemization noted by Mislow and Perlmutter (15) could have gone by inversion of the ring or through a tricyclic intermediate as shown in Chart 4 (18,20,25-27). Later work by Stiles and Salisbury (27) demonstrated that ring inversion and rearrangement of DBCOTs are two separate processes. The latter proceeding most likely by diradical intermediates.

The initial argument, depicted in Chart 5, is that if a 5,6 disubstituted DBCOT is heated:

1) the racemic 5,11 isomer should be produced

or

2) if rearrangement provides the exclusive route to racemization (prior or concurrent inversion doesn't occur)

then the rate of rearrangement should equal the rate of optical activity loss (25,26).

When (+)-5-phenyl-6-(p-carbomethoxyphenyl)-dibenzo[a,e]cyclooctatetraene (XX) was heated the racemic 5-phenyl-11-(p-carbomethoxyphenyl)-dibenzo[a,e]cyclooctatetraene (XXI) was produced. Complete loss of optical activity accompanied rearrangement.

Chart 4.

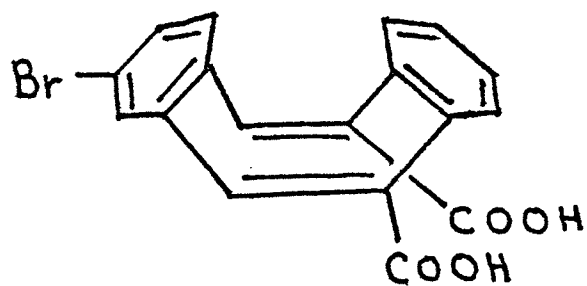
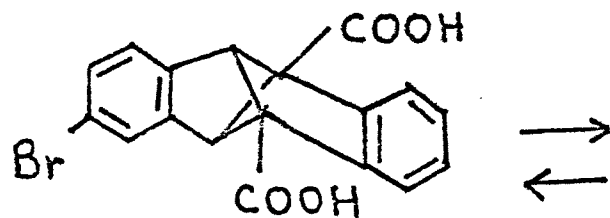
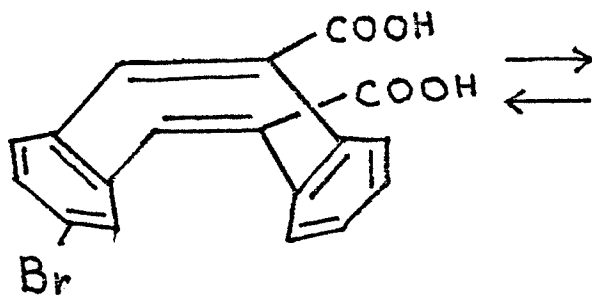
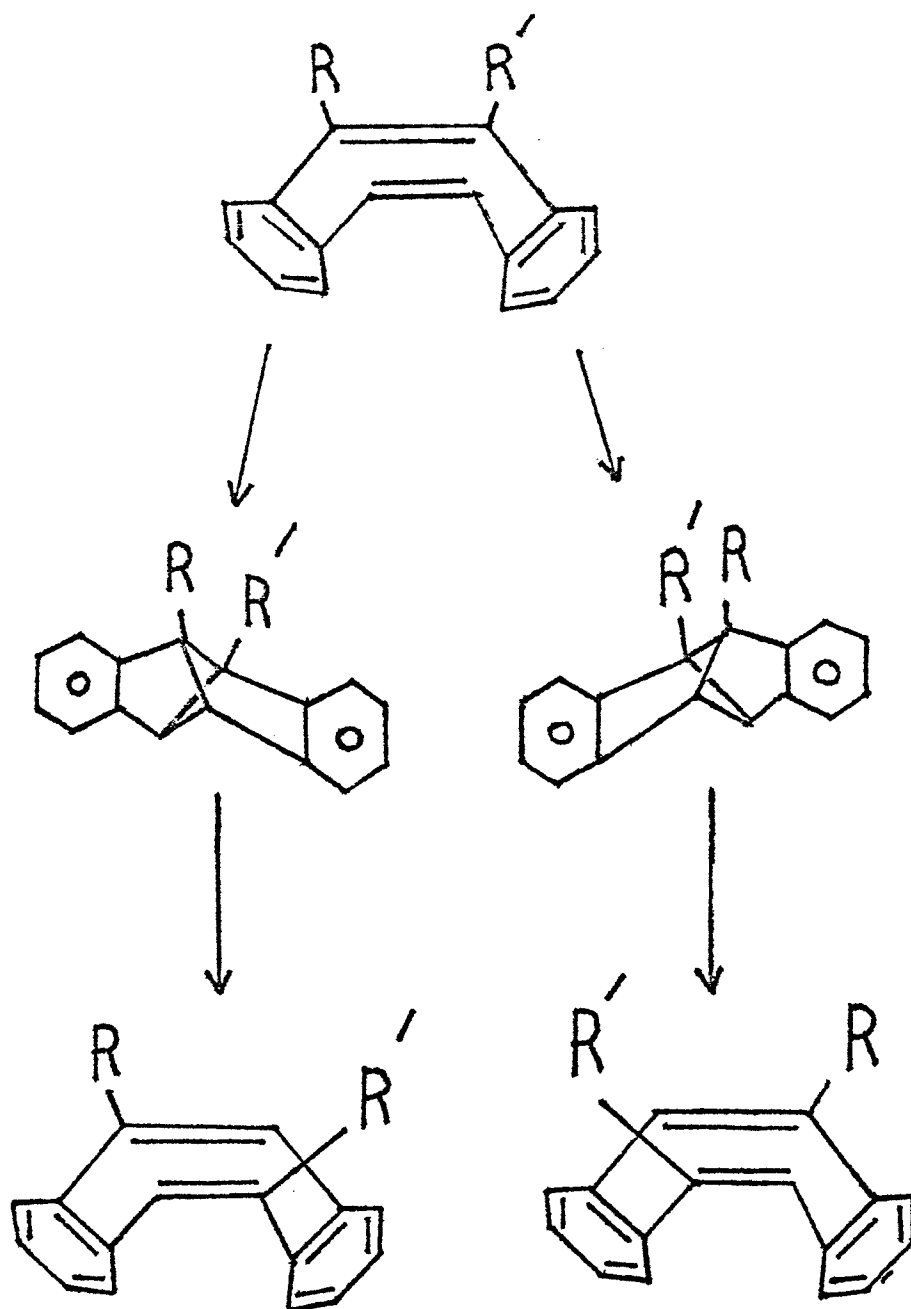
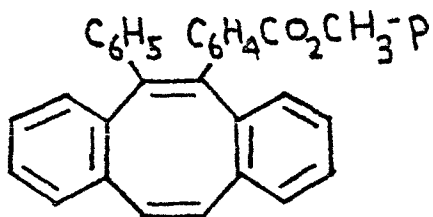
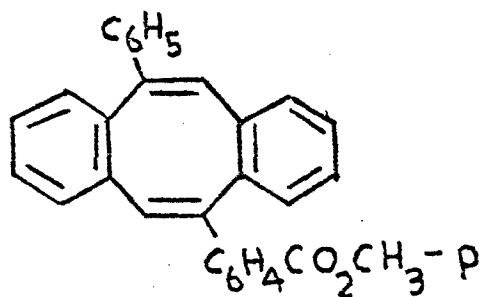


Chart 5.





XX



XXI

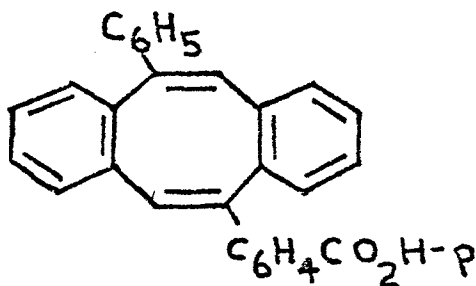
Table 2

Rearrangement and Optical Activity Loss of (+)-5-phenyl-6-(p-carbomethoxyphenyl)-dibenzo[a,e]cyclooctatetraene (XX)

Temp. C°	(k), sec ⁻¹ rate of optical activity loss	(k _r), sec ⁻¹ rearrangement rate	k/k _r
156.5	1.80x 10 ⁻⁵	1.4x 10 ⁻⁵	1.28
164.4	3.72x 10 ⁻⁵	2.92x 10 ⁻⁵	1.27
176.9	9.52x 10 ⁻⁵	7.65x 10 ⁻⁵	1.24

The rate comparison yields two conclusions. Since the rate of optical activity loss is approximately twenty per cent greater than the rearrangement rate, concurrent racemization by way of ring inversion adds to the racemization rate derived from the rearrangement pathway. Also some reversible step in the rearrangement leads to racemization of the starting material, compound XX. Since the correct choice between the two conclusions can not be made from this data another more fruitful experiment was conducted.

(-)-5-phenyl-11-(p-carboxyphenyl)-dibenzo[a,e]cycloocta-
tetraene (XXII)



The racemization of compound XXII had a rate that was much greater than that of rearrangement or loss of optical activity of the 5,6 derivative, compound XX. Table 3 shows the rate comparisons. Looking at Table 3 it seems unlikely that racemization of the 5,11 derivative, compound XXII, proceeds by way of a reversible rearrangement mechanism. This is because of the relatively close values for the rearrangement of the (+)-5,6 compound (XX) and the racemization of the 5,11 derivative (XXII). The rearrangement of the (+)-5,6 compound (XX) is at a considerable higher temperature yet the rates are very close. It is important to note that a rearrangement by a 5,11 derivative has not occurred; only the 5,6 derivatives have successfully undergone rearrangement (26,27,28). Such a racemization pathway is available only if reversal proceeds as far as the tricyclic intermediate stage. The tricyclic intermediate should lie close to the transition state of the rearrangement, bearing in mind the highly strained structure. Therefore the energy

of activation for racemization by way of a reverse rearrangement pathway should be greater than that for the rearrangement itself. This can be seen, by comparing the energies of activation in Table 4, to be just the opposite.

In conclusion, compounds such as III racemize by ring inversion while compounds such as XX lose optical activity principally by way of rearrangement. The behavior of XX is explainable by assuming that the bulky aryl groups buttress one another during ring flattening. Therefore rearrangement becomes the less energetic pathway to optical activity loss. The rearrangement proceeds via diradicals. The formation of the biradical precedes the tricyclic intermediate, (XXIII, Chart 6). Biradicals I_a and I_b have been verified by thiol trapping experiments (27). Although XXIII is proposed as the next intermediate in the reaction scheme by conjecture, actual detection is as yet unpublished.

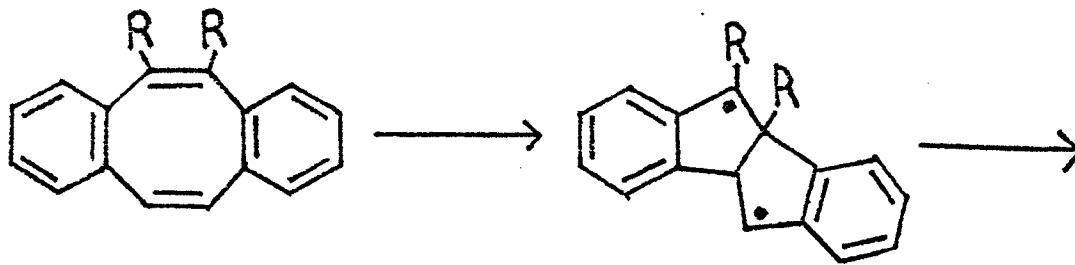
Table 3

Comparisons of the Rate Constants for 5,6 Disubstituted Di-
benzo [a,e] cyclooctatetraenes

Compound	Process	Temp. C ^o	Rate Constants
(+) XX	Rearr.	164.4	2.91 x 10 ⁻⁵
(+) XX	Op. Act. Loss	164.4	3.72 x 10 ⁻⁵
(-) XXII	Racemiza.	110.3	2.26 x 10 ⁻⁵
I	Racemiza.	110.3	3.47 x 10 ⁻⁵

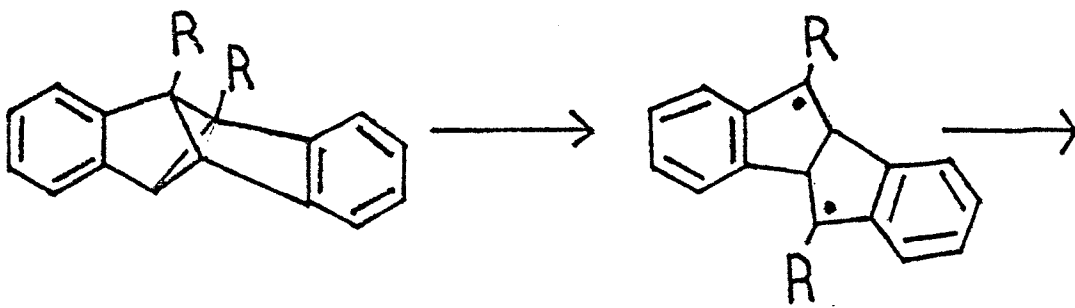
Chart 6 .

Biradical Rearrangement of 5,6 Disubstituted Dibenzo[a,e]cyclooctatetraenes



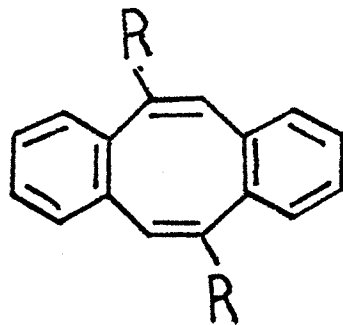
VIII

I_a



XIII

I_b



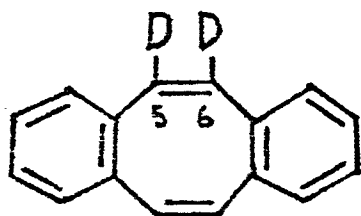
IX

Table 4

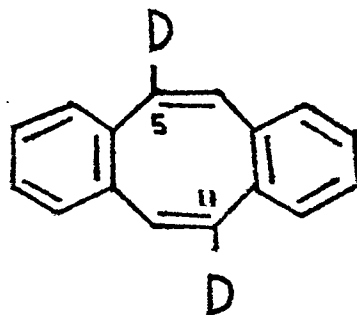
Comparisons of Energy of Activation for 5,6 Disubstituted Dibenzo [a,e] cyclooctatetraenes

Compound	Process	E_a kcal/mole	H
(+) XX	Rearr.	31.5	30.6
(+) XX	Op. Act. Loss	31.0	30.5
(-) XXII	Racemiza.	25.3	24.5
III	Racemiza.	27.5	26.7

The formation of free radicals (I_a and I_b), if involved in the rearrangement of 5,6 to 5,11 diaryl DBCOTs, would probably be prevented by removing the phenyl groups. Two compounds were synthesized in this thesis to verify the rearrangement by thermolysis without substituents that would stabilize the radical species. Labeling DBCOT in the 5,6 and 5,11 positions afforded such a means. Compounds XXIV and XXV were the two isomers of interest. Chart 7 depicts the unsuccessful approach to the 5,11 isomer, which revealed a possible synthetic technique for deuterium labeling in the course of a Wittig reaction. The successful formation of the 5,11 isomer (Chart 8) was accomplished by rationalizing the events of the Wittig reaction on compound XXXII (Chart 7). Chart 9 shows the unsuccessful attempt to procure the 5,6 isomer due to the unstable nature of the acetylene precursor (XLV) (39). The 5,6 isomer was eventually prepared by the method outlined in Chart 10. Once the two isomers were in hand thermal rearrangement experiments in a solution of decalin- d_{18} and as the pure melt were performed.



XXIV



XXV

Chart 7.

Unsuccessful Attempt at Synthesizing Compound XXV

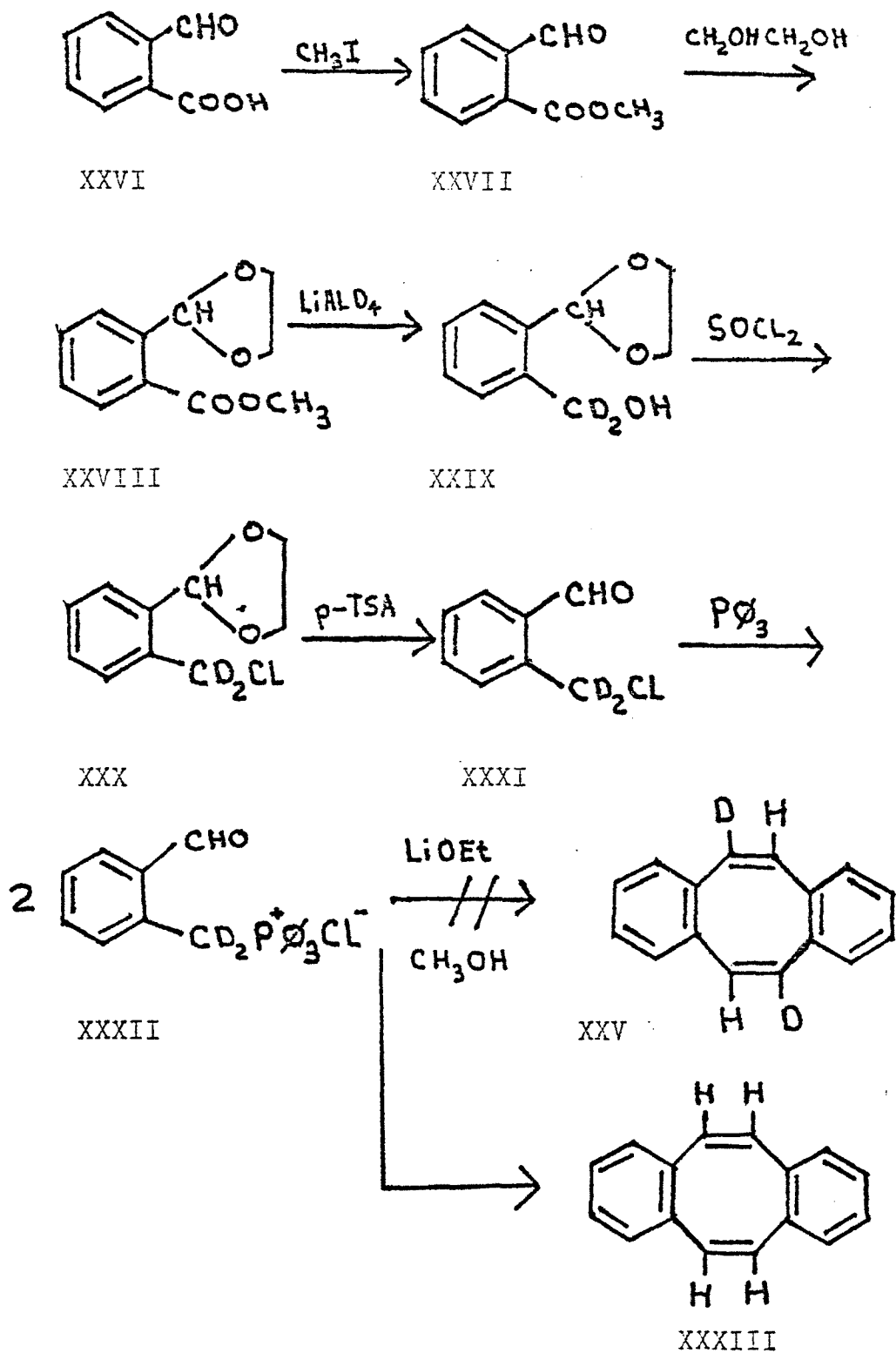


Chart 8.

Successful Attempt at Synthesizing Compound XXV

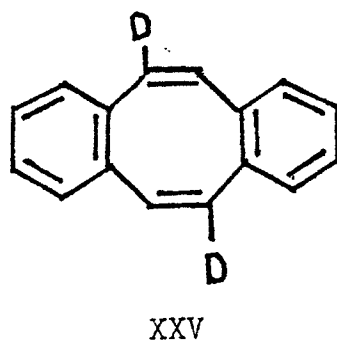
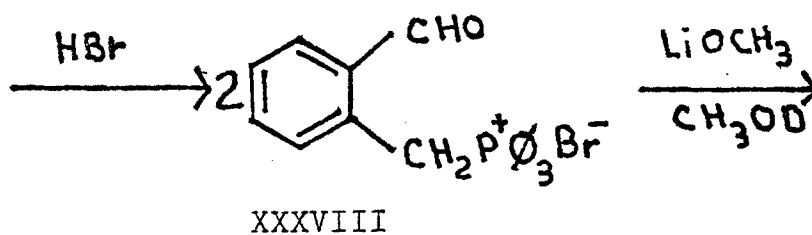
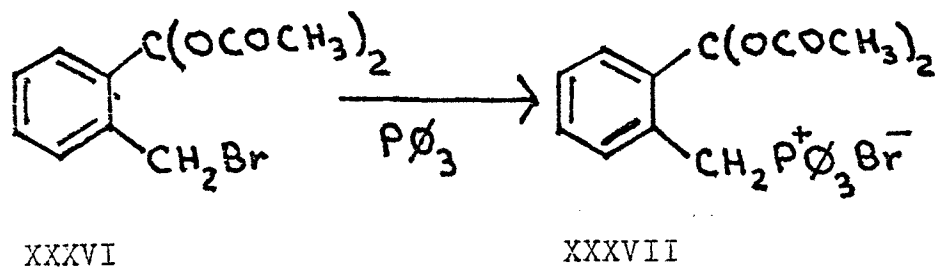
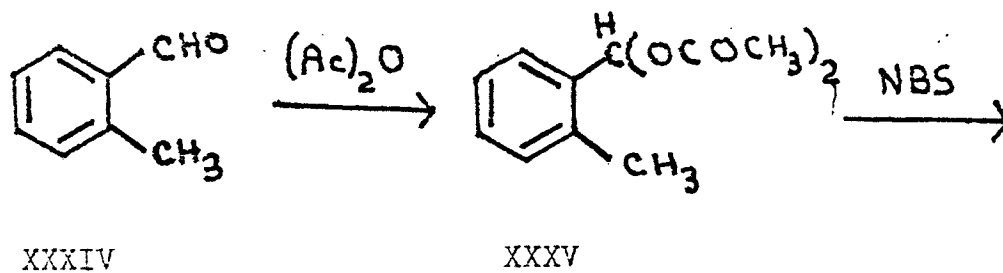


Chart 9.

Unsuccessful Attempt at Synthesizing Compound XXIV

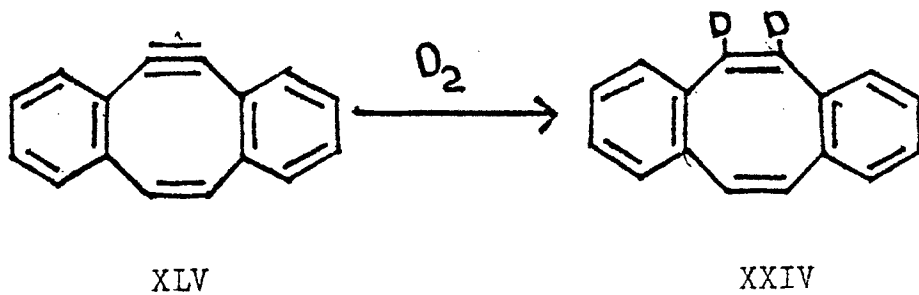
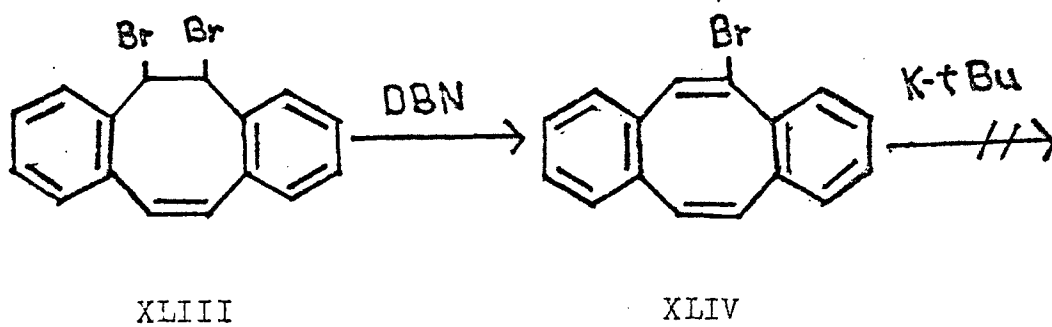
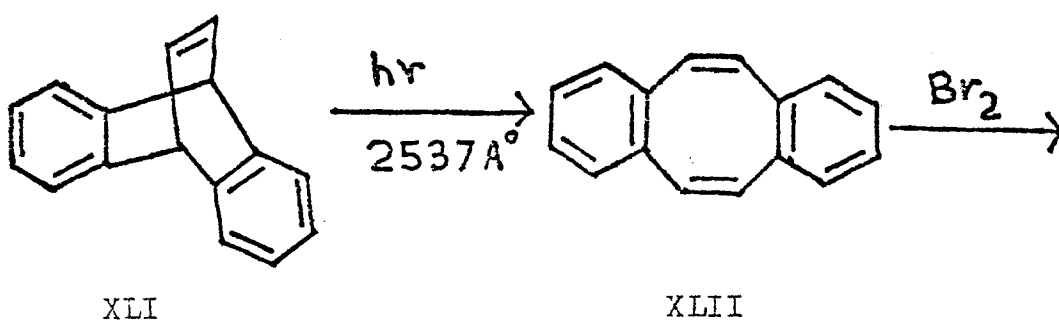
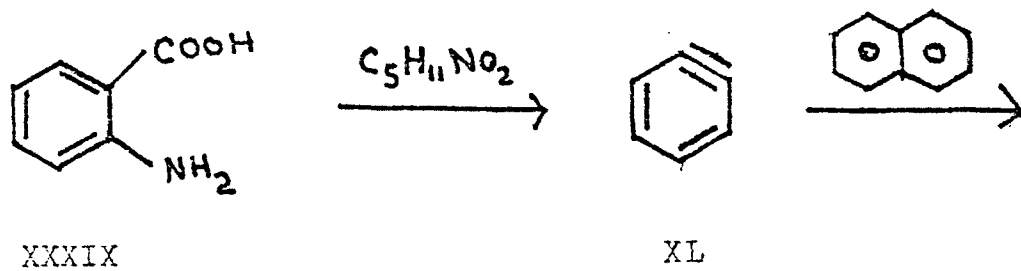
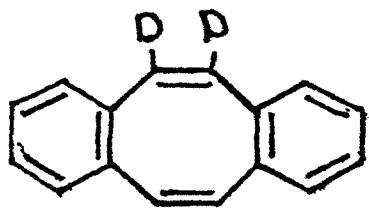
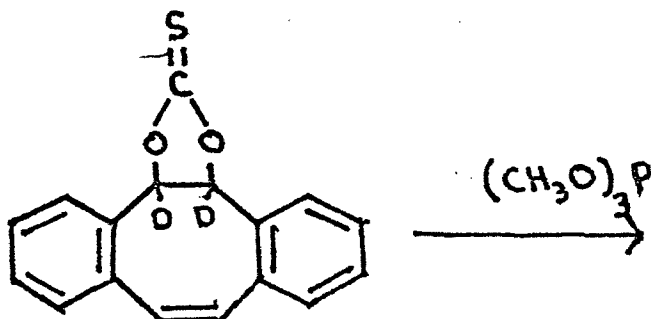
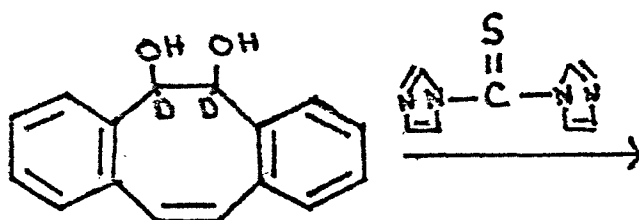
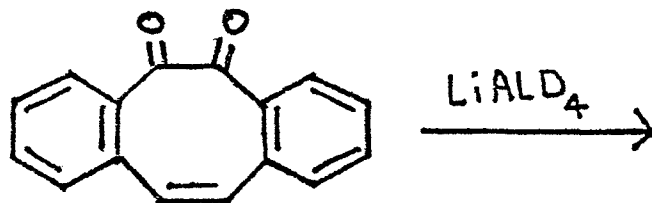


Chart 10.

Successful Attempt at Synthesizing Compound XXIV



II. Experimental

- (a) All NMRs were done on a JEOL FX-900 spectrometer, by Dr. Michael Shapiro of Sandoz, Inc. East Hanover, N.J.
- (b) All IRs were done on a Beckman 33 spectrometer.
- (c) All UVs were done on a Perkin-Elmer 571 spectrometer.
- (d) All melting points were corrected.

A. Unsuccessful Preparation of 5,11-Dideuteriodibenzo [a,e] -
cyclooctatetraene (XXV)

1. Preparation of α, α -Dideuterio-o-formylbenzyl Alcohol
Ethylene Acetal (XXIX)

The acetal (18 g. , 0.0865 mole), (XXVIII), in absolute ether (45 ml) was added dropwise to a stirred suspension of lithium aluminum deuteride (4.974 g. , 0.118 mole) in absolute ether (300 ml). The addition was done at room temperature under nitrogen. The mixture was refluxed for twelve hours. A saturated solution of $MgSO_4$ (20 ml) was added slowly to the ice-bath cooled reaction mixture. The gel was washed with methylene chloride (3 x 50 ml). The ether layer and the methylene chloride washes were combined and dried ($MgSO_4$). The compound was kept in solution over K_2CO_3 until it was to be used. An aliquot of this solution revealed the total crude product (XXIX) to be 10.0 g. (64.3 %). The ir spectrum confirmed the reduction of the ester to the alcohol.

2. Preparation of α, α -Dideuterio-o-formylbenzyl tri-
phenylphosphonium Chloride (XXXII)

The alcohol (XXIX) (10 g. , 0.055 mole) in chloroform (15 ml) and absolute pyridine (7.5 ml , 0.055 mole) was added dropwise with stirring at 0° to thionyl chloride (7.5 ml, 0.055 mole) in chloroform (12 ml). The mixture was then stirred at room temperature for 12 hrs. , after which time the reaction mixture was quenched with an equal volume of crushed ice. The organic layer was separated and washed with water

(5x5 ml), saturated sodium bicarbonate solution (10 ml) and brine (10 ml). The solution was then dried over K_2CO_3 . The residue left on removal of the solvent was dissolved in 134 ml of acetone to which 0.333 g. of p-toluenesulphonic acid had been added. The mixture was then stirred at room temperature for 48 hours. The acid was then neutralized with solid $NaHCO_3$ (0.5 g.) and the volume reduced to 33 ml under reduced pressure. Water (150 ml) was added and the product extracted with CH_2Cl_2 (3x50 ml). The CH_2Cl_2 was washed with brine (50 ml) and dried ($MgSO_4$). On removal of the solvent the residue was distilled at reduced pressure to yield α, α -dideuterio-o-formylbenzyl chloride (4 g. , 0.025 mole), b.p. $88^\circ-90^\circ/0.3$ mm (XXXI). The chloride (4 g. , 45%) was immediately refluxed with triphenylphosphine (9.0 g. , 0.034 mole) in dry benzene (60 ml) for 14 hours. The salt XXXII precipitated, was filtered, washed with ether (5x5 ml), crystallized from ether:methanol (98:2 %) and dried at $100^\circ/0.2$ mm for 2 hours. mp $233-235^\circ$, yield 51 % (5.24 g. , 0.0125 mole).

3. Preparation of 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV)

The phosphonium salt (XXXII), (5 g. , 0.0119 mole) in absolute methanol (160 ml), predried over Mg turnings, was refluxed and stirred under nitrogen during the dropwise addition over three hours of lithium ethoxide. The lithium ethoxide was prepared from 0.083 g. Li (0.0119 mole) and absolute ethanol (16 ml). The ethanol was predried over Mg turn-

ings while refluxing. The mixture was quenched with 600 ml of water, extracted with CH_2Cl_2 (5x100 ml). Then the organic layer was washed with brine (2x50 ml) and dried (MgSO_4). The solid left on removal of the solvent was washed with hot hexane (3x75 ml) to separate the phosphine oxide from the product. The compound was then purified on a preparatory silica gel plate. The elution solvent was pure hexane with the compound being separated by multiple developments (6x). The upper most band on the plate was dibenzo [a,e] cyclooctatetraene (XXXIII), mp $107.5-108^\circ$ (254 mg. , 20%). The nmr spectrum confirmed the absence of any substantial amounts of deuterium. Infrared spectroscopy revealed the absence of a strong C-D band but confirmed the DBCOT. UV confirmed the DBCOT.

B. Successful Preparation of 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV)

1. Preparation of o-Diacetoxymethyltoluene (XXXV)

o-Tolualdehyde (12.5 g. , 0.104 mole), (XXXIV), was added dropwise over 15 minutes under argon to a suspension of Dowex-50 (1.2 g. ; 8% cross linking, 100 mesh) in acetic anhydride (21 g.). The stirred mixture was then heated to 63° for 70 minutes. Then the reaction mixture was cooled, filtered and the filtrate dissolved in methylene chloride (100 ml). The organic layer was dried (MgSO_4). Once the solvent was removed, the diacetate (XXXV) was purified by distillation in

vacuo bp 127-129^o/1 mm, (18.5 g. , 0.0833 mole). The yield was 80%. The ir spectrum confirmed the absence of the aldehyde band and the presence of the ester. The nmr spectrum confirmed the ester.

2. Preparation of o-Diacetoxymethylbenzyl Bromide (XXXVI)

The diacetate (XXXV), (17 g. , 0.0766 mole), N-bromosuccinimide (NBS) (14.3 g. , 0.0766 mole) and benzoyl peroxide (0.23 g.) were added to carbon tetrachloride (100 ml). The mixture was warmed slowly to reflux over 1 hour. The reaction was exothermic so two condensers were fitted to the round bottom. After one hour of reflux the yellow NBS reacted. The succinimide floated to the top. Reaction was complete when no NBS was at the bottom of the flask. The reaction mixture was cooled and filtered. The solid was washed with CCl₄ (2x25 ml) then the CCl₄ solutions were combined and washed with water (2x35 ml) and dried (MgSO₄). Evaporation of the solvent yielded an oil (XXXVI) that was used without further purification. The yield was 82.55 % (19 g., 0.0627 mole).

3. Preparation of Triphenyl-(o-diacetoxymethylbenzyl)-phosphonium Bromide (XXXVII)

The bromide (XXXVI), (19 g. , 0.0627 mole), triphenylphosphine (21.0 g. , 0.08 mole) and dry benzene (160 ml) were refluxed for twelve hours using a drying tube. The mixture was allowed to cool, then filtered. The precipitate was washed well with ether (5x25 ml) and pumped dry under high

vacuum. The yield was 37 %, (31 g. , 0.0549 mole), mp 238-240° (Lit. 206-216°).

4. Preparation of Triphenyl-(o-formylbenzyl)-phosphonium Bromide (XXXVIII)

The diacetoxymethylbenzyl salt (XXXVII), (30 g. , 0.053 mole), was refluxed in hydrobromic acid (490 ml, 14% aq.) for 2.5 hours. Upon warming the bromide would dissolve whereupon the mixture became homogeneous. Upon cooling crystals of the aldehyde (XXXVIII) formed. The solution was refrigerated for 24 hours. It was then filtered and the crystals washed with cold water (3x75 ml). The aldehyde (XXXVIII) was dried at 56.5°/0.3 mm for one hour. mp 263-265° (Lit. 261-272°d) The ir spectrum confirmed the presence of the aldehyde.

5. Preparation of 5,11-Dideuteriodibenzo[a,e]cyclooctatetraene (XXV)

The aldehyde salt (XXXVIII), (5.5 g. , 0.012 mole), in absolute methanol-d₁ (140 ml) was stirred and refluxed under argon during the dropwise addition of Li (0.12 g. , 0.017 mole) in methanol-d₁ (14 ml) over a period of 3 hrs. The methanol-d₁ was predried by refluxing and distillation from Mg turnings. The reaction was then refluxed an additional hour. The reaction was quenched with D₂O (125 ml). After the volume of solvent was reduced under reduced pressure to about 160 ml, the solution was extracted with CH₂Cl₂ (4x50 ml). The CH₂Cl₂ was then washed with brine (D₂O: 20 ml) and dried (Mg-SO₄). The methylene chloride was filtered, the solvent removed at reduced pressure and the remaining solid extracted with

hot hexane (150 ml). The hexane was removed and the residue (1.37 g.) developed in pure hexane on preparatory silica gel plates. The uppermost band was the 5,11-dideuteriodibenzo [a,e] cyclooctatetraene (XXV), (250 mg. , 8%), mp 104-105°. Infra-red spectroscopy confirmed the presence of deuterium and the DBCOT. NMR spectroscopy also confirmed the structure as the 5,11 derivative (XXV). UV spectroscopy confirmed the DBCOT.

C. Preparation of 5,6-Dideuteriodibenzo[a,e]cyclooctatetraene (XXIV)

1. Preparation of 5,6-Dideuteriodibenzo[a,e]cyclooctene-5,6-diol (XLVII)

The dibenzo[a,e]cyclooctene-5,6-dione (XLVI), (0.8 g. , 0.34 mole) in absolute ether (18 ml) was added dropwise to a stirred solution of LiAlD_4 (0.188 g. , 0.45 mmole) in absolute ether (10 ml). The mixture was refluxed for 3 hours under nitrogen, after which time a fresh saturated solution of Na_2SO_4 (anhyd.) in D_2O (15 ml) was added. The aqueous layer becomes gelatinous. The ether layer was separated, the gel was washed with ether (3x15 ml), filtered and the ether layers combined. The ether layers were dried (MgSO_4). The solvent was removed and the solid recrystallized from benzene. The white solid (XLVII), (0.3 g. , 37.38%) had a mp of 187-188°. The ir spectrum confirmed reduction of the dione to the diol. The literature value for the diol without the deuterium was 188-189° for the melting point. The nmr spectrum also confirmed the compound.

2. Preparation of the 0,0' Thiocarbonate of 5,6 dideuterio-dibenzo [a,e] cyclooctene-5,6-diol (XLVIII)

The diol (XLVII) (0.3 g. , 0.13 mmole) and the thiocarbonyldiimidazole (0.215 g. , 0.14 mmole) were added to dry toluene (10 ml). The solution was stirred and refluxed for 90 minutes. The solution was then allowed to cool, washed with water (2 ml), brine (2 ml) and dried (CaCl_2). Removal of the solvent left a slightly yellow solid which was recrystallized from benzene:ether (3%:97%). The solid (XLVIII) had a mp of 216-217°, (0.230 g., 65%). The ir spectrum confirmed the thiocarbonate band.

3. Preparation of 5,6-Dideuteriodibenzo [a,e] cyclooctatetraene (XXIV)

The 0,0' thiocarbonate of 5,6-dideuteriodibenzo [a,e] cyclooctene-5,6-diol (XLVIII), (230 mg. , 0.82 mmole), was heated under argon and stirred for 3.5 days in trimethyl phosphite (50 ml). The system was alternately evacuated and flushed with argon several times before the reaction was commenced. After 3.5 days the reaction was quenched with 50 ml of 20% NaOH (aq.), the solution was stirred until one layer was apparent (10 hrs.). The solution was extracted with methylene chloride (2x50 ml), then with water until neutral (5x 15 ml), brine (20 ml) and dried (MgSO_4). Removal of the solvent under reduced pressure afforded a solid which was developed on a silica gel preparatory plate in pure hexane. The fastest moving band was the 5,6-dideuterio-DBCOT (XXIV), (100 mg. , 0.49 mmole, 59.5%). mp 106-107°, a mixed mp with the

nondeuterated sample showed no depression. The ir spectrum confirmed deuterium in the DBCOT compound. The nmr spectrum confirmed deuteration in the 5,6 positions. The uv spectrum substantiated the structure as that of DBCOT.

D. Thermolysis of Deuterium Labeled Dibenzo [a,e] cyclooctatetraenes

1. Thermolysis of Molten 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV) at 182°

The 5,11 derivative (XXV), (5 mg.), was placed in a sealed tube and alternately evacuated and flushed with argon (6x) to remove any oxygen. The end of the tube was then sealed under argon. The tube was submersed in an oil bath at 182° for 17 hours, after which time the tube was allowed to cool and the contents washed out of the tube with methylene chloride. The solid, on removal of the solvent, was developed on a preparatory silica gel plate in pure hexane. Multiple development (7x) yielded a top band with a mp of 105-106°, (4 mg. , 80%). The nmr spectrum showed the compound to be starting material.

2. Thermolysis of Molten 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV) at 228°

The 5,11 derivative (XXV), (5 mg.), was placed in a sealed tube and alternately evacuated and flushed with argon (6x) to remove any oxygen. The end of the tube was then sealed under argon. The tube was submersed in a Woods metal bath at 228° for 18 hours, after which time the tube was allowed to cool for a while. The contents of the tube were washed out with methylene chloride. The solid, on evaporation of the solvent, was

developed on a preparatory silica gel plate in pure hexane. Multiple development (7x) yielded a top band with an mp of 105-106°, (4 mg. , 80%). The nmr spectrum showed the compound to be starting material.

3. Thermolysis of Molten 5,6-Dideuteriodibenzo[a,e]cyclo-octatetraene (XXIV) at 182°

The 5,6 derivative (XXIV), (5 mg.), was placed in a sealed tube and alternately evacuated and flushed with argon (6x) to remove any oxygen. The end of the tube was then sealed under argon. The tube was submersed in an oil bath at 182° for 17 hours, after which time the tube was allowed to cool and the contents washed out of the tube with methylene chloride. The solid obtained on evaporation of the solvent was developed on a preparatory silica gel plate in pure hexane. Multiple development (7x) yielded the product as a top band with an mp of 105-106°, (3.4 mg. , 70%). The nmr spectrum showed the compound to be starting material.

4. Thermolysis of Molten 5,6-Dideuteriodibenzo[a,e]cyclo-octatetraene (XXIV) at 228°

The 5,6 derivative (XXIV), (5 mg.), was placed in a sealed tube and alternately evacuated (9x) and flushed with argon to remove any oxygen. The end of the tube was then sealed under argon. The tube was submersed in a Woods Metal bath at 228° for 18 hours, after which time the tube was allowed to cool. The contents were extracted with methylene chloride. The residue on evaporation of the solvent was purified on a preparatory silica gel plate with hexane as the elution solvent.

The uppermost band was collected (3 mg. , 60%). The nmr spectrum showed only starting material.

5. Thermolysis of 5,6-Dideuteriodibenzo [a,e] cyclooctatetraene (XXIV) in Decalin-d₁₈ at 182°

The 5,6 derivative (XXIV), (5 mg.), in a 0.1 ml solution of decalin-d₁₈ was placed in an nmr tube and evacuated and flushed alternately with argon (8x). The nmr tube had a ground glass joint with which to seal the tube. The solution was heated for 18 hours, in an oil bath at 182°, after which time the tube was cooled and CDCl₃ (0.2 ml) was added. An nmr spectrum of the solution showed only starting material.

6. Thermolysis of 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV) in Decalin-d₁₈ at 228°

The 5,11 derivative (XXV), (5 mg.), in 0.1 ml of decalin-d₁₈ was placed in a sealed tube and alternately evacuated and flushed with argon (9x). The tube was sealed under argon and immersed in a Woods Metal bath at 228° for 18 hours, after which the tube was allowed to cool. The contents of the tube was placed in an nmr tube with 0.18 ml CDCl₃. An nmr analysis of the contents revealed only starting material.

7. Thermolysis of 5,6-Dideuteriodibenzo [a,e] cyclooctatetraene (XXIV) in Decalin-d₁₈ at 228°

The 5,6 derivative (XXIV), (5 mg.), in 0.13 ml of decalin-d₁₈ was placed in a sealed tube and alternately evacuated and flushed with argon (9x). The tube was sealed under argon and immersed in a Woods Metal bath at 228° for 18 hours.

The tube was allowed to cool and the contents placed in an nmr tube with 0.19 ml of CDCl_3 . An nmr analysis of the contents of the tube revealed only starting material.

III. Discussion of Results

A. Preparative Part

1. α, α -Dideuterio- o-formylbenzyl Alcohol Ethylene Acetal (XXIX)¹

The method used was that of Brown and Sargent (29), who used LiAlH_4 in the reduction of the methyl o-formylbenzoate ethylene acetal (XXVIII). The alcohol (XXIX) was stable in solution in the presence of a small amount of K_2CO_3 . Isolation of the oil from solution was difficult in that on standing a short period of time (1-2 hrs.) the oil deglycolizes (39) to form a solid. The compound can not be distilled in vacuo due to the unstable nature of the compound. The compound was kept in solution over K_2CO_3 until ready for use. The ir spectrum (neat) showed bands at 3300 cm^{-1} (OH), 2200 cm^{-1} (C-D), 2100 cm^{-1} (C-D), which confirmed reduction of the ester to the alcohol and the addition of deuterium to the benzyl alcohol.

2. α, α -Dideuterio-o-formylbenzyl Triphenylphosphonium Chloride (XXXII)¹

The method used was that of Brown and Sargent (29). The aldehyde-o-benzyl chloride (XXXI) tends to decompose and should be reacted immediately with triphenylphosphine to form the salt (XXXII). The (mp $233\text{-}235^\circ$; Lit. $233\text{-}235^\circ$) ir spectrum confirmed the o-formylbenzyltriphenylphosphonium Cl (XXXII) with a band at 1692 cm^{-1} (CHO).

1. Reaction depicted on Chart 7.

3. 5,11-Dideuteriodibenzo [a,e] cyclooctatetraene (XXV)¹

The method used was that of Brown and Sargent (29). The Wittig product was extracted with hexane to separate the major portion of the triphenylphosphine oxide from the product. Exchange of deuterium with hydrogen in the methanol had occurred with 100% conversion (within error of instrumental analysis). mp 107-108°, the nmr spectrum showed peaks at δ 7.05 (s, 8H, ArH's) and δ 6.70 (s, 4H, olefinic H). The ir spectrum confirmed DBCOT without any deuterium. The uv spectrum was consistent with DBCOT, 240 m μ , (ϵ = 29,400), shoulder at 270 m μ .

4. o-Diacetoxymethyltoluene (XXXV)²

o-Tolualdehyde (XXXIV) was reacted with acetic anhydride catalyzed by use of Dowex-50 (8% cross linking, 50-100 mesh). The procedure for the diacetate was not given by Berenguer (31), so a series of similar compounds were investigated in Chemical Abstracts. The procedure of Yamada and Tsurui (32) was used. The distillation data was arrived at by comparison of data for similar compounds. The ir spectrum, using CCl₄, showed peaks at 1775 cm⁻¹ (s), 1380 cm⁻¹ (s), 1225 cm⁻¹ (triplet, s), and 1060 cm⁻¹, (doublet, m) which are consistent with the compounds structure.

5. o-Diacetoxymethylbenzyl Bromide (XXXVI)²

The method used was that of a similar compound o-nitrotoluene (33). Only an outline of steps were given by Berenguer (31). The diacetate (XXXV) was brominated with N-bromo-

1. Reaction depicted in Chart 7.

2. Reaction depicted in Chart 8.

succinimide in CCl_4 with benzoyl peroxide added to initiate reaction. The product was an oil that decomposed on distillation even under high vacuum, eg. 0.1-0.3 mm. Attempts to check purity on the G.C. were thwarted since the bromide (XXXVI) decomposed in the injection needle on insertion in the septum due to the heat of the injector. The product used was the crude. The ir spectrum peaks at 1600 cm^{-1} (W), 1425 cm^{-1} (M), and 750 cm^{-1} (S) were consistent with the structure of the compound as compared to the values given by Berenguer (31). The nmr spectrum substantiated the structure of the compound with values of δ 2.23 (6H's, OCOCH_3 , S), δ 3.51 (2H's, CH_2Br , S), δ 8.0 (4H's, Aro, Multi.) and δ 8.45 (1H, S).

6. Triphenyl (o-diacetoxymethylbenzyl)-phosphonium Bromide (XXXVII)¹

The method used was that of Brown and Sargent (29) for the formation of the phosphonium salt with the chloride. The yield here for the bromide (XXXVII), (87%), was much higher than the same reaction with the chloride salt (XXXII), (51%). The mp of $238-240^\circ$ was indicative of the salt, by comparison with literature it was much more pure ($206-216^\circ$, Lit.). The ir spectrum (KBr 2%) showed peaks at 1760 cm^{-1} and 1743 cm^{-1} which are consistent with the structure of the compound.

These values were equivalent to literature values.

7. Triphenyl (o-formylbenzyl) Phosphonium Bromide (XXXVIII)¹

The literature procedure was for o-nitrobenzaldiacetate.

1. Reaction depicted in Chart 3.

The method used was that of Tsang and Wood (34) by refluxing the salt in aqueous HBr acid. The aldehyde was produced in 71% yield. The mp of 263-265°d was sharper than the literature value (29) of 261-272°d. The ir spectrum (KBr 2%) showed peaks at 2858 cm⁻¹, 2825 cm⁻¹, 2768 cm⁻¹ and 1675 cm⁻¹ which proved consistent with the structure of the compound as compared to values given by Berenguer (31).

8. 5,11-Dideuteriodibenzo[a,e]cyclooctatetraene (XXIV)¹

The method of Brown and Sargent (29) was used for the Wittig reaction. Modification by use of deuterated solvents and methanol-d₁ for the base rather than ethanol proved rewarding. The methanol-d₁ was easier to dry than the ethanol. The yield on the Wittig reaction for the 5,11 derivative (XXIV) was 8% whereas the literature has noted 6% (31). The use of deuterated methanol affected the exchange of deuterium for the labile hydrogen in the ylide with its carbanion character. The deuteration yielded a 5,11 derivative of DBCOT with 100% conversion (within error of instrumental analysis). The nmr spectrum had peaks at δ 7.05 for 8H's aromatic, and δ 6.70 for 2H's olefinic, (triplet at δ 6.70 due to adjacent ²H, I=1). The uv spectrum was consistent with that of DBCOT, 240 m μ , (ϵ = 29,400), shoulder at 270 m μ . The ir spectrum confirmed DBCOT.

1. Reaction depicted in Chart 8.

9. 5,6-Dideuteriodibenzo [a,e]cyclooctene-5,6-diol (XLVII)¹

The method used was that of Bendall (35) wherein LiAlH_4 was used. LiAlD_4 was substituted in order to place deuterium on the carbon skeleton of the COE ring in the 5,6 positions. The ir spectrum confirmed the structure of the compound, 3375 cm^{-1} (s), (OH); 2500 cm^{-1} (s), (doublet, O-D); 1490 cm^{-1} , 1400 cm^{-1} , and 1130 cm^{-1} which were equivalent with literature values given by Berenguer (31).

10. 0,0' Thiocarbonate of Dibenzo [a,e] cyclooctene-5,6-diol (XLVII)¹

The method used was that of Corey and Winter (36,37). N,N' thiocarbonyldiimidazole reacted with the diol (XLVII) in dry toluene to form the cyclic thionocarbonate in 65% yield. The ir spectrum of the thiocarbonate has two bands that are broad and strong, 1260 cm^{-1} and 1320 cm^{-1} .

11. 5,6-Dideuteriodibenzo [a,e] cyclooctatetraene (XXIV)¹

The method used was that of Corey and Winter (36,37). The olefin was formed by desulfurization-decarboxylation of the thiocarbonate ring by refluxing the thiocarbonate (XLVII) in trimethyl phosphite for 72 hours. After which time the trimethyl phosphite was reacted with aqueous NaOH. On removal of the solvent the solid was purified on silica gel plates. The nmr spectrum had peaks at δ 7.05 (8Hs, ArH's), δ 6.72 (2H's, olefinic). The ir spectrum showed peaks at 2230 cm^{-1}

1. Reaction depicted in Chart 10.

(C-D) and 2200 cm^{-1} (C-D). The UV spectrum was that of DBCOT, $240\text{ m}\mu$, ($\epsilon=29,400$), shoulder at $270\text{ m}\mu$.

B. Comparisons of the Spectral Data of the Dibenzo[a,e]cyclooctatetraene, 5,6- and 5,11-Dideuteriodibenzo[a,e]cyclooctatetraenes.

The ir spectra of the 5,6-dideuteriodibenzo[a,e]cyclooctatetraene (Fig. 4) and the 5,11-dideuteriodibenzo[a,e]cyclooctatetraene (Fig. 5) are identical, with C-D bands at 2230 cm^{-1} and 2200 cm^{-1} . The bands between 2000 cm^{-1} and 1700 cm^{-1} are indicative of 1,2 disubstitution on the aryl ring. Bands at 1500 cm^{-1} (m), 1440 cm^{-1} (m), 1150 cm^{-1} (w) and 750 cm^{-1} (s) are typical of dibenzo[a,e]cyclooctatetraene from known spectra (7,39). The unreacted dibenzo[a,e]cyclooctatetraene spectrum (Fig. 6) was similar to the reacted 5,6 and 5,11 dideuterio isomers, except for the C-D bands, which shows that the compounds are still dibenzo[a,e]cyclooctatetraenes.

The uv spectrum of the 5,6 isomer, 5,11 isomer and the dibenzo[a,e]cyclooctatetraene have identical spectra with an absorption at $240\text{ m}\mu$, ($\epsilon=29,400$), and a shoulder at $270\text{ m}\mu$ (Fig. 7).

The mass spectrum of the 5,6 isomer (Fig. 8) and the 5,11 isomer (Fig. 9) have identical fragmentation peaks as that of the DBCOT (Fig. 10), except for the increase in mass (+2) of the molecular ion in the deuterated compounds.

The nmr spectra were crucial in that they were used to distinguish between the 5,6 and 5,11 isomers. The nmr spectrum of the 5,11 isomer (Fig. 12) had peaks at $\delta 7.05$ (M) for 8H's aromatic and $\delta 6.70$ (T) for 2H's olefinic, (triplet at $\delta 6.70$ due to adjacent ^2H , $I=1$). The 5,6 isomer was identical to the DBCOT except for the integration of the olefinic hydrogens, 2:1, respectively (Fig 11 and Fig. 13).

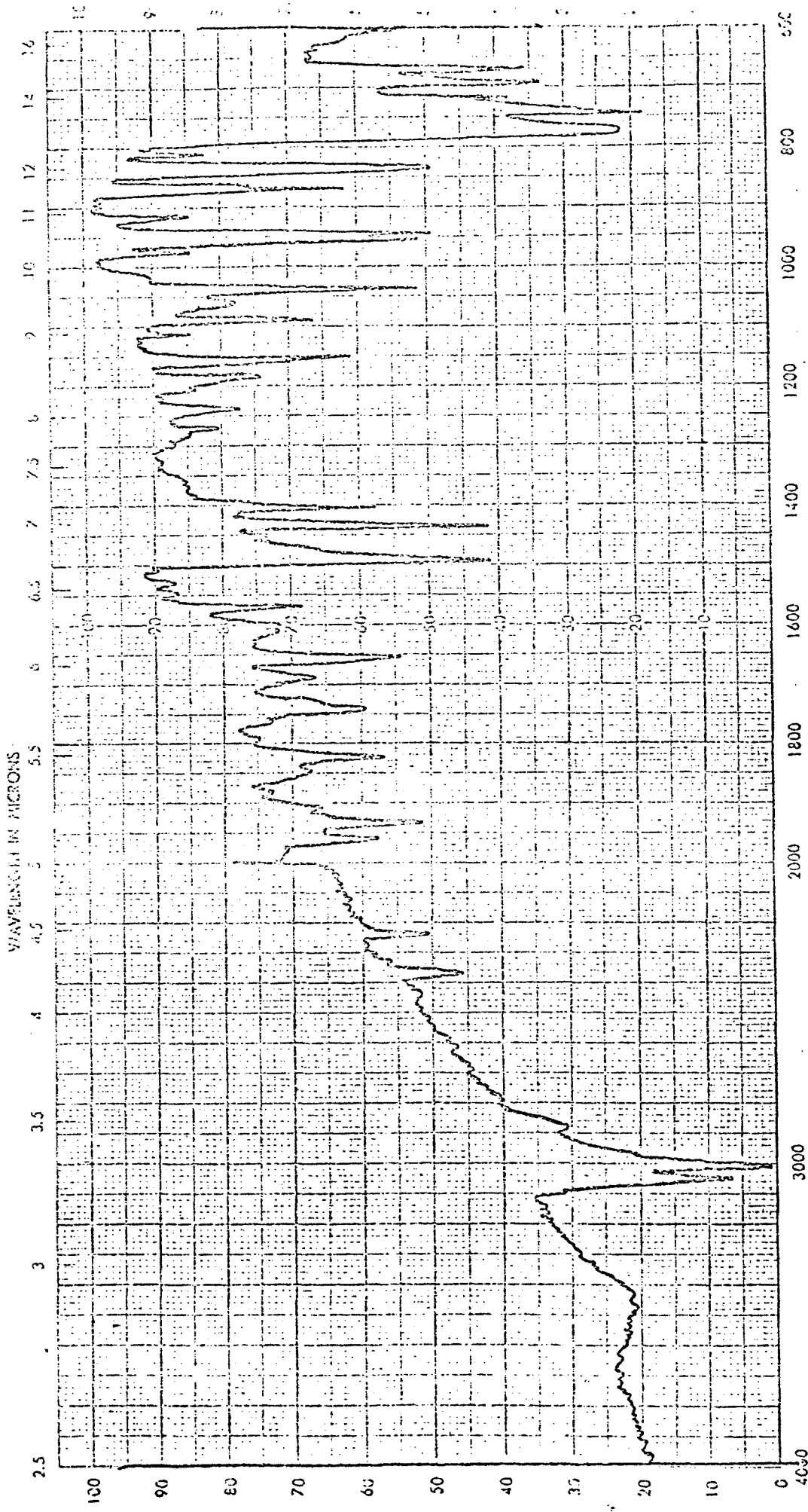
c. Thermolysis of 5,6- and 5,11-Dideuteriodibenzo [a,e] cyclooctatetraenes (XXIV) and (XXV)

The nmr spectroscopy results are tabulated below. There wasn't any rearrangement in any of the experimental runs made.

<u>Conditions</u>	<u>5,6 derivative</u>	<u>5,11 derivative</u> ¹
Molten, 182°	7.05 (8H's, Aro): 6.72 (2H's, olefinic), sharp singlet	7.05 (8H's, Aro): 6.72 (2H's, olefinic), unresolved triplet
Molten, 228°	*same*	*same*
Decalin-d ₁₈ , 182°	*same*	-----
Decalin-d ₁₈ , 228°	*same*	*same*

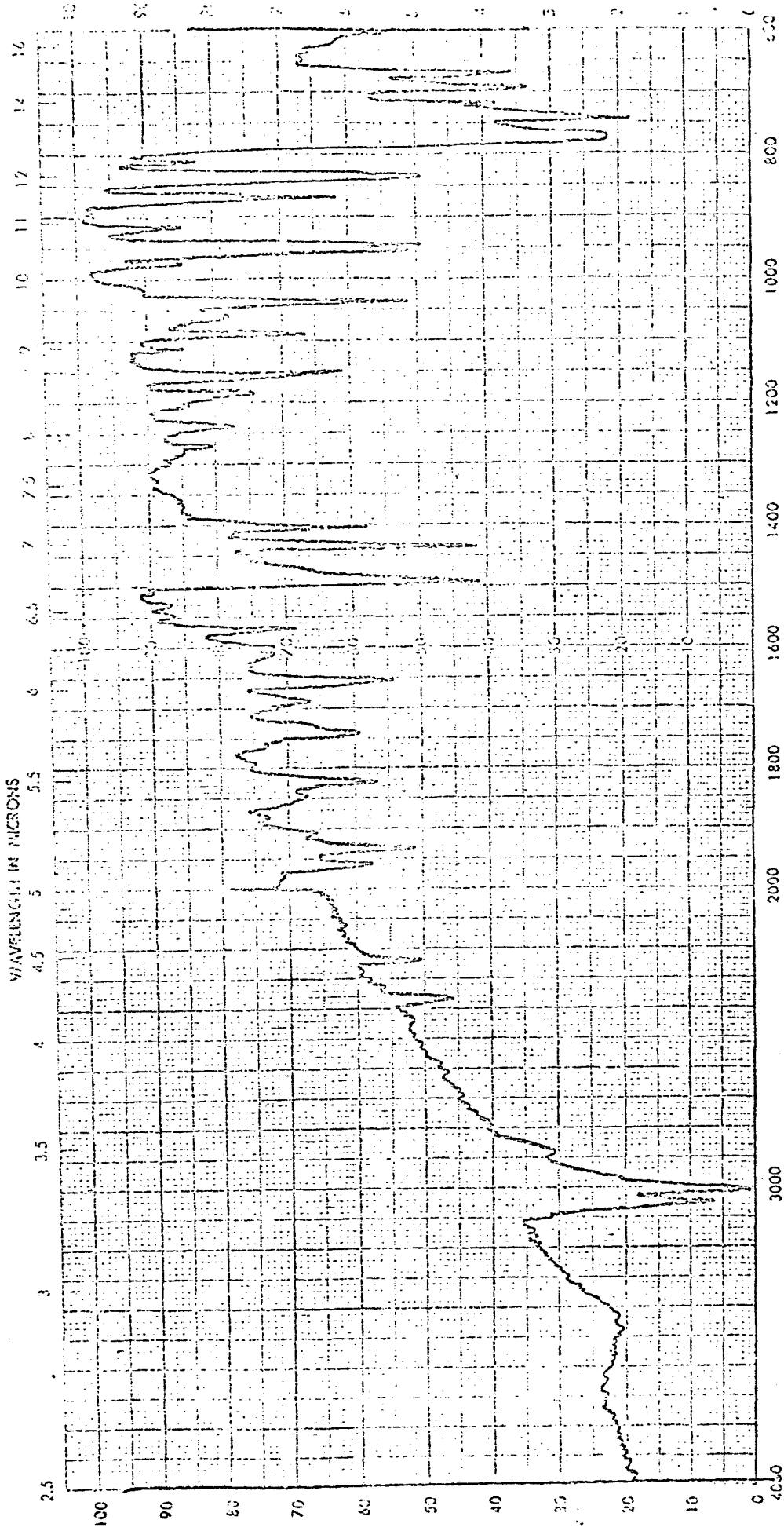
1. The unresolved triplet was due to the adjacent deuterium (²H) where the spin state I is equal to 1.

Figure 4 : I.R. Spectrum (2% KBr pellet)
of 5,6-Dideuteriodibenzo [a,e]
cyclooctatetraene



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Figure 5 : I.R. Spectrum (2% KBr pellet)
of 5,11-Dideuteriodibenzo [a,e]
cyclooctatetraene



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WAVENUMBER SPECIFIC CHART NO. 106568

Figure 6 : I.R. Spectrum (2% KBr pellet)
of Dibenzo [a,e] cyclooctatetraene

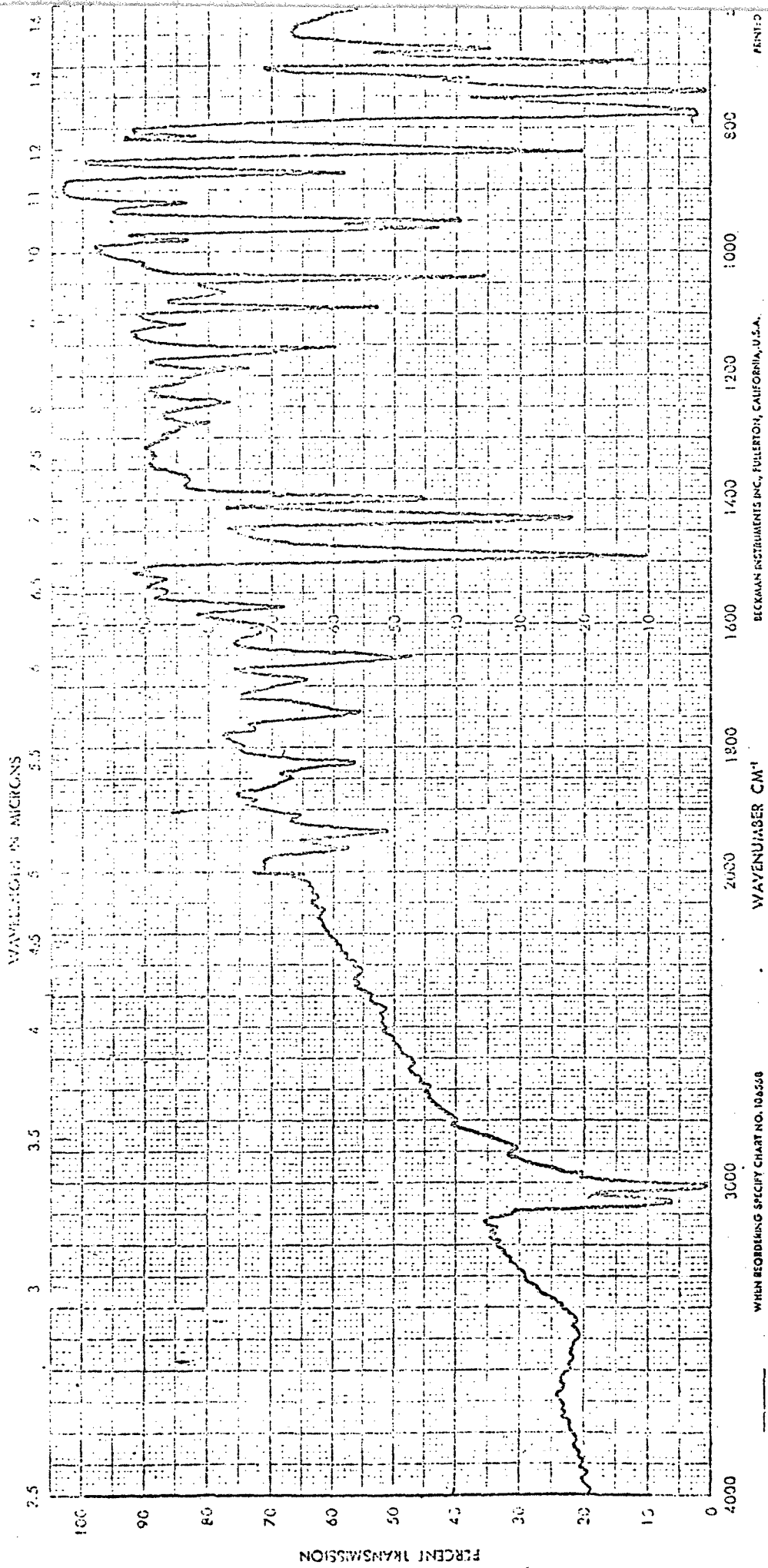


Figure 7 : U.V Spectrum (95% ethanol) of
5,6-Dideuteriodibenzo [a,e] cyclo-
octatetraene ,
5,11-Dideuteriodibenzo [a,e] cyclo-
octatetraene ,
and
Dibenzo [a,e] cyclooctatetraene

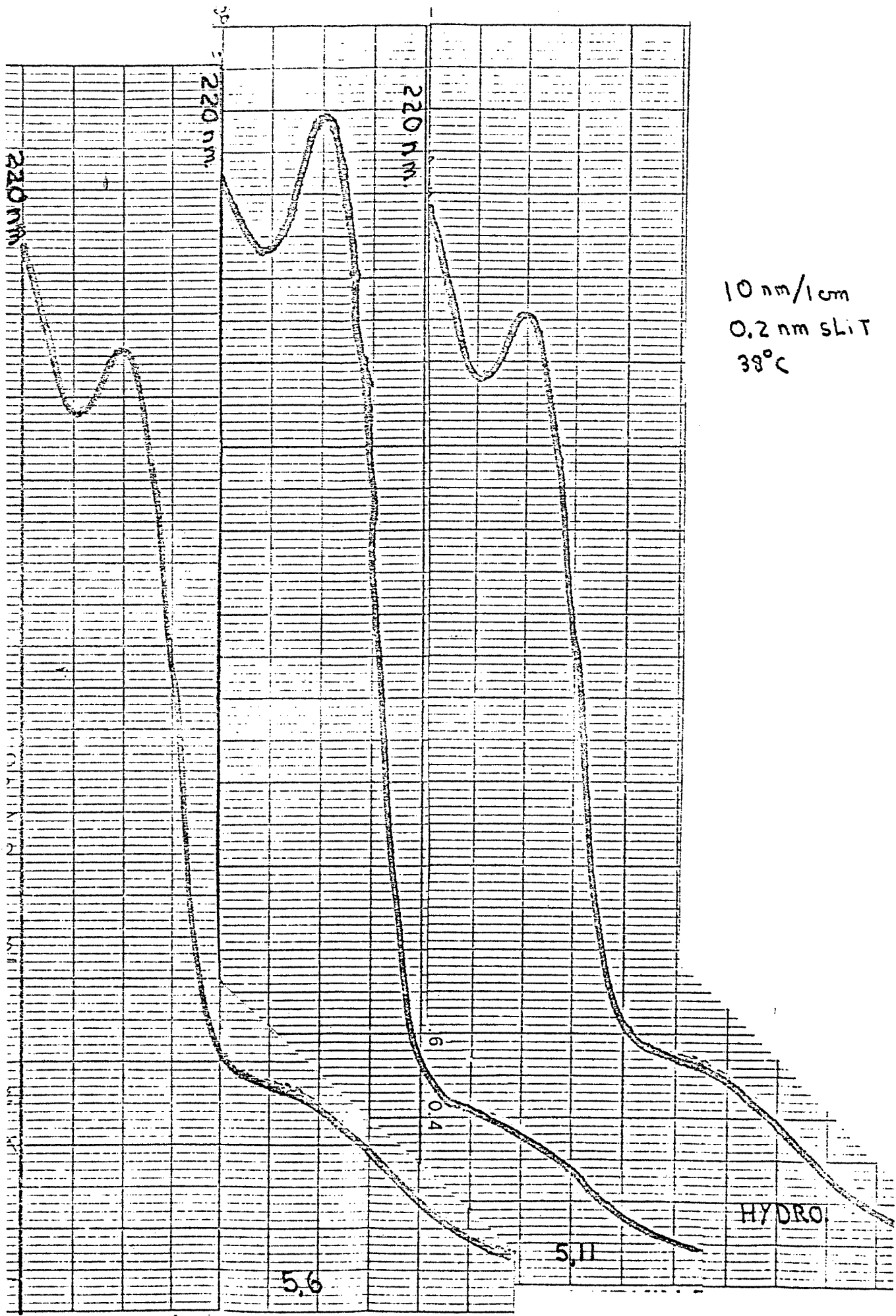
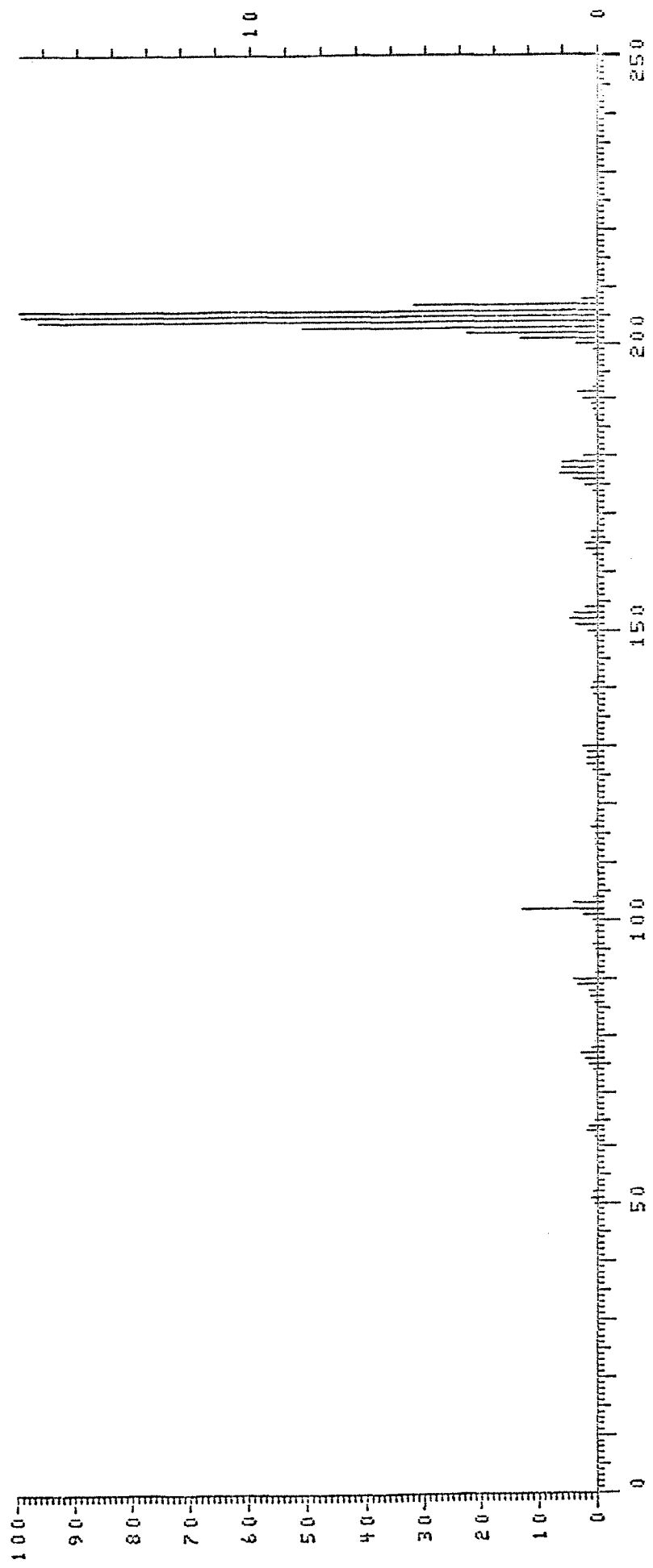
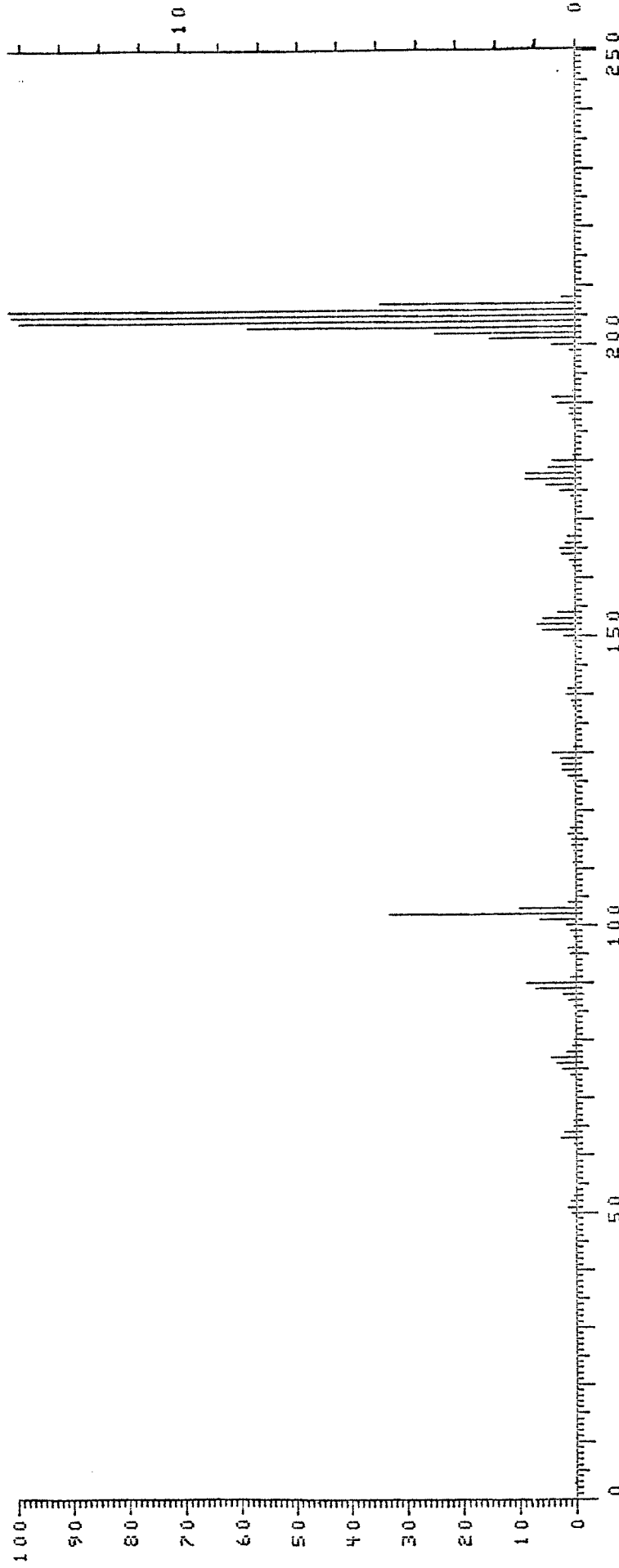


Figure 8 : Mass Spectrum of
5,6-Dideuteriodibenzo [a,e]
cyclooctatetraene



SPEC# 0 LM 5-6 PG106H C.WENGER M.L. STEP MASS=1, I/B/S.C= 1%

Figure 9 : Mass Spectrum of
5,11-Dideuteriodibenzo [a, e]cyclo-
octatetraene

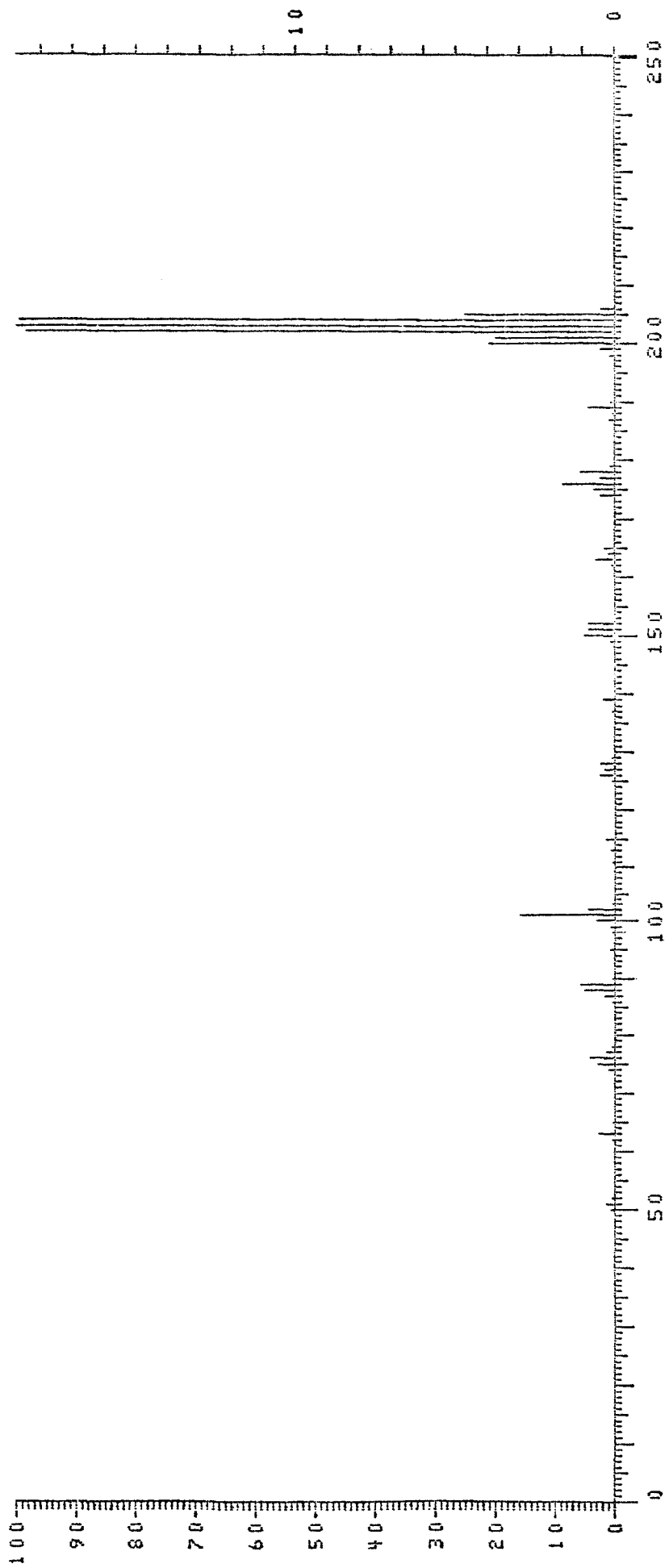


SPEC# 0 LM 5,11 P01068 C.WENGER

N.L.

STEP MASS=1, I/B/S,C= 12

Figure 10 : Mass Spectrum of
Dibenzo [a,e] cyclooctatetraene



REC# 0 LM HYDRO P6106C C.WENGER N.L. STEP MASS=1, I/B/S,C= 1X

Figure 11 : N.M.R. Spectrum of
5,6-Dideuteriodibenzo [a,e] cyclo-
octatetraene

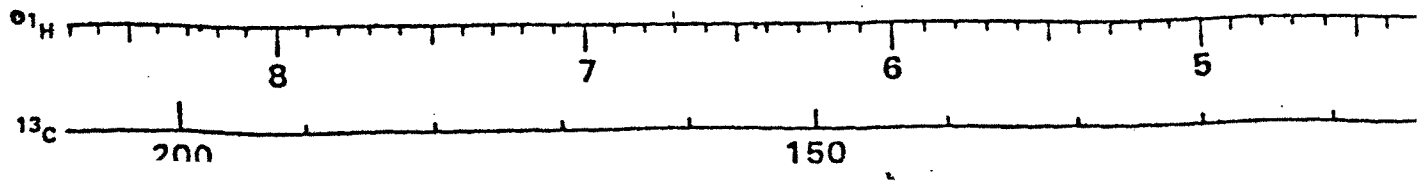
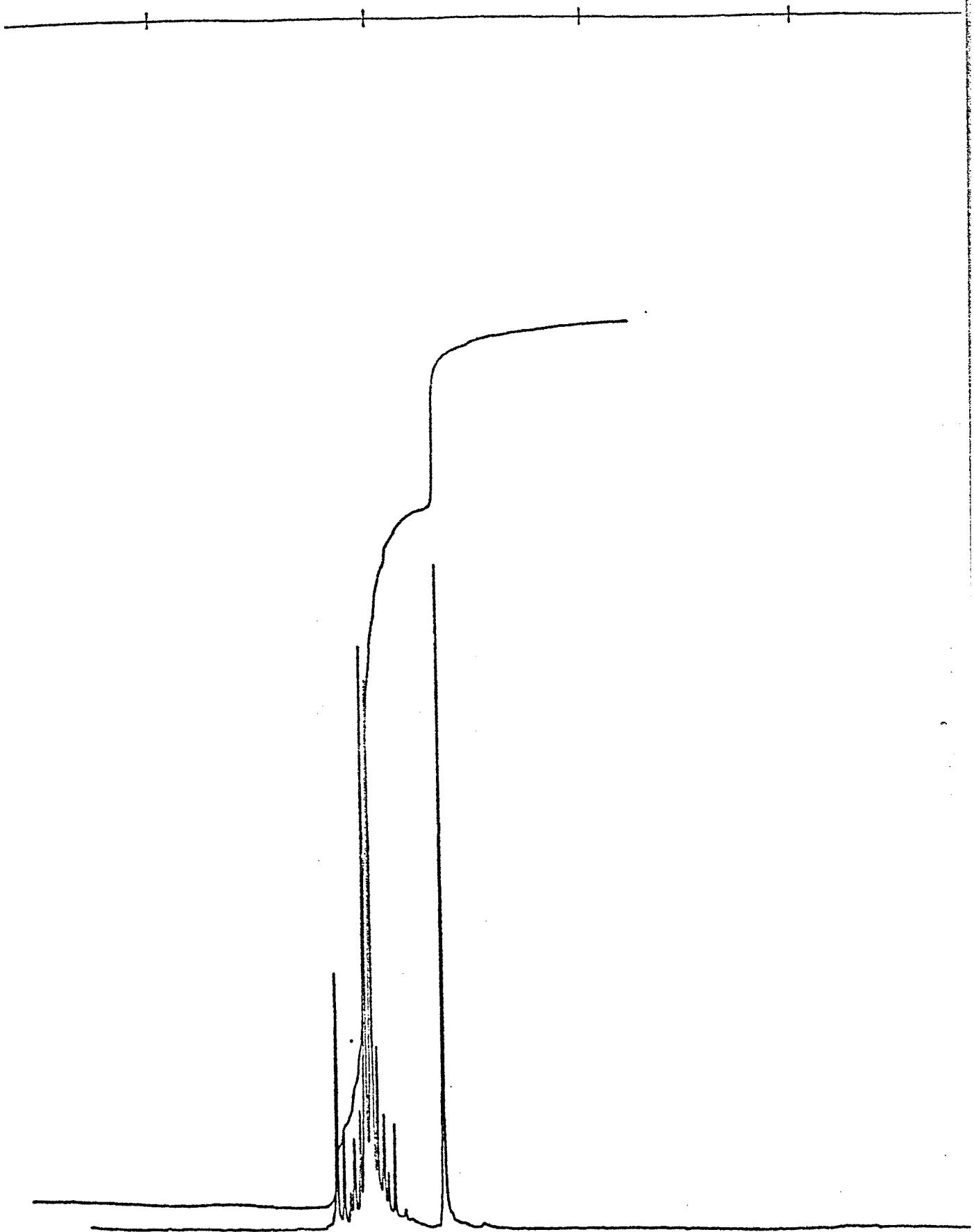


Figure 12 : N.M.R. Spectrum of
5,11-Dideuteriodibenzo [a, e] cyclo-
octatetraene

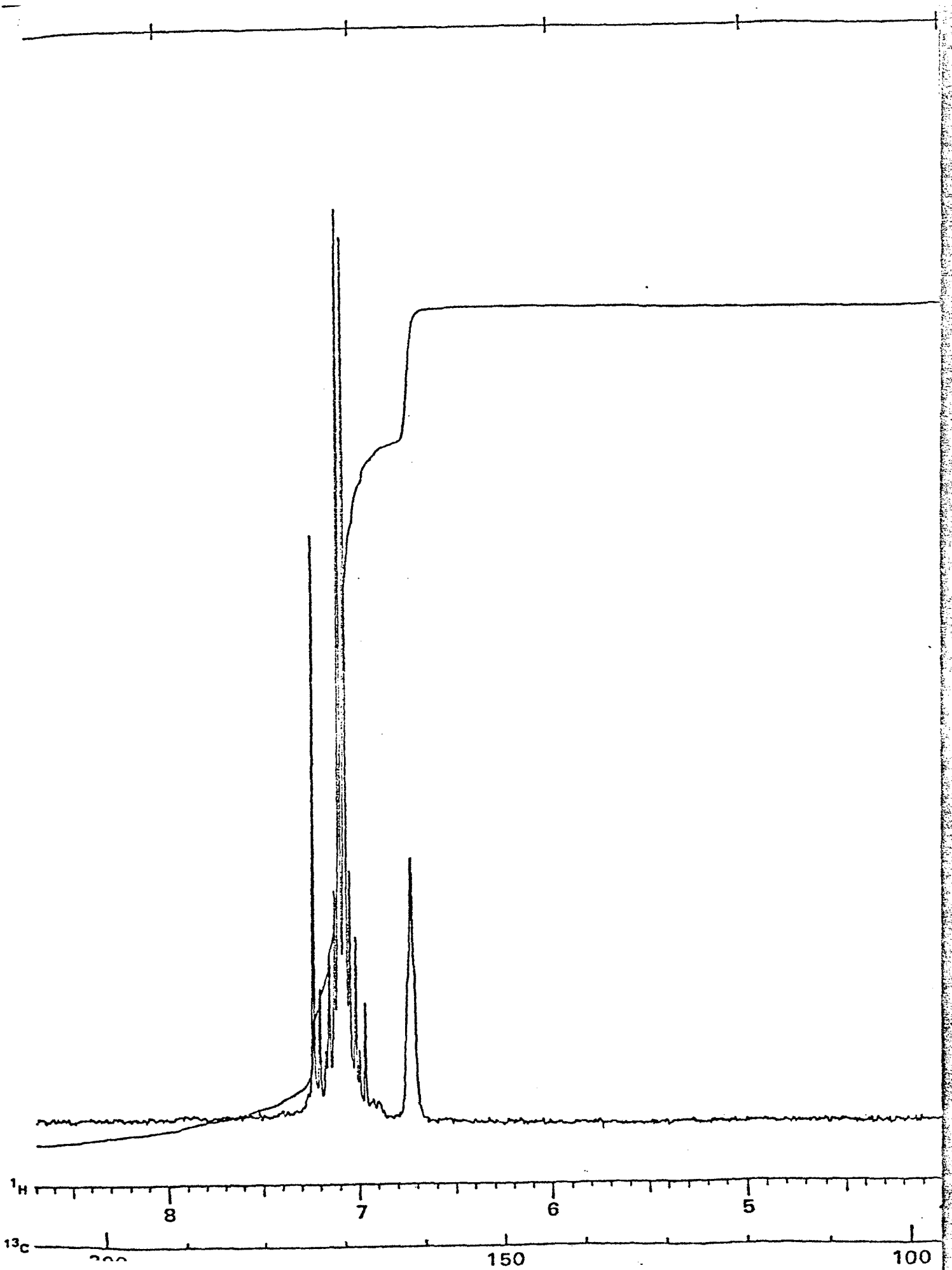
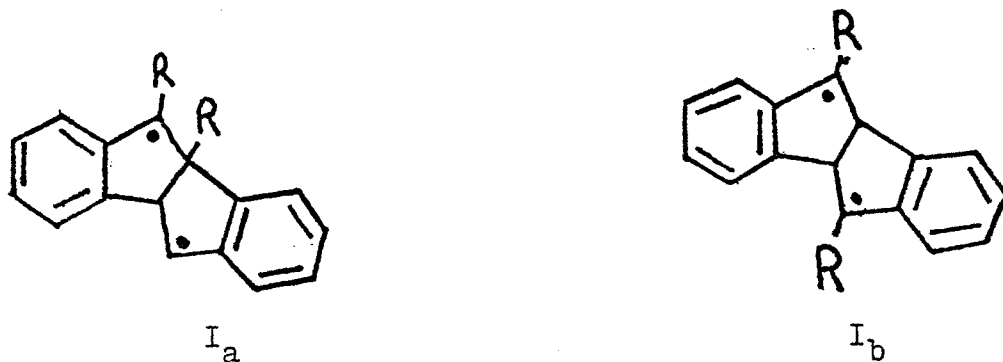


Figure 13 : N.M.R. Spectrum of
Dibenzo [a,e] cyclooctatetraene



B. Discussion of Thermolysis

The two processes of ring inversion and rearrangement were delineated as separate processes. The diradical species I_a and I_b may be the intermediates in the rearrangement of the 5,6 derivative of DBCOT to the 5,11 derivative. It was the intention of our work to attempt such a rearrangement with deuterium in place of the aryl substituents. All of the thermolysis runs, both in the molten state and in solution, revealed no rearrangement. The temperatures were well above other published values. It is our conclusion that due to the results the diradical intermediate may very well be the path to rearrangement.



Certainly the removal of the phenyl groups would tend to destabilize the diradical species. This in turn would prevent the subsequent formation of the rearranged isomers. If rearrangement is possible with the deuterium in the compounds, the energy barrier was not attained in this study. Published values of temperature for rearrangement range from $156-177^\circ$, whereas our experiments were conducted at 182° and 228° . At the higher temperature of 228° increased decomposition was noted.

In an attempt to rationalize the order of magnitude of the rates of reaction of our compounds versus published values Table 5 was compiled. Literature values for the rates of reaction range from 4.6×10^{-5} to $7.1 \times 10^{-5} \text{ sec}^{-1}$ for a temperature range of 164.0° to 164.9° . Considering a ten percent yield the following values have been computed.

Table 5.

isomer	temperature ($^{\circ}\text{C}$)	time (hrs.)	$k \times 10^{-6} \text{ sec}^{-1}$
5,11	182°	17	1.72
5,11	228°	18	1.62
5,6	182°	17	1.72
5,6	228°	18	1.62

These values are an upper limit for the rate of reaction of the 5,6 and 5,11 derivatives. Additional experiments with these isomers can be performed using a photolytic procedure and trapping experiments. The $2+2$ transannular cycloaddition product is forbidden by the Woodward-Hoffman rules for the thermal process. But such a reaction is not forbidden for the photolytic process.

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