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Studies on the photochemistry and mass spectrometry of isotopically labelled 2-phenoxy-4, 5-benztropones

Ming-ta Sung
Iowa State University

STUDIES ON THE PHOTOCHEMISTRY AND MASS SPECTROMETRY OF ISOTOPICALLY LABELLED 2-PHENOXY-4,5-BENZTROPONES

by

Ming-ta Sung

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Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967

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INTRODUCTION

The photochemistry of troponoid compounds has been reviewed by Pasto (1) and Koch (2). A variety of interesting photochemical reactions including valence tautomerizations, dimerizations, gross structural rearrangements has been observed with different tropolone compounds. The complexicity of the photoinduced reactions of troponoids varies greatly depending on the structure of the starting material and the photoreactivity of the initial photoproducts formed.

The work described here is a study of photochemical dimerizations and mass spectrometry of a series of benztropolone ethers. Several isotopically labelled derivatives of 2-phenoxy-4,5-benztropone and related compounds have been synthesized to study the dimerization process and the structural rearrangements. Mass spectroscopic examination of the labelled derivatives revealed a novel rearrangement induced by electron impact. The importance of alkyl group migrations using labelled derivatives of 2-methoxy-4,5-benztropone has been evaluated.

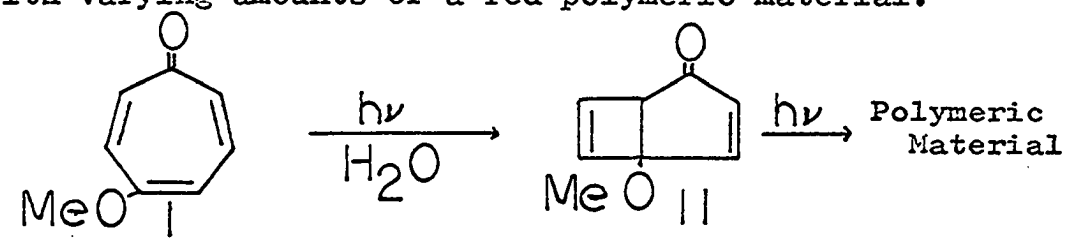
HISTORICAL

The Photochemistry of Troponoid Compounds

The photochemistry of troponoid compounds dates back to 1865 when Hübler (3) observed that solutions of colchicine turned brown when irradiated with sunlight. In the following years Struve (4), Jacobi (5) and Scoville (6) reported similar observations with colchicine. It was not until 1945, however, that the basic structure of troponoid compounds was established following Dewar's suggestion that troponoid compounds contained the cycloheptatrienolone system. It was only after this that an assault on the structure of the photoproducts could be made.

Simple troponoid compounds

γ-Tropolone methyl ether (I) was the first of the simple troponoid compounds reported by Chapman and Pasto (7) to undergo photochemical reaction. Irradiation of an aqueous solution of I in a Pyrex vessel produced a single monomeric photoproduct (II) in up to 60% yield, based on recovered I, with varying amounts of a red polymeric material.



The photoinduced reactions involving α-tropolone and substituted α-tropolone methyl ethers present a much more complex picture than γ-tropolone methyl ether. Dauben et al. (8) investigated the irradiation of α-tropolone methyl ether (IIIa) in methanol gives a similar bicyclic product (IVa) initially (see Figure 1, page 4). Continued irradiation of IVa gives the rearranged product Va. Further irradiation after the addition of water to the solution gives the methyl ester VIa. This sequence of photochemical reactions was clarified by studying the products from the irradiation of substituted α-tropolone methyl ether (IIIb,c,d). Dauben et al. have proposed the general mechanistic scheme for the process.

Forbes and Ripley (9) irradiated α-tropolone methyl ether (IIIa) in aqueous solution and observed the formation of the methyl ester of 4-oxo-2-cyclopentene-1-acetic acid (VIa). In addition to the formation of VIa they also isolated three solid products with melting points of 112 to 114°, 145 to 146°,and 185° (decomposition). The authors indicated that these products may be dimeric products.

Recently, Mukai et al. (10) showed that irradiation of 2-methoxy-6-phenyltropone (IIIc) gave,in addition to 1-methoxy-4-phenyl-$\Delta^{3,6}$-bicyclo[3,2,0]heptadien-2-one (IVe), 3-methoxy-7-phenyl-$\Delta^{3,6}$-bicyclo[3,2,0]heptadien-2-one (IVe') and methyl 4-oxo-2-phenylcyclopentenylacetate (VIe), a new

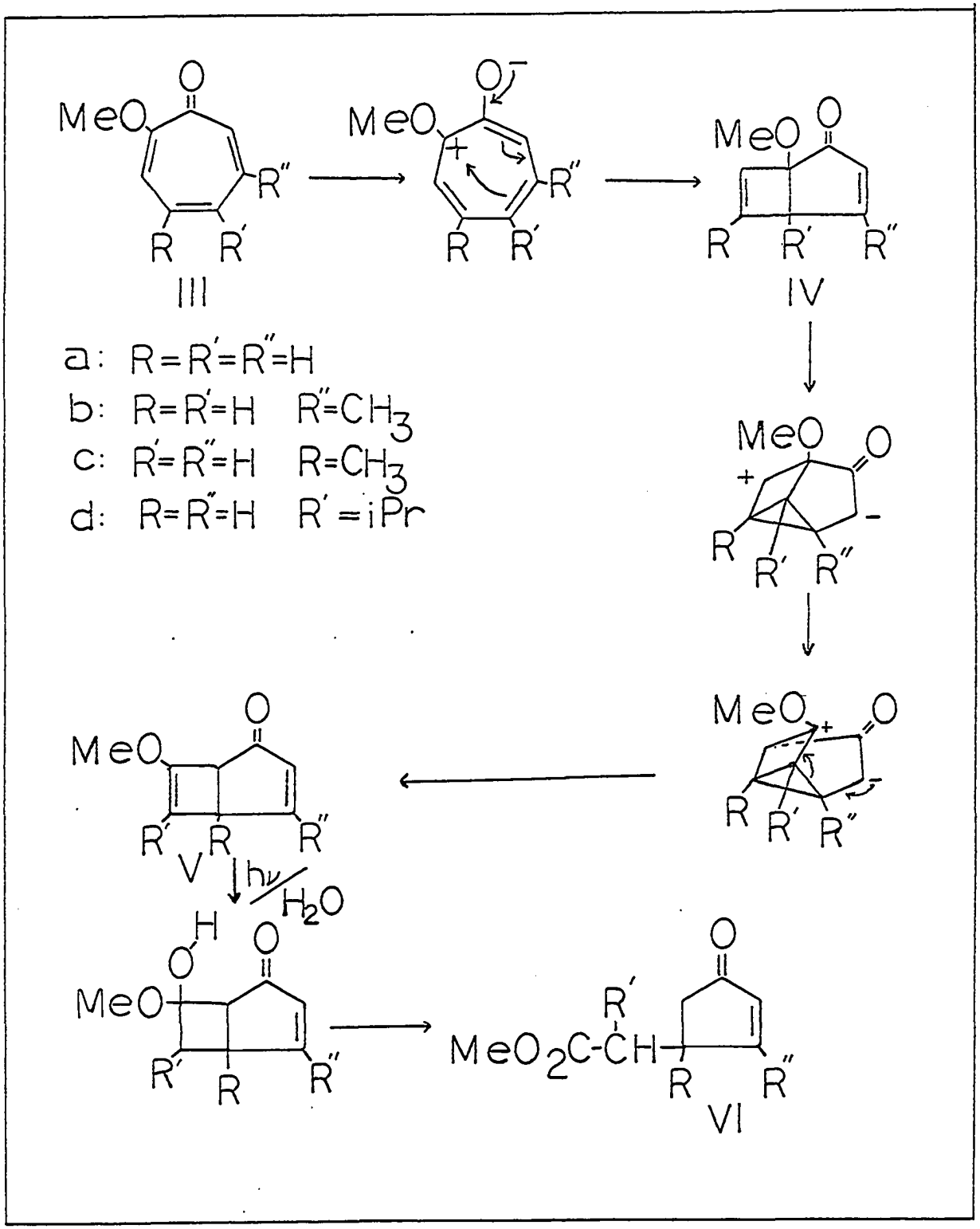
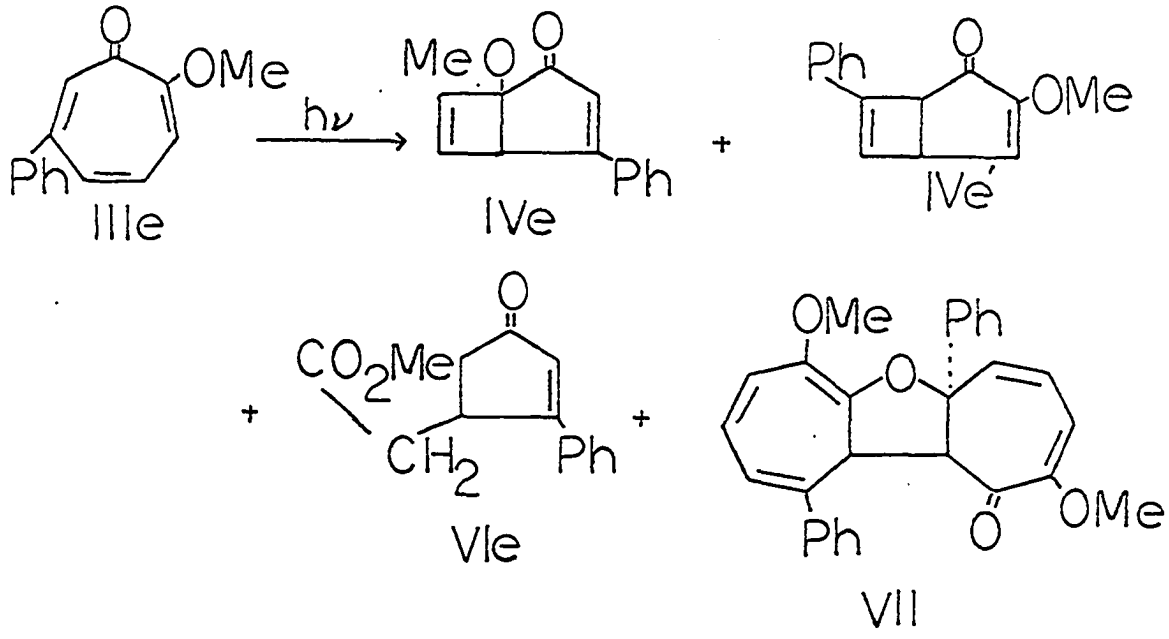


Figure 1. The photochemistry and mechanism of α-tropolone methyl ethers

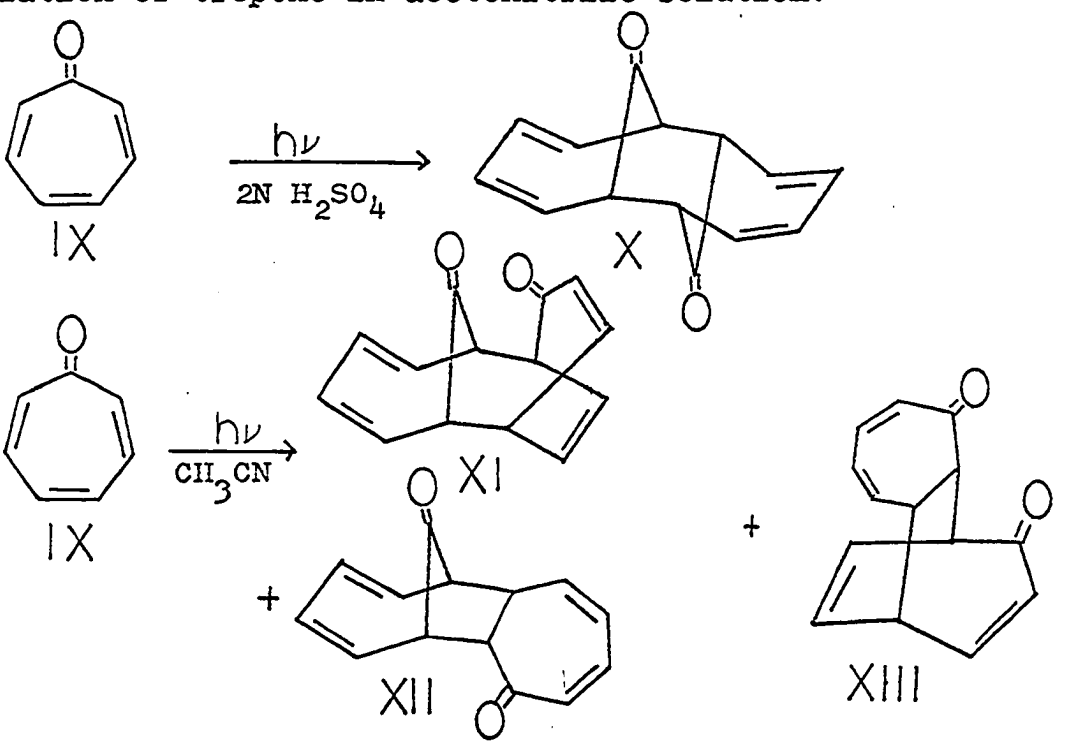
type of dimerization product (VII) in 4% yield.



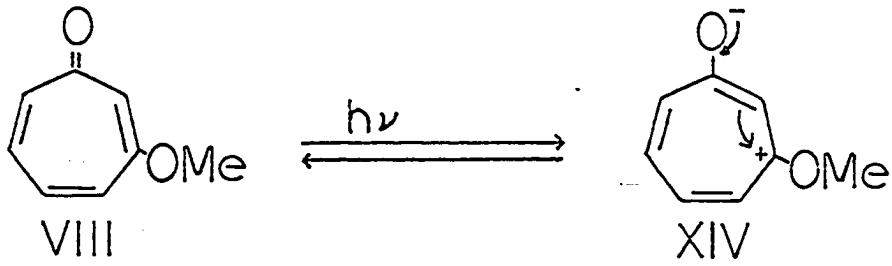
The photochemistry of β-tropolone methyl ether (VIII) and tropone (IX) evidently follows quite different path and no bicyclic products have been isolated (11). The irradiation of β-tropolone methyl ether in benzene (12) gives two white solid products in 10% yield. Both products were found to have dimeric molecular weights. The dimer 1 has a carbonyl peak in the infrared spectrum at 5.7μ with melting point at 193-195°. The dimer 2 with melting point at 158-160° has a single carbonyl peak at 5.86 μ. The structure determination of these dimers is being continued in this group.

Irradiation of tropone (13) in 2 N sulfuric acid with a mercury lamp in a Pyrex vessel afforded 7.5% dimeric product X, which has a structure of tricyclo[6,4,1,$1^{2,7}$]tetradeca-3,5-

9,11-tetracne-13,14-dione. This is the first example of (6 + 6) π-type cycloaddition according to Woodward and Hoffmann's selection rule (14). Kende (15) isolated three dimeric products XI, XII and XIII in 50% yield from the irradiation of tropone in acetonitrile solution.



The distinct difference in photochemical properties of α-tropolone methyl ether and the γ-tropolone methyl ethers on one hand and β-tropolone and tropone on the other hand must be a result of the presence and position of the methoxy group. The dipolar intermediate (XIV) for the β isomer can only return to the starting material. Whereas with tropone there is no methoxy group to give any directing influence, thus increasing the probability of a less favored reaction occurring.



VIII XIV

Colchicine and related compounds

Aqueous solutions of colchicine (XV) when exposed to sunlight give varying quantities of three photoproducts, α-, β-, and γ-lumicolchicine (15-21). Structure XVI and XVII has been assigned to β and γ-lumicolchicine, respectively (17,18, 22). The structure of α-lumicolchicine (XVIII) is a dimer of β-lumicolchicine (19) (Figure 2, page 8).

The photoisomerization of isocolchicine (XIX) has been investigated by Chapman et al. (23) and by Dauben et al. (24). The photoisomerization of XIX could conceivably produce either, or both, the valence tautomers (XX) and (XXI). Both photoisomers should possess about equal strain energy; however, the formation of XX will preserve a trimethoxystyryl chromophore, whereas in XXI interaction between the cyclobutene double bond and the benzene ring is not possible. The competition between the formation of XX and XXI should therefore give an indication of the importance of electronic factors in the formation of the photoisomers. Both groups of investigators observed the formation of only valence tautomer XX. The photochemistry of colchicine is governed almost

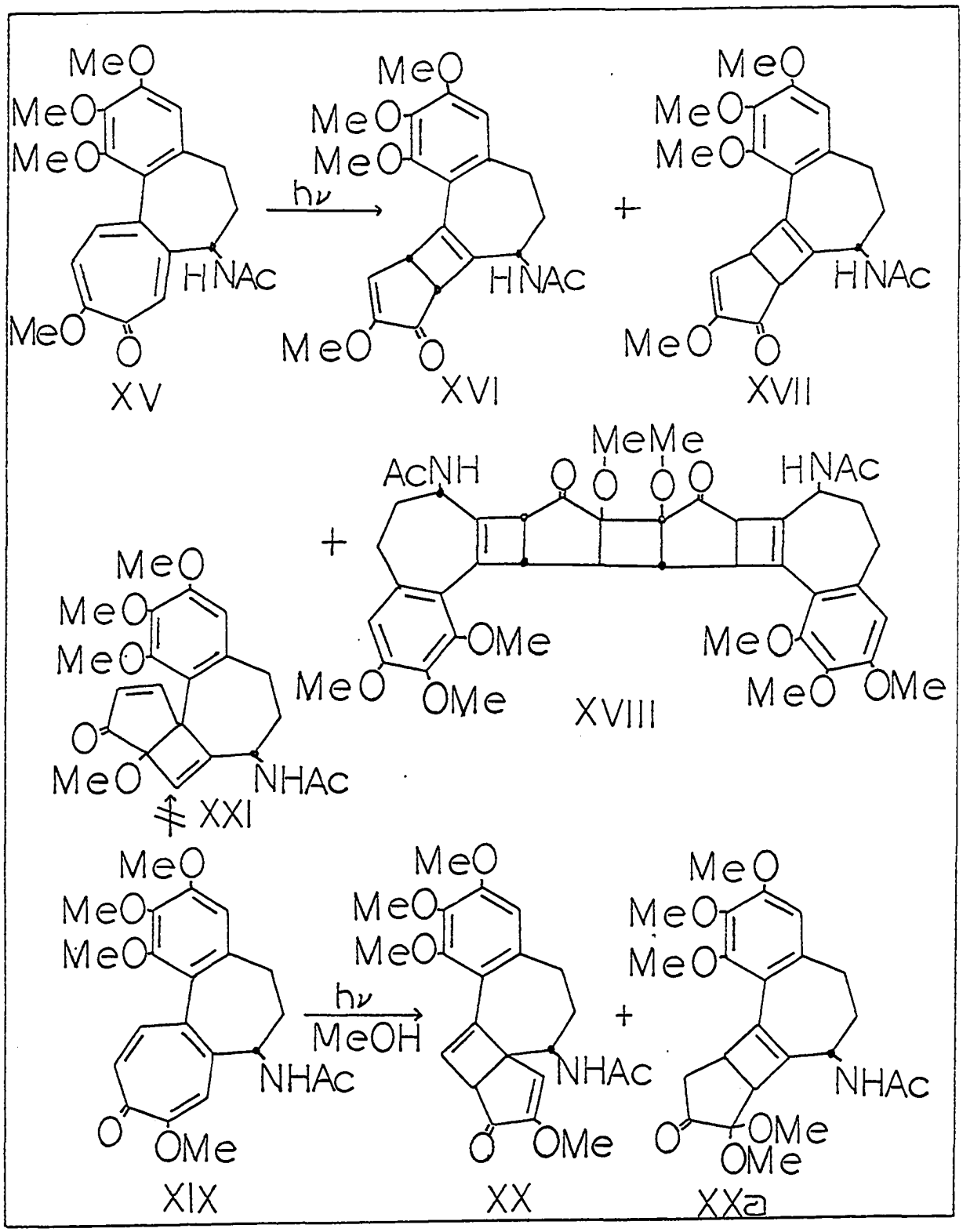
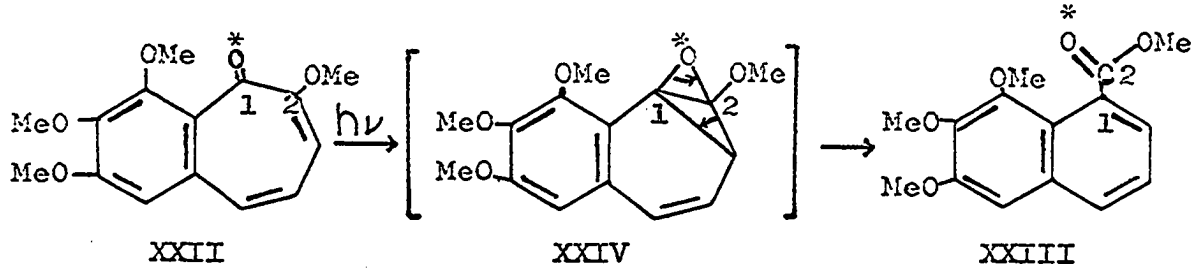


Figure 2. Photochemical transformations of colchicine and isocolchicine

exclusively by electronic factors in which the preservation of a trimethoxylstyryl chromophore is the most important factor. The effect of the methoxy group on the troponoid ring in stabilizing the electron distribution in the " excited" state is overweighted by the apparent desire to preserve the trimethoxystyryl chromophore. Several derivatives of colchicine have been subjected to ultraviolet irradiation. The mode of reaction in the colchicine series seems to be little affected by substituents.

Benztropones

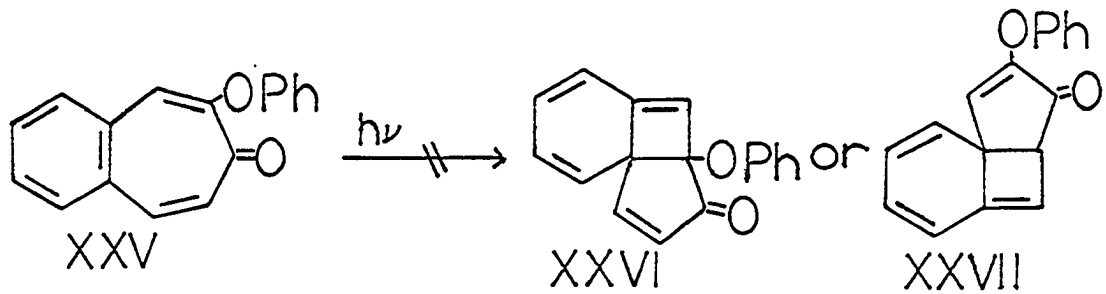
Forbes and Ripley (25) have reported that purpurogallin tetramethyl ether (XXII) on irradiation in ethanolic solution gives a photoisomer XXIII. The photoisomerization of XXII to XXIII represents a new mode of troponoid photoisomerization. Insight as to the mechanism of this rearrangement has been gained by Chapman and Murphy (26) employing labelled XXII. Irradiation of XXII-$^{14}C_2$ results in the formation of XXIII carbonyl-^{14}C and the photoisomerization of XXII carbonyl-^{18}O gives XXIII carbonyl-^{18}O. These results are consistent with but do not require Forbes suggestion of an



XXII XXIV XXIII

oxabicyclobutane intermediate XXIV.

Of the troponoid compounds, the photochemistry of 2-phenoxy-4,5-benztropone (XXV) is by far the most complex and interesting one. Simple photochemical valence tautomerization to give XXVI or XXVII, as observed in the previously discussed troponoid compounds, is virtually forbidden for XXV owing to both electronic and steric factors. Both valence tautomers represent a complete loss of the resonance energy of the benzenoid and troponoid systems, and the bond angle strain and steric crowding inherent in the systems would appear to be rather large. This system seemed to be an ideal one for investigating the less favored photochemical transformations of a troponoid system which might otherwise be obscured by the more facile valence tautomerization reactions. Irradiation of



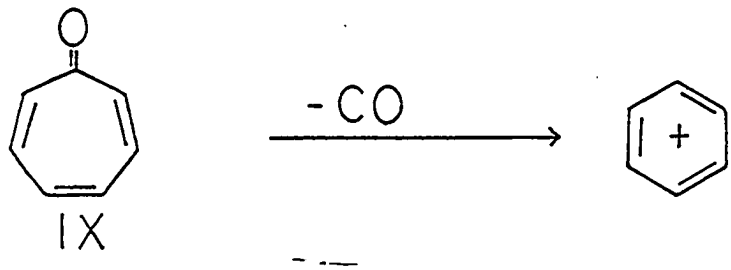
XXV XXVI XXVII

2-phenoxy-4,5-benztropone gives three dimers A, B and C. The structures of the dimers have been determined (27). A mechanism for the formation of the dimers has been proposed. (27). The work described in this thesis was undertaken with two goals in mind. First, we sought to provide evidence of the phenyl group migration in the formation of the dimers. Second, we wished to label the atoms in the tropolone ring to

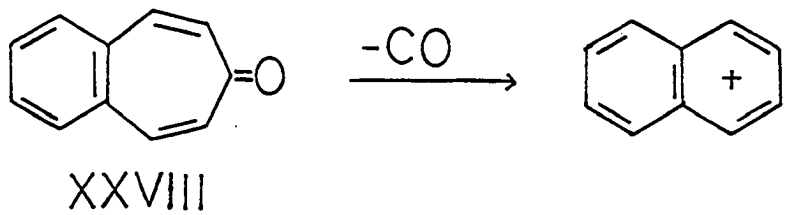
be certain that other skeletal rearrangements were not occurring. In the course of this work the mass spectra of the labelled compounds proved to be of such interest that they were investigated in detail.

The Mass Spectrometry of Troponoid Compounds

The mass spectrometry of troponoid compounds has been reviewed by Budzikiewicz, Djerassi and Williams (28,29). The most characteristic feature in the spectrum of tropone is the pronounced loss of carbon monoxide (M - 28) (30,31). An analogous observation has been made with benztropone (XXVIII) (32), the primary step being expulsion of carbon monoxide with generation of the naphthalene ion. A detailed study of various tropone derivatives has shown that the elimination of carbon monoxide with formation of an M - 28 species, which



IX

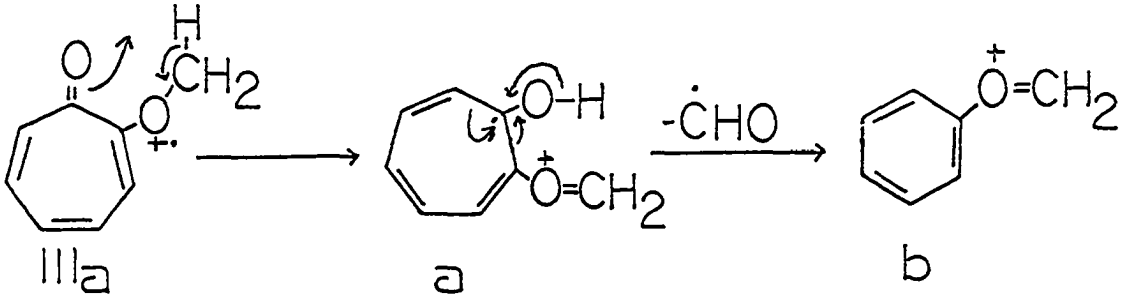


XXVIII

behaves like the analogous benzene derivative, is the main process in this class.

The mass spectrum of tropolone exhibits a much more intense molecular ion peak than was found in the tropone spectrum.

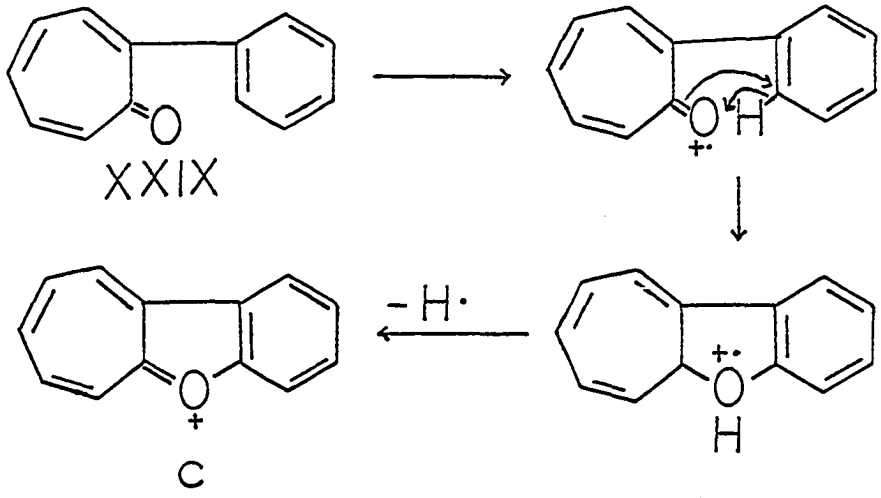
Several interesting features may be noted in the spectrum of tropolone methyl ether. The elimination of carbon monoxide from the molecular ion, so characteristic of tropone and tropolone, occurs only to a minor extent. Expulsion of a CHO rather than CO predominates. A possible explanation may be the occurrence of a hydrogen transfer in the molecular ion to give species a, which could yield the stable carbonium ion b on loss of CHO (28).



IIIa a b

Introduction of a phenyl group may alter the mass spectrum in a marked fashion depending upon the site of substitution. As expected, the base peaks in the spectra of 4- and 5-phenyltropolone occur at m/e 170 due to the loss of carbon monoxide. However, in 2-phenyltropone (XXIX) the most abundant ion is formed by loss of one hydrogen atom. This unique feature can be employed as a convenient criterion for

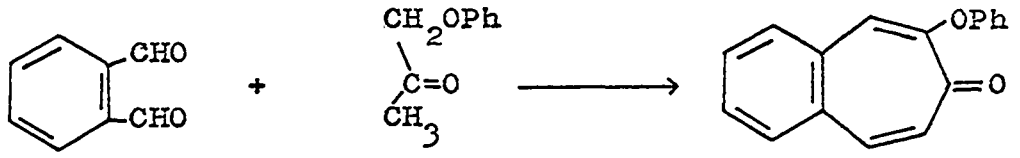
setting the point of attachment of an aromatic substituent in a tropone. The most plausible explanation for the occurrence of such ion is the abstraction of an ortho hydrogen atom to provide the cyclic species c. Elimination of carbon monoxide from the molecular ion or from the M - 1 fragment c accounts for the remaining intense peaks in the upper mass range of the mass spectrum of 2-phenyltropone (31).



RESULTS AND DISCUSSION

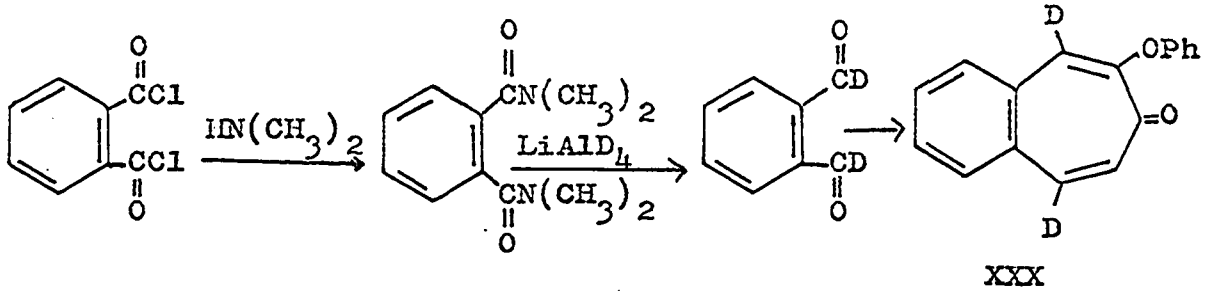
Synthesis of 2-Phenoxy-4,5-benztropone and Related Compounds

Synthesis of 2-phenoxy-4,5-benztropone (XXV) was readily achieved by the method of Tarbell *et al.* (33). This method also proved readily adaptable to the synthesis of isotopically labelled derivatives of 2-phenoxy-4,5-benztropone. Condensation of o-phthalaldehyde with phenoxyacetone in basic solution gave crude XXV.



XXV

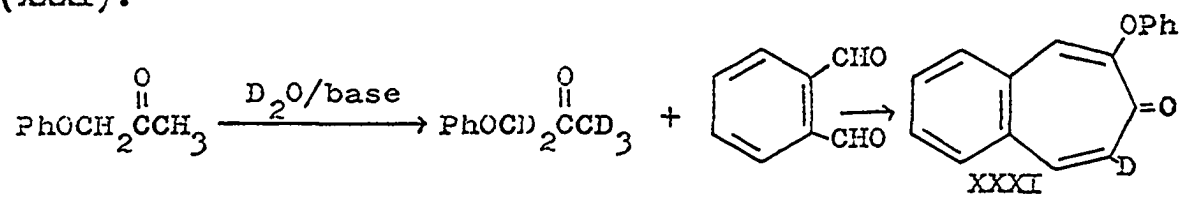
Treatment of phthaloyl chloride with dimethylamine gave the bis-amide. Reduction of the bis-amide with lithium aluminum deuteride gave o-phthalaldehyde with deuterium in each aldehyde group. Condensation with phenoxyacetone gave 2-phenoxy-4,5-benztropone-3,6-d_2 (XXX).



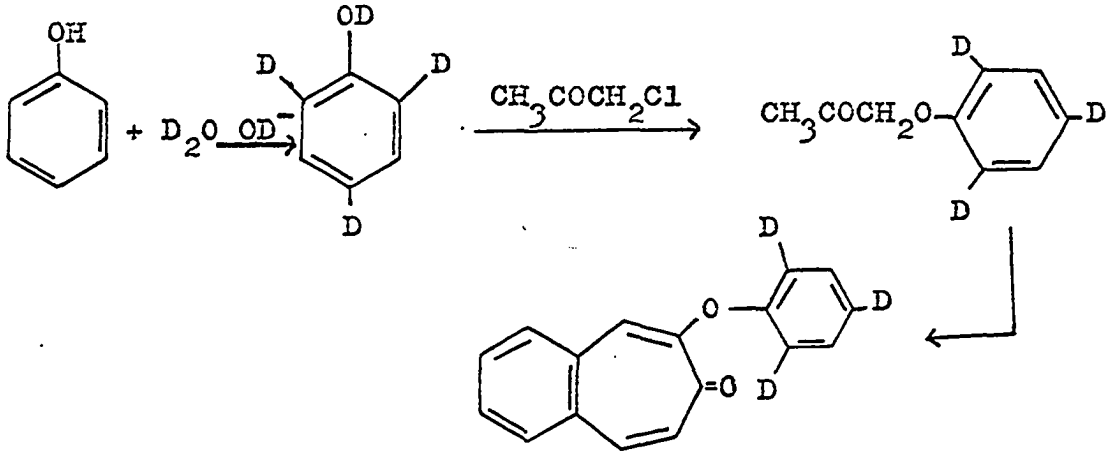
XXX

Equilibration of phenoxyacetone with deuterium oxide

in the presence of base gave phenoxyacetone-d_5. Condensation with o-phthalaldehyde gave 2-phenoxy-4,5-benztropone-7-d (XXXI).



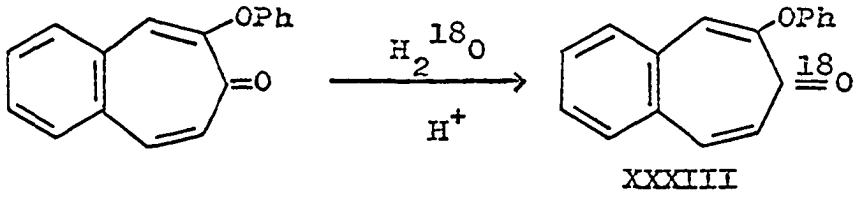
Equilibration of phenol with deuterium oxide in basic solution gave phenol-2,4,6,O-d_4. Reaction of sodium phenoxide-2,4,6-d_3 with iodoacetone gave 2,4,6-trideuteriophenoxyacetone, which on condensation with o-phthalaldehyde gave 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone (XXXII). The infrared and nuclear magnetic resonance spectra of these deuterium labelled derivatives are similiar to 2-phenoxy-4,5-benztropone itself.



XXXII

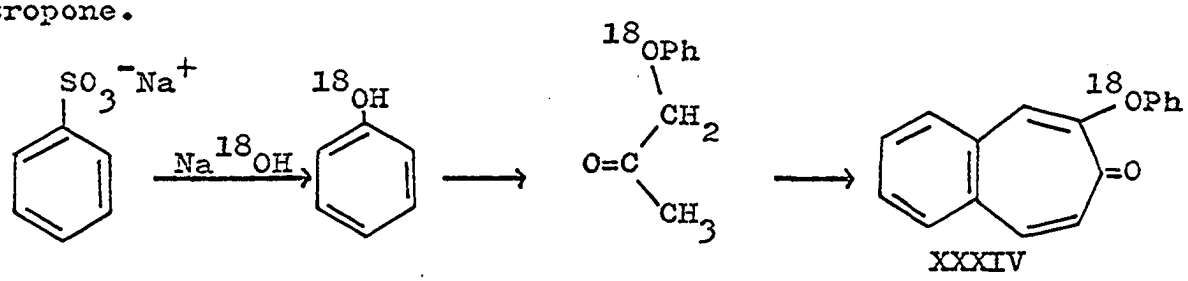
The oxygen of aldehydes and ketones can be exchanged by water. The exchange is catalysed by hydrogen and hydroxide ions (34). In most cases the organic compound is dissolved in water. When the compounds are not very soluble in water,

mixed solvents are used. Carbonyl-^{18}O -labelled 2-phenoxy-4,5-benztropone (XXXIII) was prepared by acid catalyzed exchange with ^{18}O-labelled water in tetrahydrofuran. It was shown that XXXIII contained 29% excess ^{18}O by mass spectrometry. The infrared spectrum (Figure 13, page 56) shows two carbonyl absorption peaks at 1600 cm^{-1} (C=O) and 1570cm^{-1} (C=^{18}O).



XXXIII

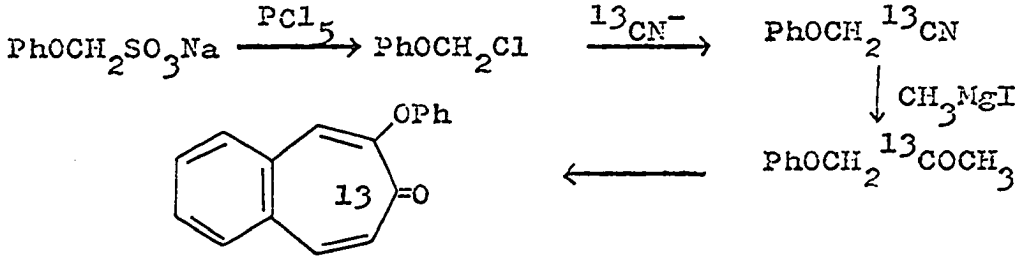
Labelling the ether oxygen proved more difficult. Phenol containing oxygen-18 was prepared by fusion of sodium benzenesulfonate with ^{18}O-labelled sodium hydroxide. The ^{18}O-labelled phenol was converted to phenoxyacetone and then to 2-(^{18}O-phenoxy)-4,5-benztropone (XXXIV) (16% excess ^{18}O by mass spectrometry). The infrared spectrum of XXXIV (Figure 13, page 56)is essentially identical with 2-phenoxy-4,5-benztropone.



XXXIV

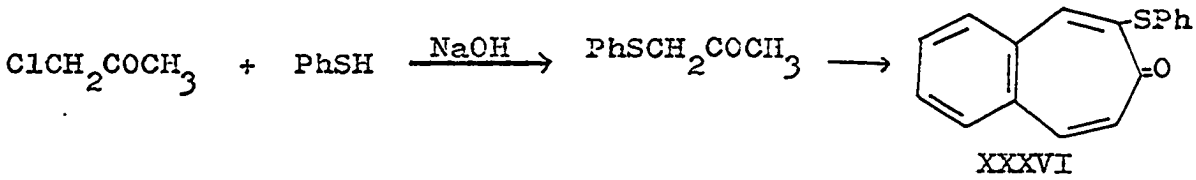
Synthesis of 2-phenoxy-4,5-benztropone-1-^{13}C (XXXV) utilized potassium cyanide-^{13}C. Phenol was converted to phenyl chloromethyl ether via the phenoxymethane sulfonate by

treatment with phosphorous pentachloride (35). Displacement of the chlorine by cyanide-^{13}C followed by Grignard reaction with methyl magnesium iodide gave phenoxyacetone-2-^{13}C which then condensed with o-phthalaldehyde to give XXXV.



XXXV

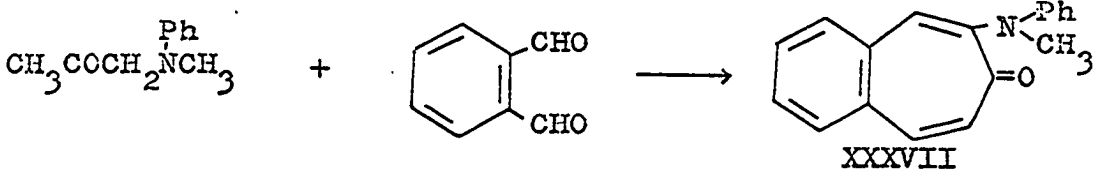
2-Thiophenoxy-4,5-benztropone (XXXVI) was prepared by condensation of o-phthalaldehyde with thiophenoxyacetone prepared in modest yield by treatment of chloroacetone with thiophenol in aqueous sodium hydroxide solution. The infrared



XXXVI

spectrum (Figure 14, page 58) and nuclear magnetic resonance spectrum (Figure 28, page 86) of XXXVI were similiar to those of XXV.

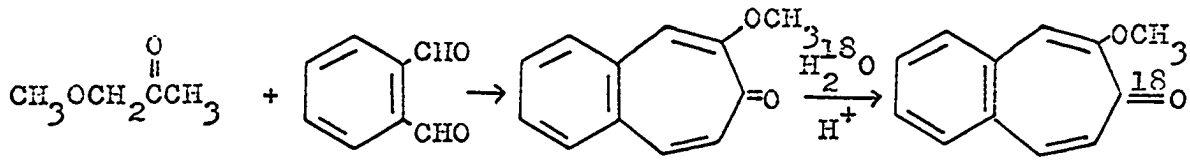
Condensation of N-methylanilinoacetone with o-phthalaldehyle gave 2-(N-methylanilino)-4,5-benztropone (XXXVII). The nuclear magnetic resonance spectrum of XXXVII showed the aromatic protons at 2.87 and the methyl protons at 6.73 τ



XXXVII

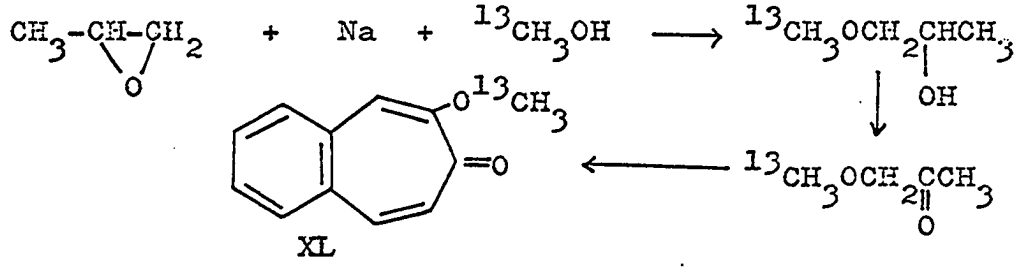
(Figure 27,page 84).

2-Methoxy-4,5-benztropone (XXXVIII) was prepared by the condensation of o-phthalaldehyde with methoxyacetone (36). The carbonyl-^{18}O-labelled derivative (XXXIX) was prepared by acid catalyzed exchange using ^{18}O-enriched water in tetrahydrofuran.



XXXVIII XXXIX

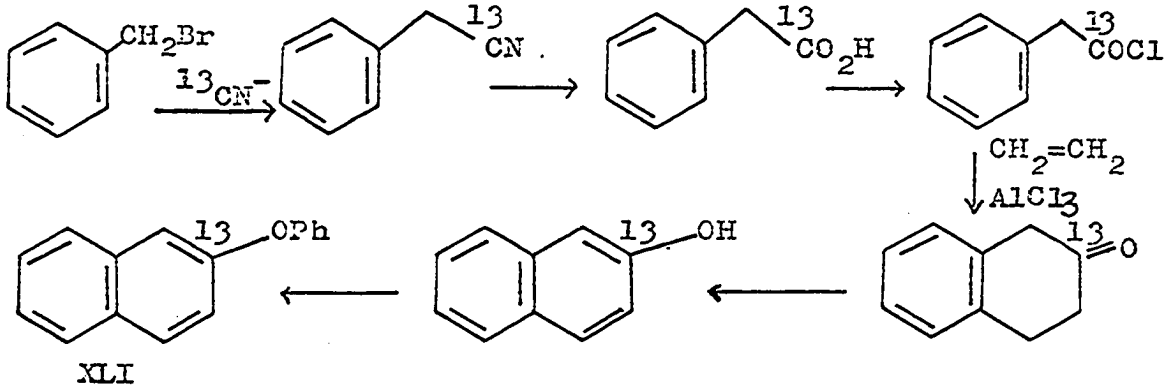
The synthesis of 2-(methoxy-^{13}C)-4,5-benztropone (XL) utilized methanol-^{13}C as the source of the label. Treatment of propylene oxide with methanol-^{13}C and sodium at 100° produced 1-(methoxy-^{13}C)-2-propanol which was oxidized to the ketone and condensed in the usual manner. The nuclear magnetic resonance spectrum (Figure 27,page 84) shows the aromatic protons at 2.70 and the methyl protons at 6.08τ which was splitted to doublet by ^{13}C ($J_{^{13}CH}$ = 146 c.p.s.).



XL

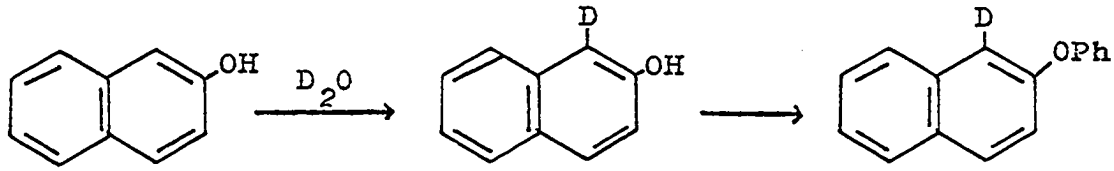
Synthesis of 2-Phenoxynaphthalene-2-^{13}C (XLI) started with potassium cyanide-^{13}C. Treatment of benzyl bromide with

potassium cyanide-^{13}C gave phenylacetonitrile-1-^{13}C. Hydrolysis gave carboxyl labelled phenylacetic acid which was converted to the acid chloride. Condensation of the acid chloride with ethylene gave 2-tetralone-2-^{13}C. Bromine oxidation of 2-tetralone-2-^{13}C gave 2-naphthol-2-^{13}C. Treatment of 2-naphthoxide with refluxing bromobenzene gave 2-phenoxynaphthalene-2-^{13}C (XLI).



XLI

1-Deuterio-2-phenoxynaphthalene (XLII) was prepared. Exchange of 2-naphthol with deuterium oxide gave 1-deuterio-2-naphthol whose sodium salt was condensed with bromobenzene to give XLII.



XLII

Irradiation of 2-Phenoxy-4,5-benztropone and Related Compounds

The irradiation of 2-phenoxy-4,5-benztropone (XXV) gives a number of products. The irradiations were carried out in isopropanol or tetrahydrofuran, using a mercury arc lamp with a Pyrex filter. If the irradiation was stopped before all of the starting material was destroyed, two dimeric photoproducts XLIII and XLIV (Figure 3, page 21) were isolated which were separated by column chromatography. Compound XLIII and XLIV were designated Dimer A and Dimer B, respectively. Treatment of either dimer with acid results in the formation of 4,5-benztropolone and phenol. This precludes gross rearrangement of the carbon skeleton of the troponoid ring. Dimer B can be converted to Dimer A by heating it slightly above its melting point (220-230°). If either dimer is heated to a slightly higher temperature (230-240°) it is converted to the starting material (XXV).

The spectra of the dimers are very useful in the determination of their structures (27). The infrared spectrum of Dimer B (Figure 19, page 68) displays a single carbonyl peak at 1737 cm^{-1}. The low wavelength carbonyl band would indicate the presence of a saturated carbonyl chromophore. The nuclear magnetic resonance spectrum of Dimer B (Figure 28, page 86) shows aromatic protons at 2.87 τ, a single AB system

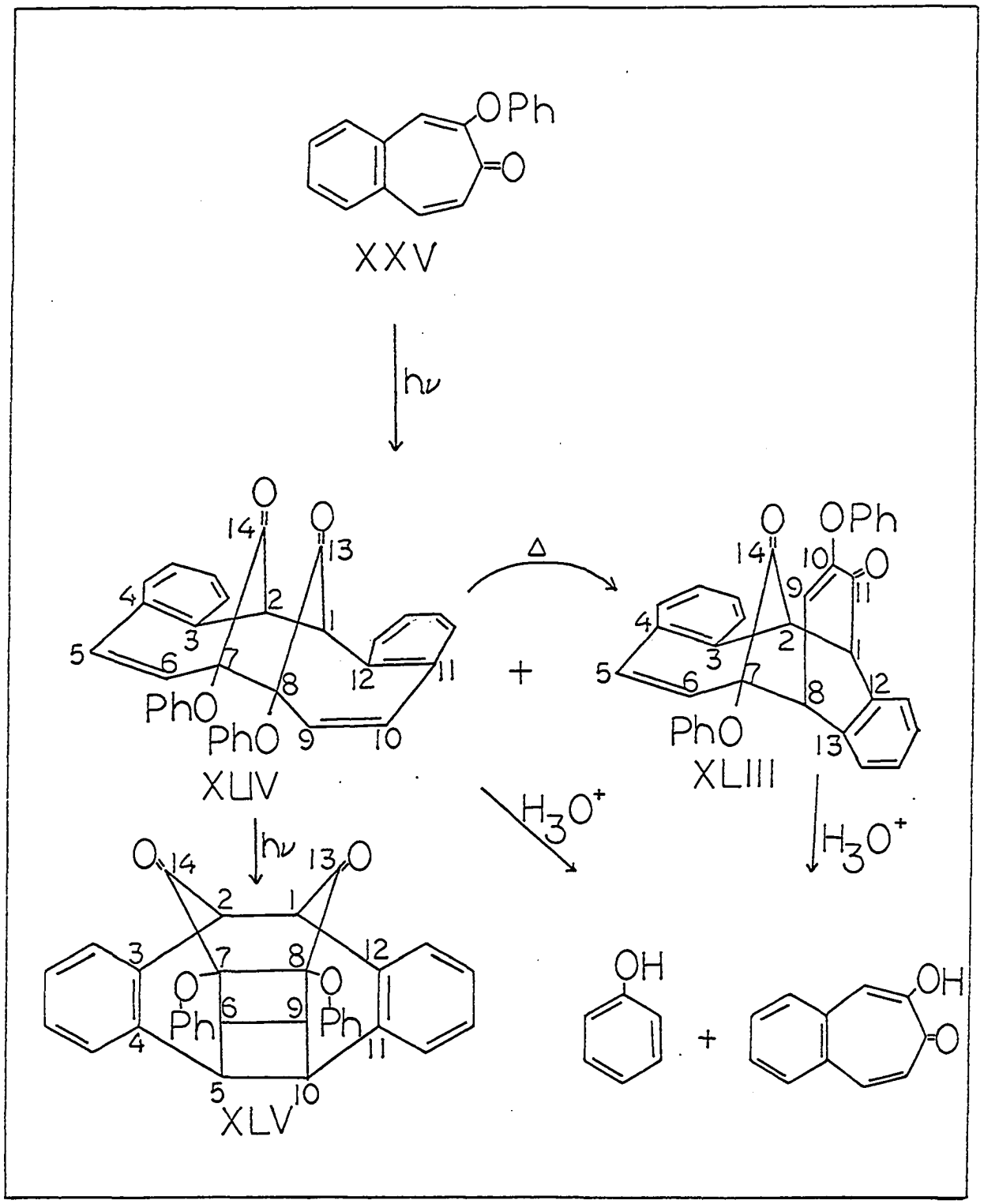
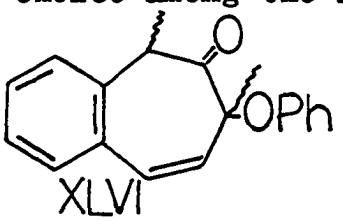


Figure 3. Photochemical transformation of 2-phenoxy-4,5-benztropone

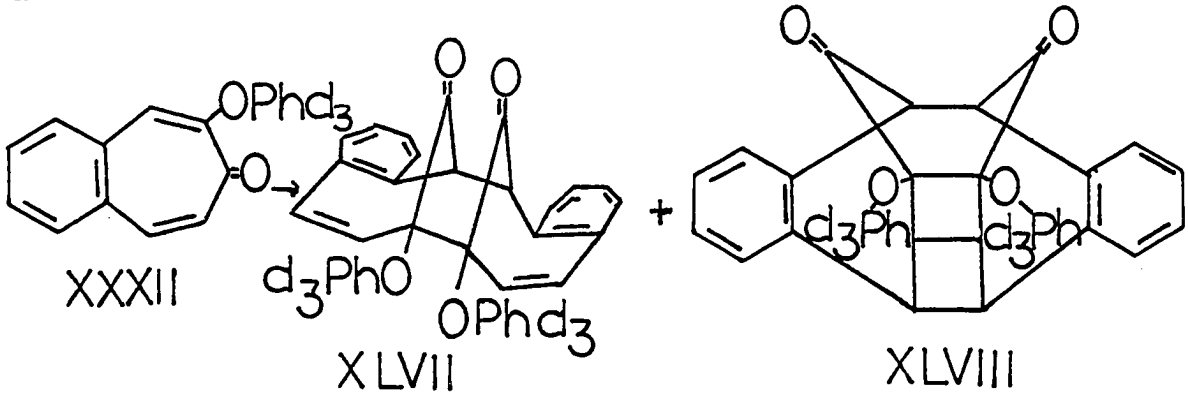
with doublets at 3.41 τ and 4.12 τ, J_{AB}= 12.3 c.p.s. characteristic of an isolated styryl system, and a single isolated aliphatic proton at 5.97 τ (Table 1, page 27). The simplicity of the nuclear magnetic resonance spectrum immediately suggests a symmetric dimer composed of two units of XLVI. A unique choice among the four possible dimers based



XLVI

on XLVI is provided by the observation that irradiation of XLIV in low yield of a new dimer (XLV) which was designated Dimer C. Dimer C can be formed from XXV in addition to Dimer B if the irradiation is allowed to proceed until no starting material remains. Dimer C shows a single carbonyl absorption in the infrared spectrum (Figure 23, page 76) at 1707 cm^{-1}. The nuclear magnetic resonance spectrum (Figure 39, page 108) shows no olefinic protons. An A_2B_2 pattern appears at 5.55 and 6.35 τ which is ascribed to a cyclobutane ring formed by the cycloaddition of the styryl double bonds of Dimer B. The isolated bridgehead proton appears as a singlet at 5.46 τ. The aromatic region of the spectrum shows a remarkable change from that of Dimer B. The aromatic protons of the benzo-group appear as a sharp singlet at 2.66 τ. The phenoxy protons 3:2 appear at 3.01 and 3.70 τ (Table 2, page 28). The o,p-trideuteriophenoxy derivative of Dimer C (XLVIII), which was

prepared by irradiation of 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone, shows two singlet signals for the aromatic protons (Figure 40, page 110). The one at 2.66 τ is due to the protons of the benzo-group. The signal at 3.01 τ is the m,p-protons of phenoxy group. The chemical shift at 3.70 τ corresponding to the o-phenoxy protons is absent. The chemical shift of the phenoxy protons of Dimer C is higher than Dimer B. This can be accounted for by diamagnetic shielding from the carbonyl groups. An examination of models shows that the phenyl protons, especially those ortho to the ethereal oxygens, can spend an appreciable amount of time in the shielding cone (37) of the carbonyl groups. The formation of Dimer C from Dimer B can occur reasonably only if Dimer B has structure XLIV.



Dimer A can be obtained from the irradiation of XXV, but since it is usually not produced in good yield, the easiest method of preparation is the thermal isomerization of Dimer B at 220-230°. Dimer A shows two carbonyl absorptions in the infrared spectrum (Figure 16, page 62) at 1718 cm^{-1} and 1683 cm^{-1}

suggesting the presence of conjugated and nonconjugated carbonyl groups.

The nuclear magnetic resonance spectrum of Dimer A (Figure 32, page 94) shows aromatic protons at 2.95 τ (eighteen aromatic protons plus one low field olefinic proton); a styryl AB pattern at 3.95 and 4.50 τ, J_{AB}= 13 c.p.s.; a higher field AB pattern at 5.33 and 5.75 τ, J_{AB}= 5 c.p.s. due to the adjacent, non-equivalent bridgehead protons and the high field half of an AX system at 5.64 τ, J_{AX}=9.7 c.p.s. (Table 3, page 29). A double resonance experiment identified the low field olefinic proton as the other half of the AX system. Reduction of Dimer A gives a diol (XLIX) which on reaction with acid forms the internal ether (L). The formation of L from Dimer A diol requires that the carbonyl bridges of Dimer A be on the same side of the molecule. Structure XLIII fits all of the spectral and chemical data for Dimer A and can be formed reasonable from Dimer B by heating.

In agreement with the gross structural assignments, the photochemistry of two deuterium labelled derivatives of 2-phenoxy-4,5-benztropone has been studied. Irradiation of 2-phenoxy-4,5-benztropone-3,6-d_2(XXX) until no starting material left gave tetradeuterodimers, Dimer B-1,2,5,10-d_4 (LI) and Dimer C-1,2,5,10-d_4 (LII) as shown by their infrared spectra. Dimer A-1,2,5,8-d_4 (LIII) was formed by thermal transformation of Dimer B-1,2,5,10-d_4 (Figure 4, page 25).

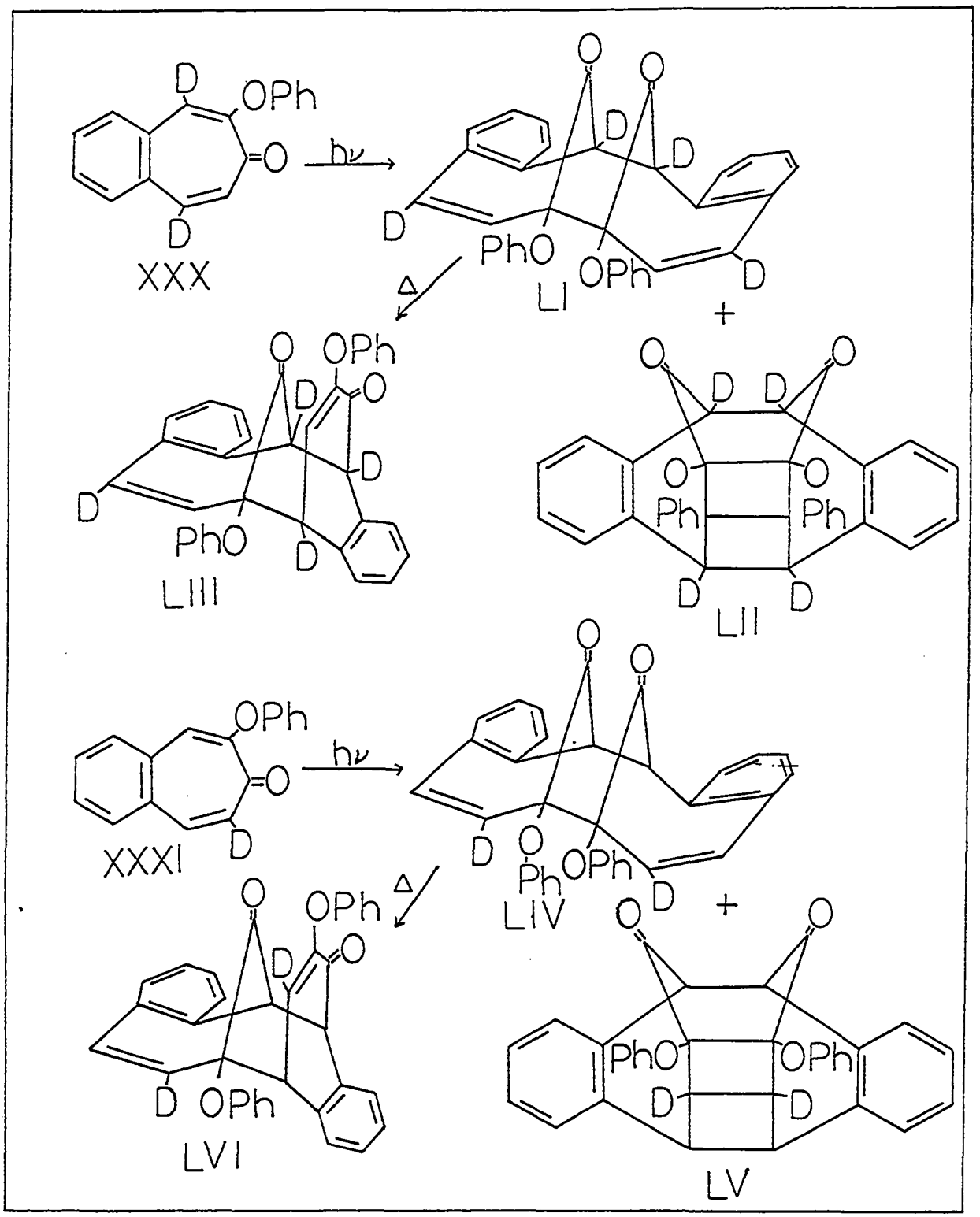


Figure 4. Photochemical transformation of 2-phenoxy-4,5-benztropone-3,6-d_2 and 2-phenoxy-4,5-benztropone-7-d

The position of deuterium incorporation was determined by nuclear magnetic resonance spectroscopy and was consistent with the earlier spectral interpretations.

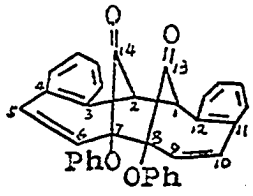
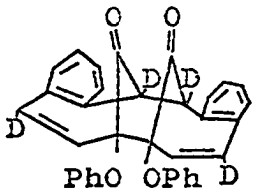
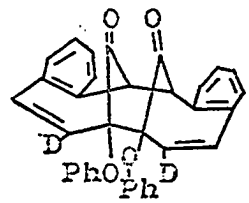
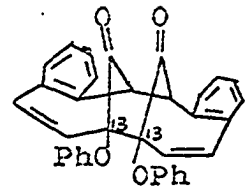
The nuclear magnetic resonance spectrum of Dimer B-1,2,5,10-d_4 (Figure 31, page 92) shows absence of bridgehead protons at 5.97 τ and the lower field absorption from the α-proton of the styryl double bond at 3.41 τ, the higher field absorption from the β-proton of the styryl double bond as a singlet at 4.12 τ.

The nuclear magnetic resonance spectrum of Dimer C-1,2,5,10-d_4 (Figure 39,page 104) shows aromatic protons at 2.66,3.03 and 3.70 τ. The A_2B_2 pattern at 5.55 and 6.35 τ shows one singlet at 6.35 τ,and the protons at 5.55 τ are absent. The isolated bridgehead protons at 5.46 τ are absent.

The nuclear magnetic resonance spectrum of Dimer A-1,2,5,8-d_4 (Figure 32, page 94) shows nineteen aromatic protons at 2.95 τ and a one proton singlet at 4.5 τ. The bridgehead protons at 5.33 and 5.75 τ and the proton at 5.64 τ are absent. The α-proton of the styryl double bond at 3.95 τ is also absent.

Irradiation of 2-phenoxy-4,5-benztropone-7-d (XXXI) gave dideuterodimers, Dimer B-6,9-d_2(LIV) and Dimer C-6,9-d_2 (LV). Dimer A-6,9-d_2(LVI) was prepared by thermal rearrangement of Dimer B-6,9-d_2. The infrared spectra of dideuterodimers are similiar to the unlabelled coumpouds.

Table 1. The nuclear magnetic resonance spectra of Dimer B and its labelled derivatives[a]

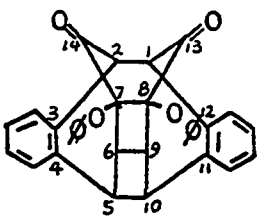
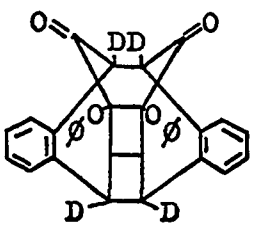
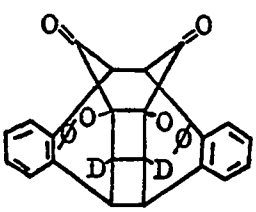
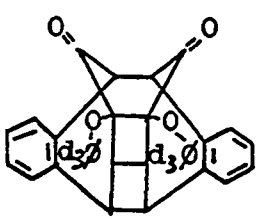
Proton	 XLIV	 LI	 LIV	 LXXV
Aromatic	2.87(m)	2.87(m)	2.87(m)	2.87(m)
H_5, H_{10}	3.41(d)J=12.3	-	3.41(s)	3.41(m)$J_{^{13}CCCH}$=12
H_6, H_9	4.12(d)J=12.3	4.12(s)	-	4.12(m)$J_{^{13}CCH}$=4
H_1, H_2	5.97(s)	-	5.97(s)	5.97(d)$J_{^{13}CCCH}$=4.5

[a]Chemical shifts in tau with respect to tetramethylsilane; J values in c.p.s.

The nuclear magnetic resonance spectrum of Dimer B-6,9-d_2(Figure 29, page 88) indicates clearly the position of the deuterium. The bridgehead proton is apparent at 5.97 τ. The higher field absorption from the β proton of the styryl double bond at 4.12 τ is absent while the lower field absorption of the α-proton at 3.41 τ appears as a singlet.

The nuclear magnetic resonance spectrum of Dimer C-6,9-d_2 (Figure 40, page110) shows aromatic protons of the benzo-group at 2.66 τ, the phenoxy protons at 3.01 and 3.71τ. The A_2B_2 pattern at 5.55 and 6.35 τ of the cyclobutane ring

Table 2. The nuclear magnetic resonance spectra of Dimer C and its labelled derivatives[a]

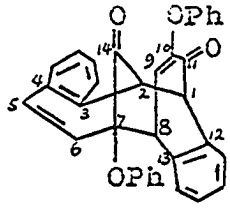
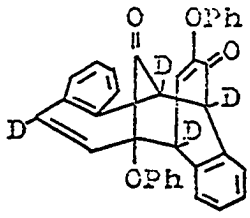
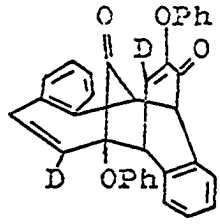
Proton	 XLV	 LII	 LV	 XLVIII
Benzo	2.66(s)	2.66(s)	2.66(s)	2.66(s)
m,p-OPh	3.03(m)	3.03(m)	3.03(m)	3.03(s)
o-OPh	3.70(m)	3.70(m)	3.70(m)	-
H_1, H_2	5.46(s)	-	5.46(s)	5.46(s)
H_5, H_{10}	5.55(m)	-	5.55(s)	5.55(m)
H_6, H_9	6.35(m)	6.35(s)	-	6.35(m)

[a]Chemical shifts in tau with respect to tetramethylsilane

shows only one singlet at 5.55 τ, which is due to the protons α to the benzene ring. The bridgehead protons appear at 5.46 τ.

The nuclear magnetic resonance spectrum of Dimer A-6,9-d_2 (Figure 33, page 96) shows eighteen aromatic protons at 2.95 τ. The styryl AB pattern only shows one singlet at 3.95τ. The higher field AB pattern appears at 5.33 and 5.75 τ. The high field half of the AX system shows a singlet at 5.64 τ.

Table 3. The nuclear magnetic resonance spectra of Dimer A and its labelled derivatives[a]

Proton	 XLIII	 LIII	 LVI
Aromatic	2.95(m)	2.95(m)	2.95(m)
H_5	3.95(d)J=13	-	3.95(s)
H_6	4.50(d)J=13	4.50(s)	-
H_1	5.75(d)J=5	-	5.75(d)
H_2	5.33(d)J=5	-	5.33(d)
H_8	5.64(d)J=9.7	-	5.64(s)

[a]Chemical shifts in tau with respect to tetramethylsilane; J value in c.p.s.

The latter result is equivalent to the earlier double resonance experiment and confirms that result.

All the dimers can be reduced to the corresponding diols. Sodium borohydride reduction of Dimer A gives Dimer A diol (XLIX). The nuclear magnetic resonance spectrum of XLIX (Figure 33, page 96) shows aromatic protons at 2.91 τ. AB styryl protons appear at 4.16 and 4.52 τ, J_{AB}=13 c.p.s.

Hydroxyl protons appear at 5.64 and 6.34 τ and are lost on treatment with deuterium oxide. The multiplets at 5.70, 4.90 and 5.33 τ correspond to one proton. The multiplet at 6.36 τ corresponds to two protons. The assignment of these protons was achieved by study of the nuclear magnetic resonance spectra of Dimer A diol-11,14,0-d_4 ($LVII_a$) (Figure 35, page 100) and Dimer A diol-6,9,0-d_4 ($LVIII_a$) (Figure 36, page 102). Reduction of Dimer A with sodium borodeuteride gave Dimer A diol-11,14-d_2(LVII) which was exchanged with deuterium oxide to $LVII_a$. Reduction of Dimer A-6,9-d_2 with sodium borohydride gave Dimer A diol-6,9-d_2(LVIII) (Figure 5, page 31) which was exchanged with deuterium oxide to $LVIII_a$. The nuclear magnetic resonance spectrum of Dimer A diol-11,14,0-d_4 shows the peaks at 4.90 and 5.33 τ due to the C_{11},C_{14} protons are missing. The peak at 5.70 τ is a doublet J=5 c.p.s. which is part of the AB pattern. The other part is at 6.36 τ superimposed upon the upper half of the AX system, J=10 c.p.s. The AX system is the C_8,C_9 protons. The C_9 proton is in the aromatic region. The C_8 proton appears as a singlet in the nuclear magnetic resonance spectrum of Dimer A diol-6,9,0-d_4 (see Table 4, page 32).

Treatment of Dimer A diol with acid forms the internal ether (L) (Figure 5, page 31). The nuclear magnetic resonance spectrum of Dimer A alcohol ether (Figure 37, page 104) shows aromatic protons at 2.85 τ. The AB styryl protons at 4.07 and

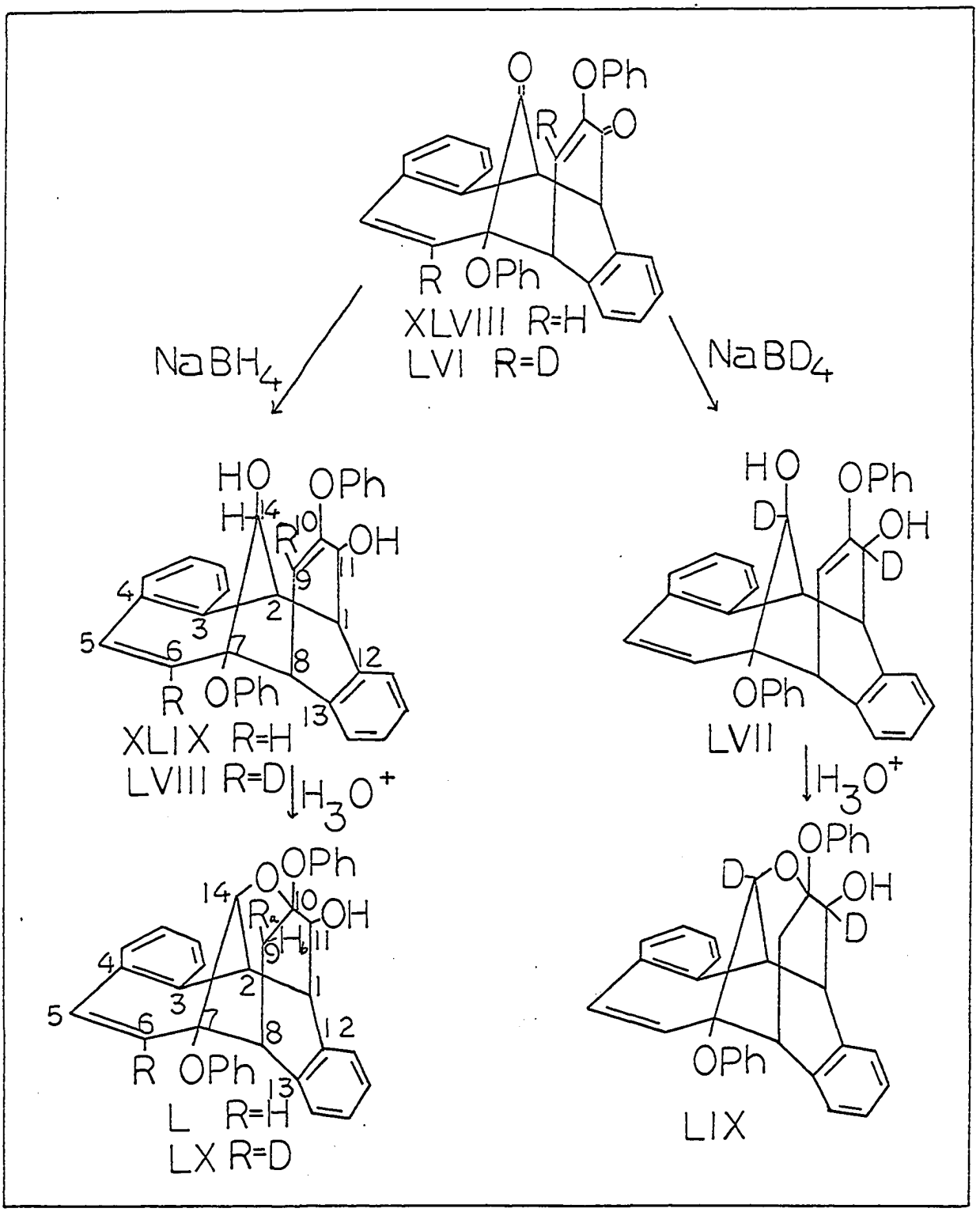
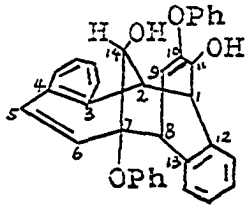
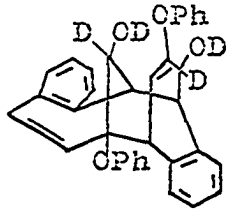
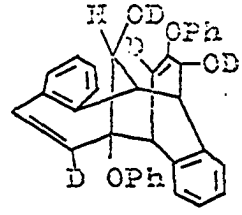


Figure 5. Reduction of Dimer A and formation of Dimer A alcohol ether

Table 4. The nuclear magnetic resonance spectra of Dimer A diol and its labelled derivatives[a]

Proton	 XLIX	 LVIIa	 LVIIIa
Aromatic	2.91(m)	2.91(m)	2.91(m)
H_5	4.16(d)J=13	4.16(d)	4.16(s)
H_6	4.52(d)J=13	4.52(d)	-
H_{14}	4.90(s)[b]	-	4.90(s)[b]
H_{11}	5.33(m)$J_{H_{10}OH}=11$ $J_{H_1H_{11}}=6.5$	-	5.33(d)J=6.5
$C_{14}OH$	5.64(s)	-	-
H_2	5.70(m)$J_{H_1H_2}=5$ $J_{H_2H_{14}}=2$	5.70(d)J=5	5.70(m)
$C_{11}OH$	6.34(m)[c]	-	-
H_8	6.34(m)[c]	6.34(d)J=9.5	6.31(s)[d]
H_1	6.36(m)[c]	6.36(d)J=5	6.36(m)[c]

[a]Chemical shifts in tau with respect to tetramethylsilane; J value in c.p.s.

[b]Broad singlet

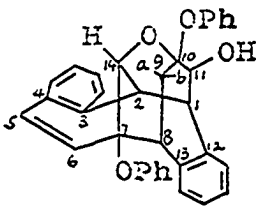
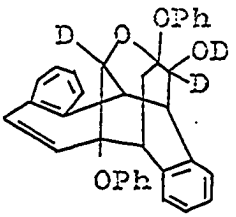
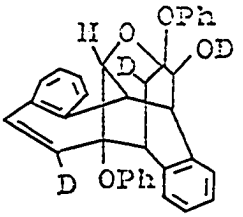
[c]Part of the complex multiplet

[d]Singlet on the top of the multiplet

4.42 τ, J_{AB}=13 c.p.s., the hydroxyl proton at 6.57 τ which disappears on treatment with deuterium oxide. The peaks at 4.90(d), 5.61(t), 6.06(d), 6.60(d), 6.63(m), 6.77(q) and 8.19(d) τ correspond to one proton. The assignment of these protons was achieved by study of the nuclear magnetic resonance spectra of Dimer A alcohol ether-11,14,O-d_3 (LIX$_a$) and Dimer A alcohol ether-6,9a,O-d_3 (LXa) which were prepared from the corresponding Dimer A diol. The peaks at 4.90,6.06 and 6.57 τ are missing in the nuclear magnetic resonance spectrum of Dimer A alcohol ether-11,14,O-d_3. The peaks at 4.42, 6.57 and 6.77 τ are missing in the nuclear magnetic resonance spectrum of Dimer A alcohol ether-6,9a,O-d_3. The 4.90 τ peak is the proton at C_{14}, $J_{H_2H_{14}}$=5 c.p.s. The peak at 5.61 τ is the proton at C_2, $J_{H_1H_2}$=$J_{H_2H_{14}}$=5 c.p.s. The peak at 6.60 τ is the proton at C_8, $J_{H_8H_{9b}}$=7 c.p.s. The peak at 6.63 τ is the proton at C_1, $J_{H_1H_2}$=5 c.p.s. and $J_{H_1H_{11}}$=2 c.p.s. The doublet at 8.19 τ which changes to a singlet in the nuclear magnetic resonance spectrum of Dimer A alcohol ether-6,9a,O-d_3 is the C_{9b} proton $J_{H_{9a}H_{9b}}$=12 c.p.s., $J_{H_8H_{9b}}$=0 because the dihedral angle =90°. The quartet at 6.77 τ is the C_{9a} proton (see Table 5, page 34).

Dimer B can be reduced to Dimer B diol (LXI) by sodium borohydride (38) (Figure 6, page 35). The infrared spectrum (Figure 21, page 72) shows no carbonyl absorption peak. The nuclear magnetic resonance spectrum (Figure 30,

Table 5. The nuclear magnetic resonance spectra of Dimer A alcohol ether and its labelled derivatives[a]

			
Proton	L	LIXa	LXa
Aromatic	2.85(m)	2.85(m)	2.85(m)
H_5	4.07(d)J=13	4.07(d)	4.07(s)
H_6	4.42(d)J=13	4.42(d)	-
H_{14}	4.90(d)J=5	-	4.90(d)
H_2	5.61(t)J=5	5.61(d)J=5	5.61(t)
H_{11}	6.06(d)J=2	-	6.06(d)
OH	6.57(s)	-	-
H_8	6.60(d)J=7	6.60(d)	6.60(d)
H_1	6.63(m)$J_{H_1H_2}=5$ $J_{H_1H_{11}}=2$	6.63(d)J=5	6.63(m)
H_{9a}	6.77(q)$J_{H_8H_{9a}}=7$ $J_{H_{9a}H_{9b}}=12$	6.77(q)	-
H_{9b}	8.19(d)J=12	8.19(d)	8.19(s)

[a]Chemical shifts in tau with respect to tetramethylsilane; J value in c.p.s.

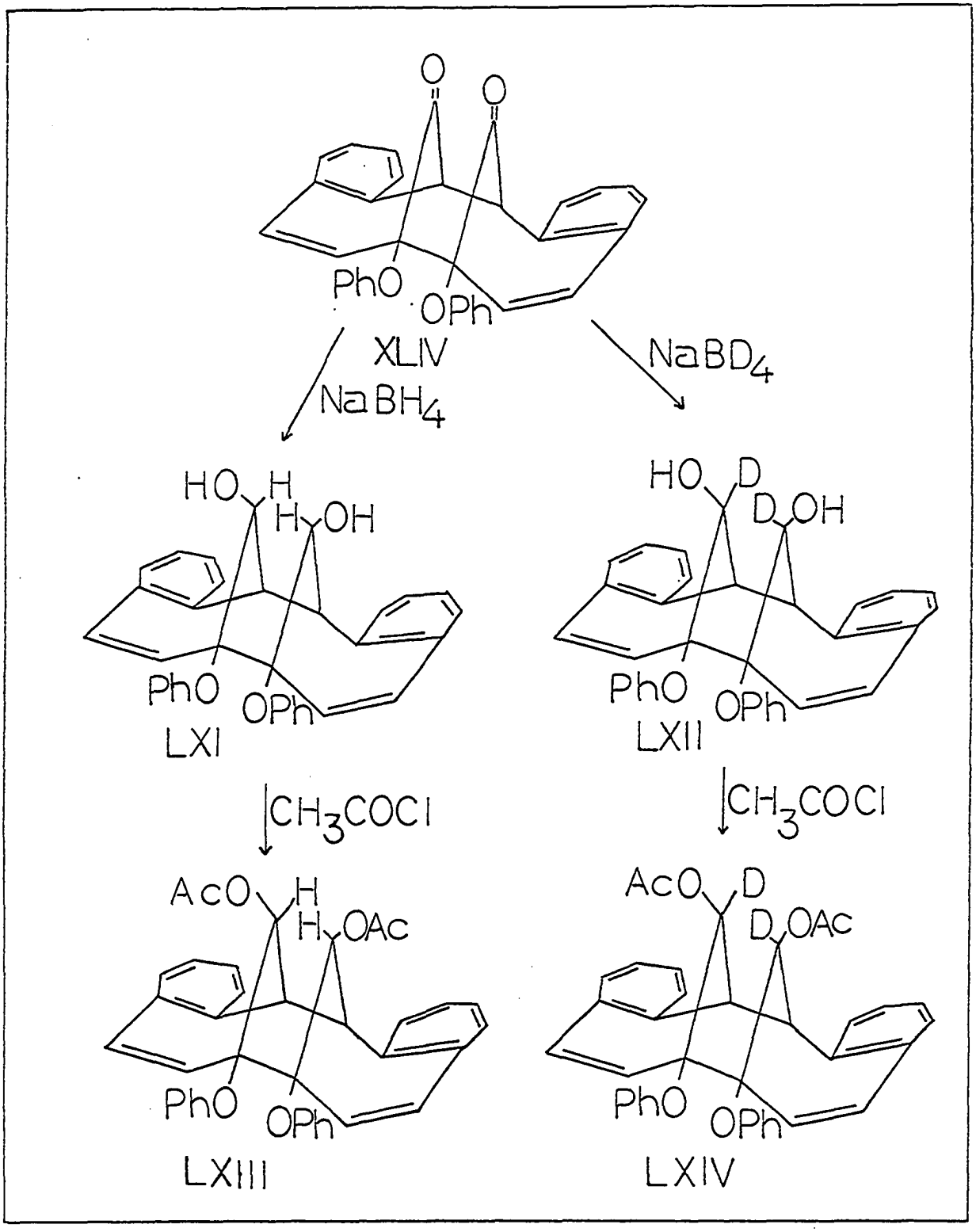
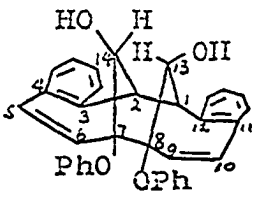
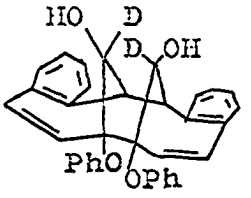
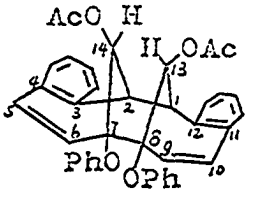
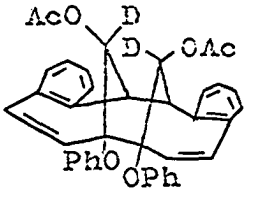


Figure 6. Reduction of Dimer B and acetylation of the resulting Dimer B diol

page 90) shows a pair of doublets at 3.55 and 3.90 τ corresponding to the styryl protons (J=13 c.p.s.). The chemical shifts between these doublets is greatly reduced upon reduction of Dimer B to the alcohol indicating a closer similarity of the protons. The aromatic protons appear as an unusually intense singlet at 2.80 τ. The signal at 6.10 τ is the bridgehead protons. The signal at 7.0 τ is the alcohol proton which can be exchanged by deuterium oxide. The protons on the carbon bearing alcohol group appear at 5.0 τ. In order to establish the assignments, Dimer B diol-13,14-d_2 (LXII) was prepared. Dimer B was reduced by sodium borodeuteride to give LXII. The nuclear magnetic resonance spectrum of LXII (Figure 35, page 100) is similiar to LXI except that the signal at 5.0 τ is absent. (Table 6, page 37). Dimer B diol has been oxidized back to Dimer B (39).

Dimer B diol can be acetylated to diacetate (LXIII) by acetyl chloride. The infrared spectrum (Figure 22, page 74) shows carbonyl absorption at 1718 cm^{-1}. The nuclear magnetic resonance spectrum (Figure 31, page 92) shows AB styryl protons at 3.51 and 3.53 τ. The chemical shifts of the AB system are very close indicating an even greater similarity of the α, β styryl protons. The protons of the methyl group of the acetoxy group are at 8.70 τ. The signal for these protons appears at an abnormally high field position, displaying a diamagnetic shift of 0.8 p.p.m. from the normal position. The

Table 6. The nuclear magnetic resonance spectra of Dimer B diol and Dimer B diol diacetate[a]

Proton	 LXI	 LXII	 LXIII	 LXIV
Benzo	2.80(m)	2.80(m)	2.80(s)	2.80(s)
OPh	2.80(m)	2.80(m)	2.88(s)	2.88(s)
H_5, H_{10}	3.55(d)J=12	3.55(d)	3.51(d)J=12	3.51(d)
H_6, H_9	3.90(d)J=12	3.90(d)	3.53(d)J=12	3.53(d)
H_{13}, H_{14}	5.00(d)J=2	-	3.90(d)J=2	-
H_1, H_2	6.12(d)J=2	6.12(s)	6.30(d)J=2	6.30(s)
OH	7.00(s)	7.00(s)	-	-
CH_3CO	-	-	8.70(s)	8.70(s)

[a]Chemical shifts in tau with respect to tetramethylsilane; J value in c.p.s.

location of the methyl group is at exceptionally high field for $\overset{O}{\overset{\|}{C}}CH_3$. The abnormal nuclear magnetic resonance spectrum must be a consequence of the stereochemistry or strain in the molecule. The aromatic protons appear as two peaks at 2.80 and 2.88 τ. The bridgehead protons and the protons at the

carbon bearing OAc group appear as AX signal at 6.30 and 3.90 τ (J_{AX}=2 c.p.s.). The assignment of these protons was achieved by looking at the nuclear magnetic resonance spectrum of Dimer B diol diacetate-13,14-d_2 (LXIV). Since the signal at 3.90 τ is absent in LXIV, the signal at 6.30 τ is the bridgehead protons (Table 6, page 37).

Reduction of Dimer C with sodium borohydride gave Dimer C diol (LXV). The nuclear magnetic resonance spectrum (Figure 41, page 112) shows the aromatic protons as multiplet centered at 3.0 τ. The bridgehead protons are no longer a singlet. Complex multiplets are observed at 6.00 and 6.55 τ. A hydroxy proton appears at 8.42 τ which disappears on treatment with deuterium oxide. The infrared spectrum (Figure 24, page 78) shows hydroxyl peak at 3570 cm^{-1}.

In the study of a photochemical reaction it is of interest to learn something about the excited state which is involved in the formation of products. In most cases the first excited state formed in the irradiation of a compound is an excited singlet state; the absorption of light promotes one electron to a vacant orbital, but the two electrons remain spin-paired. Since the singlet-singlet transition is spectroscopically allowed, the lifetime of the excited singlet state is relatively short. In some cased the excited singlet intermediate can undergo intersystem crossing to the triplet state, in which one electron inverts its spin and is no longer

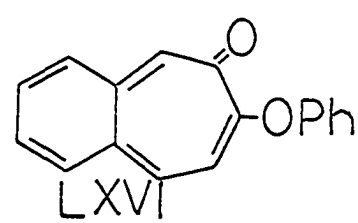
paired. The triplet state intermediate has a relatively longer lifetime than the excited singlet state. Therefore, the triplet state has been considered the most likely species to be involved in an intermolecular reaction (40). Triplet state intermediates often can be quenched by oxygen and certain other molecules which can deactivate the intermediate by energy transfer. The triplet state may be attained also by a photosensitization process rather than as a result of direct irradiation. In this process energy absorbed by the sensitizer is transferred to the molecule involved in the photochemical reaction. Sensitizers which undergo intersystem crossing efficiently to the triplet state will produce the triplet state in the acceptor molecule when energy is transferred. Energy transfer is most efficient when the triplet energy of the sensitizer is above the triplet energy of the acceptor molecule (41).

It was found that the formation of dimers from 2-(p-halophenoxy)-4,5-benztropones is unaffected by the presence of oxygen or sensitizer (42). The involvement of a short-lived excited singlet state in an intermolecular reaction would be more credible if evidence could be found for the existence of a ground state complex between two or more molecules of the phenoxybenztropones. No evidence was found for complex formation in the ground state of the phenoxybenztropone (42).

If the dimerization proceeds through the triplet state,

phenoxybenztropone itself could be a photosensitizer in photochemical cis-trans isomerization (43). The effect of 2-phenoxy-4,5-benztropone on the sensitization of photochemical cis-trans isomerization was studied. Piperylene was irradiated under the same conditions with and without 2-phenoxy-4,5-benztropone. The cis to trans ratio of piperylene was not appreciable changed. Irradiation of trans-stilbene in the presence of 2-phenoxy-4,5-benztropone at 366 mμ gave 84% cis stilbene. trans-Stilbene has no absorption at 366 mμ. The triplet energy of piperylene and trans-stilbene is 53 and 47 Kcal/mole, respectively. Since 2-phenoxy-4,5-benztropone has no effect on the cis-trans isomerization of piperylene and has effect on the cis-trans isomerization of stilbene, the triplet energy of 2-phenoxy-4,5-benztropone is in the vicinity of 50 Kcal/mole. Without more evidence it would be premature to draw further conclusions concerning the excited species involved in the dimerization process.

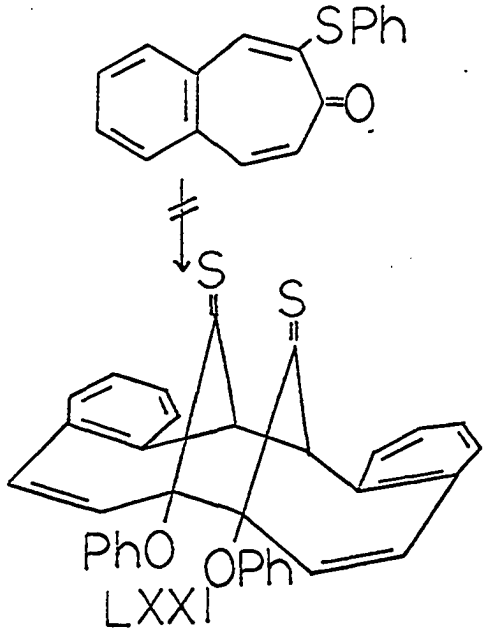
The dimers appear to be derived formally from LXVI rather than XXV. All attempts to trap LXVI with dienophiles have failed (39). Dimer formation continues in the presence of dicarbomethoxyacetylene, maleic anhydride and tetracyanoethylene suggesting that dimerization does not involve LXVI as a discrete intermediate.



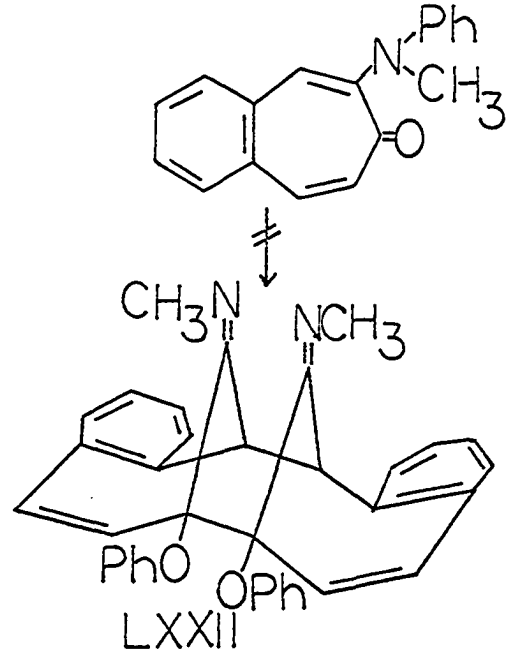
LXVI

One of the interesting aspects of the dimerization process is an apparent oxygen to oxygen phenyl shift in going from the starting material to the dimers. Examples of phenyl shifts from carbon to oxygen are known in the photoreactions of tetrabenzoylethylene (LXVII) (44) and the cis-1,2-dibenzoylethylenes (LXVIII) (45) (Figure 7, page 42). A diradical intermediate (LXIX) was proposed for the latter. Examples of phenyl shifts from oxygen to oxygen are known in cases where the O-phenoxybenzoyloxy radical (LXX) is produced (46).

The effect of replacement of the phenoxy oxygen atom of 2-phenoxy-4,5-benztropone with different heteroatoms(S and N) was studied. If dimerization of 2-thiophenoxy-4,5-benztropone or 2-(N-methylanilino)-4,5-benztropone was to occur with the accompanying phenyl shift, the heteroatom should be located in the carbonyl position as in LXXI or LXXII.



LXXI



LXXII

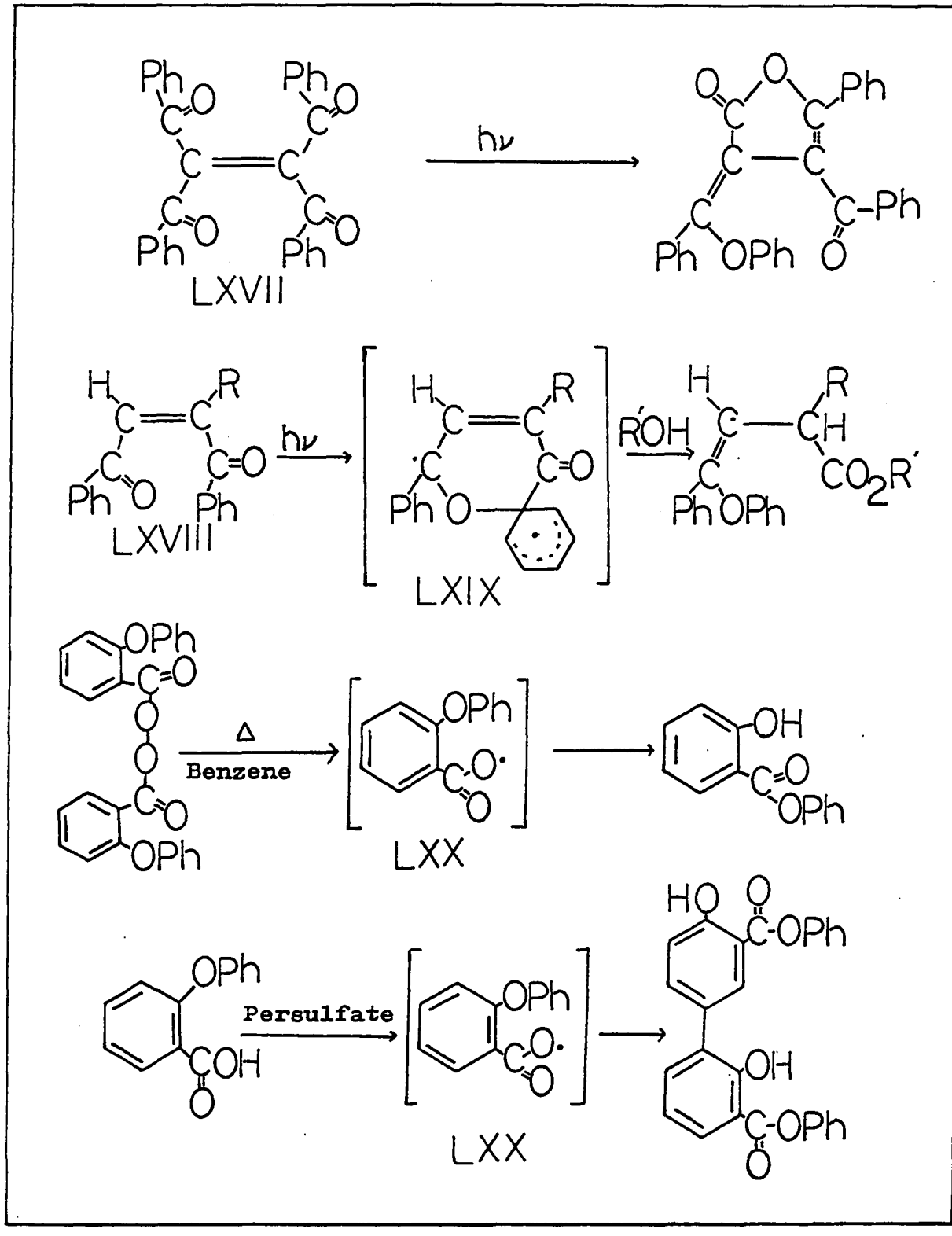


Figure 7. Examples of phenyl migrations

Irradiation of 2-thiophenoxy-4,5-benztropone(XXXVI)(42) and 2-(N-methylanilino)-4,5-benztropone (XXXVII) under the same condition as 2-phenoxy-4,5-benztropone gave only starting material and tars. No dimer could be found. Although the results were not as hoped, they do indicate that the atom attached to the phenyl group plays an important role in the dimerization. Substitution of the oxygen by sulfur or nitrogen prevents dimer formation.

The best way to study the phenyl migration from oxygen to oxygen is to study the ^{18}O-labelled compounds. If the carbonyl oxygen atom of 2-phenoxy-4,5-benztropone is labelled with ^{18}O, the labelled oxygen should become the phenoxy oxygen atom in the dimers by phenyl shift. If the ether oxygen of the starting material is labelled, the labelled oxygen should be located in the carbonyl position in the dimers. The location of the labelled oxygen can be detected by the infra-red spectrum (47).

The stretching frequency ν of a diatomic molecule of atoms with masses m_x and m_y can be expressed by equation (1):

$$\nu = \frac{1}{2\pi c} = \sqrt{\frac{f(m_x + m_y)}{m_x m_y}} \qquad (1)$$

where c is the velocity of light, and f is the force constant (bond strength or bond order corresponding to Hooke's constant of springs). The stretching frequencies of x-y bonds and multiple bonds can also be approximated by the same expression,

and it can be seen that the heavier the atoms concerned the lower the frequency. If it is assumed that force constants of x-y and x-y', where y' is the isotope of y, are identical, the wave number ratio of stretching frequencies deduced from equation (1) becomes:

$$\frac{\nu_{x-y}}{\nu_{x-y'}} = \sqrt{\frac{m_x m_{y'} + m_y m_{y'}}{m_x m_y + m_y m_{y'}}} \qquad (2)$$

where m_x, m_y, $m_{y'}$ are the mass of atom x, y, y', respectively. Thus, the ratio of bonds C=O:C=^{18}O is 1.024.

If labelled oxygen locates in the carbonyl position, it will show two carbonyl absorption peaks in the infrared spectrum. The labelled carbonyl absorption peak is the lower frequency one. Irradiation of carbonyl ^{18}O-labelled 2-phenoxy-4,5-benztropone (XXXIII), which shows two carbonyl absorption at 1600 cm^{-1} and 1570 cm^{-1}, in the same manner gave LXXIII (Figure 8, page 45). The infrared spectrum of LXXIII (Figure 20, page 70) shows one carbonyl absorption and is essentially identical with Dimer B. The labelled oxygen is located at the ether position (phenyl migration). Irradiation of 2-(^{18}O-phenoxy)-4,5-benztropone in the usual manner gave carbonyl ^{18}O-labelled Dimer B (LXXIV). The infrared spectrum of LXXIV (Figure 20, page 70) shows two carbonyl absorption peaks at 1690 cm^{-1}(C=^{18}O) and 1737 cm^{-1}(C=O). It proves that the labelled oxygen is located at carbonyl position. To check the observation, photochemistry of 2-phenoxy-4,5-benztropone-

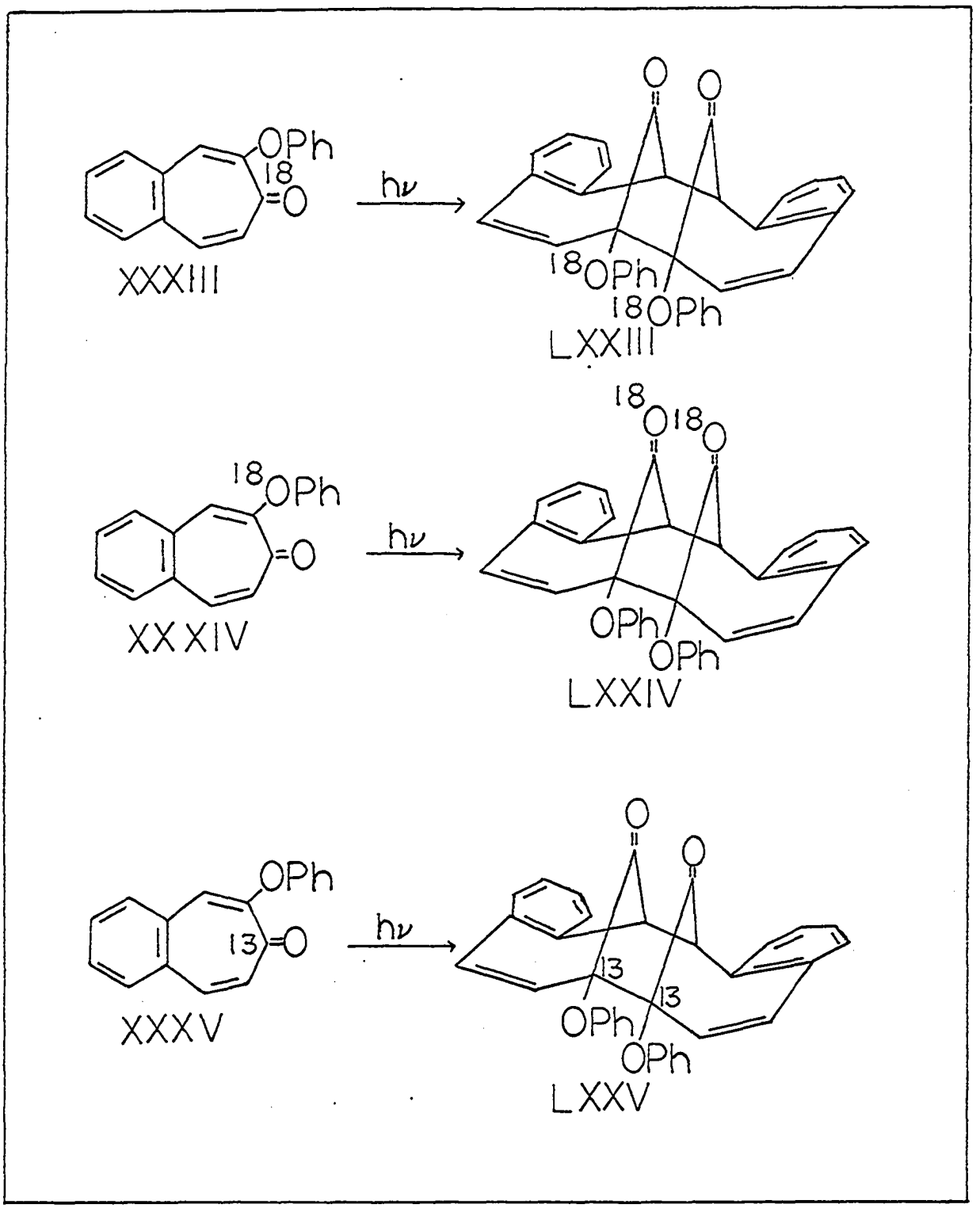


Figure 8. Photochemical transformation of ^{18}O-labelled and ^{13}C-labelled 2-phenoxy-4,5-benztropones

1-^{13}C was studied. Irradiation of 2-phenoxy-4,5-benztropone-1-^{13}C in tetrahydrofuran gave Dimer B with ^{13}C at bridgehead carbon (LXXV) by phenyl shift. The infrared spectrum of LXXV (Figure 20, page 70) shows only one carbonyl absorption peak at 1737 cm^{-1}. The nuclear magnetic resonance spectrum (Figure 30, page 90) shows aromatic protons at 2.87 τ. The AB system doublets at 3.41 and 4.12 τ are split by ^{13}C to two doublets with $J_{^{13}CCCH}$=12 c.p.s. and $J_{^{13}CCH}$=4 c.p.s., respectively. The aliphatic protons at 5.97 τ are split by ^{13}C to a doublet with $J_{^{13}CCH}$=4.5 c.p.s. It was reported (48) that $J_{^{13}CCH}$ for sp^3 hybridized ^{13}C has values of about 4.0 c.p.s. and $J_{^{13}CCCH}$ is larger than $J_{^{13}CCH}$. Recently Roberts reported that $J_{^{13}CC=CH}$ is 4 c.p.s. larger than $J_{^{13}CCH}$ in the cyclobutene case (49). From these observations,the phenyl group does migrate during dimerization of 2-phenoxy-4,5-benztropone.

As mentioned previously, Dimer B can be converted to Dimer A by heating it slightly above its melting point (220-230°). The rearrangement can be visualized as starting by homolytic cleavage of the bond between the two phenoxy-bearing carbons to give diradical (LXXVI) (Figure 9, page 47). Rebonding of the two unpaired electron of LXXVI can give either Dimer B or Dimer A. The rearrangement of Dimer B to Dimer A would be expected to be favored thermodynamically because of the decrease in angle strain and electronic and steric repulsions. Evidence was found indicating that an

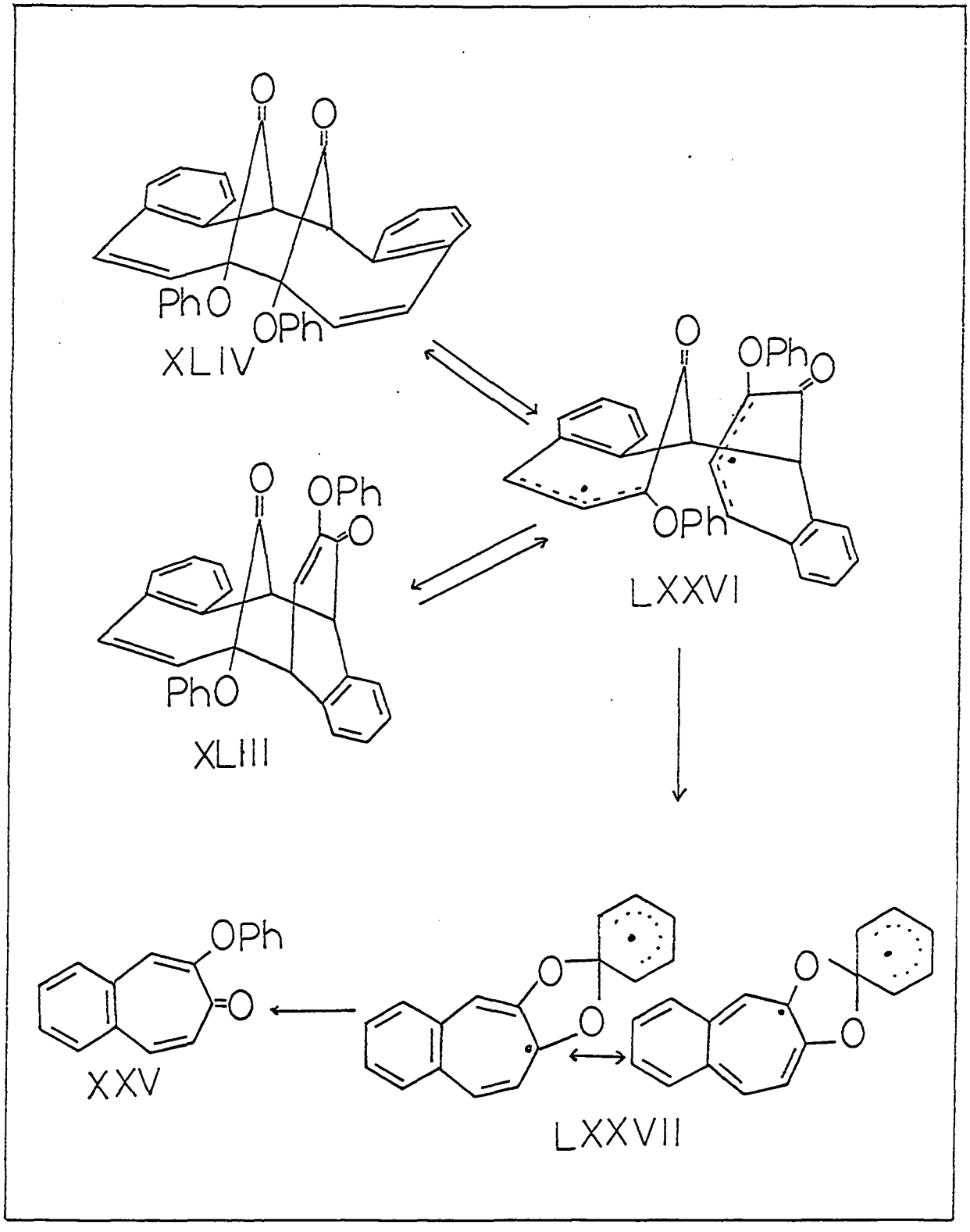


Figure 9. Thermal reactions of Dimer B and Dimer A

equilibrium actually exists between the dimers at the temperature of the rearrangement. After Dimer A was heated at 220-230° for a short period, Dimer B was detected in the mixture by the observation of a pair of peaks in the infrared spectrum at 975 and 967 cm^{-1}, a characteristic pattern for Dimer B. Not enough Dimer B was present to attempt to isolate it, as the equilibrium does favor Dimer A.

The thermal cleavage of the dimers to monomer poses more difficult mechanistic problems. The phenyl shift must occur again to give XXV. The possibility of LXVI being an intermediate in the thermal cleavage was tested by cleaving both p-chloro derivatives of Dimer A and Dimer B in the presence of maleic anhydride (42). No adduct of p-chloro derivative of LXVI could be detected in either case. The pyrolysis could involve a bridged intermediate such as LXXVII which is not trapped by maleic anhydride.

Any mechanism for dimerization of the 2-phenoxy-4,5-benztropone must meet certain requirement. Dimer B is not derived photochemically from Dimer A. It is known that Dimer B is converted to Dimer C on irradiation and to Dimer A on thermal rearrangement. It would seem reasonable that the primary mechanistic problem is to account for the formation of Dimer B. Any mechanism must account for an exchange in relative position of the phenoxy group and carbonyl group in going from 2-phenoxy-4,5-benztropone to the dimers. In study

of the isomerization and rearrangement of other tropolone systems suggests that a mechanism involving polar intermediates should be considered in the case of the 2-phenoxy-4,5-benztropone (Mechanism 1) (Figure 10, page 50). Polarization of the carbonyl and a rearrangement of the double bonds gives the intermediate LXXVIII. Return of the electron pair on the carbonyl oxygen and rearrangement gives a benzobicyclo[3,2,0]-heptadienone (LXXIX). Opening of the bicyclic system to a seven-membered ring gives the previously discussed intermediate (LXVI) which can dimerize to give Dimer B. The fact that all attempts to trap the intermediate LXVI have failed casts some doubt on the validity of the Mechanism 1. Mechanism 1 exchange the relative position of C_3 and C_7. In the study the photochemistry of 2-phenoxy-4,5-benztropone-3,6-d_2 and 2-phenoxy-4,5-benztropone-7-d, the carbon skeleton does not rearrange; therefore, Mechanism 1 is eliminated.

An alternate Mechanism 2 has been proposed (27) (Figure 11, page 51). Collision of a photochemically excited molecule with a ground state molecule gives LXXX in which the two molecules are joined by a bond between the two carbonyl carbons. LXXX also can be formed by excitation of the complex formed between two molecules of 2-phenoxy-4,5-benztropone with dipoles opposed. An oxygen-oxygen phenyl shift gives LXXXI via the bridged intermediate LXXXII. Rotation about the newly formed carbon-carbon bond in LXXXI gives LXXXIII and collapse

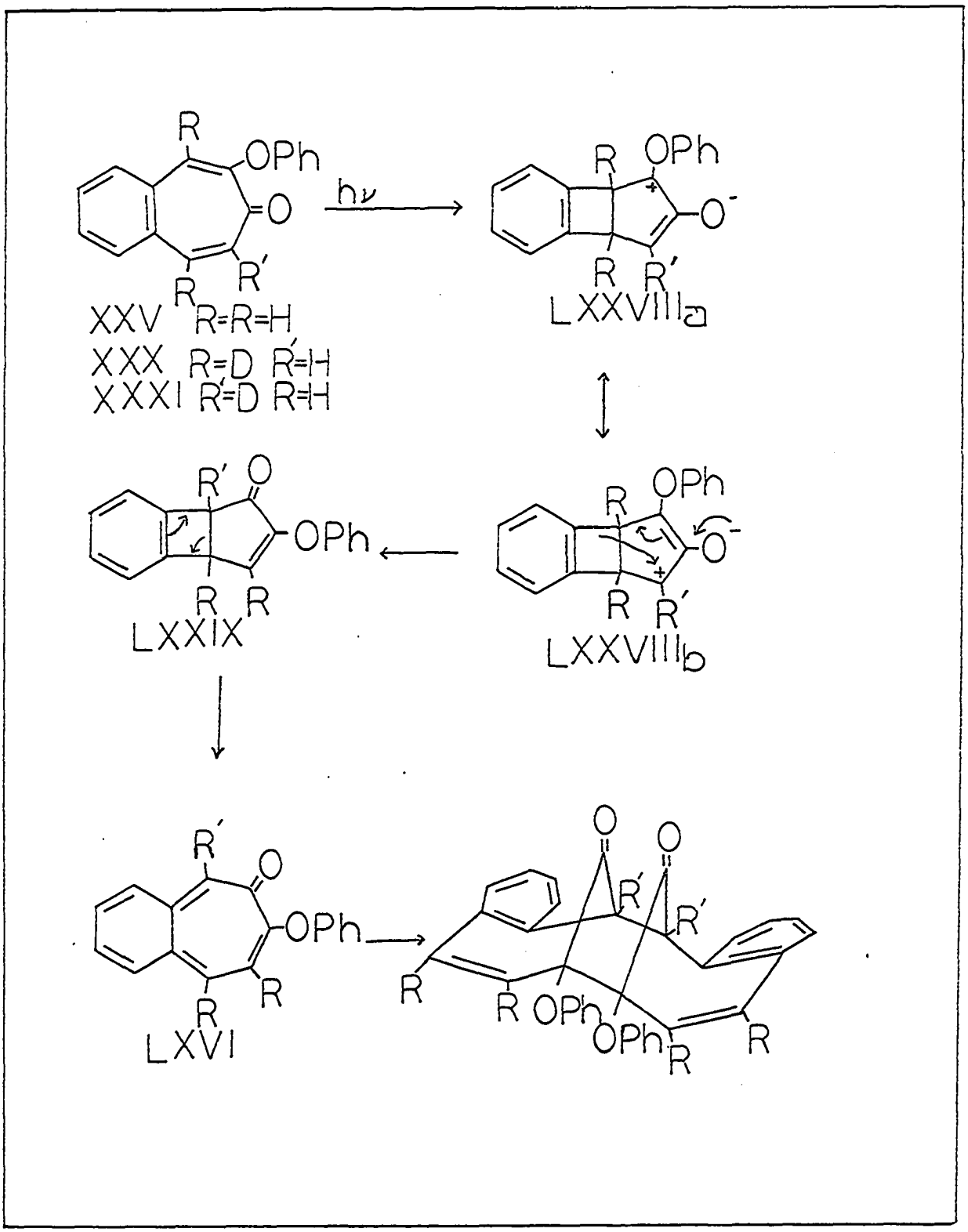


Figure 10. Mechanism 1 for the formation of Dimer B

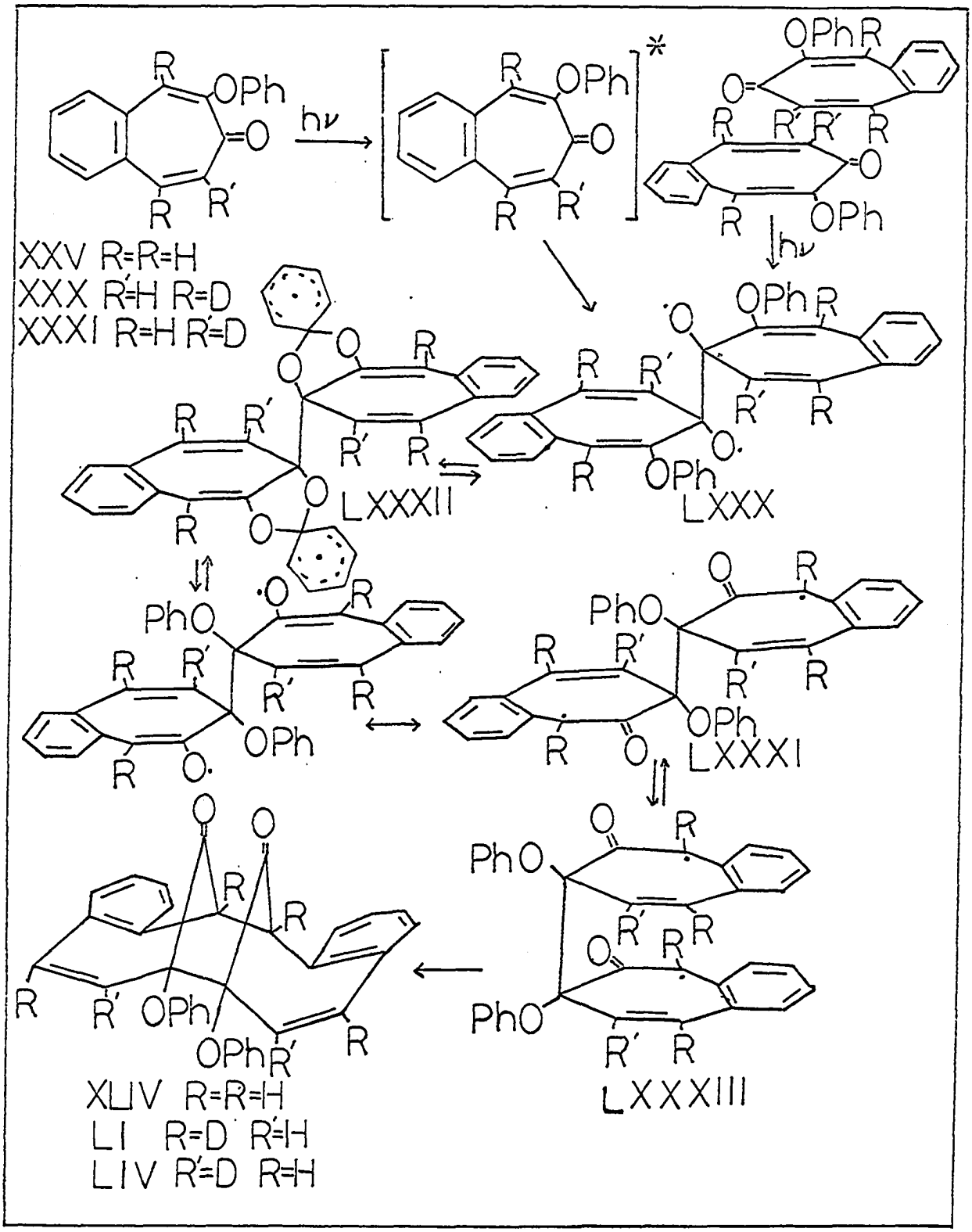


Figure 11. Mechanism 2 for the formation of Dimer B

of the diradical produces Dimer B.

Mechanism 2 accounts for the phenyl migration without any rearrangement of the carbon atoms in the tropolone ring. It does not involve the rearrangement monomer unit LXVI. The photochemistry of 2-phenoxy-4,5-benztropone-3,6-d_2 and 2-phenoxy-4,5-benztropone-7-d agrees with the mechanism.

Evidence for this type of mechanistic path is provided by the nonphotoreactivity of 2-methoxy-4,5-benztropone (XXXVIII). The methyl migration as illustrated for the phenyl migration would not be expected to occur. Irradiation of 2-methoxy-4,5-benztropone in several different solvents gave only starting material and polymers.

Mass Spectrometry of 2-Phenoxy-4,5-benztropone and Related Compounds

Mass spectrometry of 2-phenoxy-4,5-benztropone

The 70 ev mass spectra of 2-phenoxy-4,5-benztropone (XXV) and its derivatives are shown in Table 7. The principle features, summarized in Table 7,page 113, are (1)a sequence of fragmentations 248 (M^+) $\longrightarrow$ 220 (M - 28) $\longrightarrow$ 192 $\longrightarrow$ 191 $\longrightarrow$ 165 each correlated by a metastable ion signal, (2) 249 (M^+) $\longrightarrow$ 231 (M - 17) peak, (3) significant peaks at m/e 144, 127 and 77 and (4) an intense peak at m/e 115.

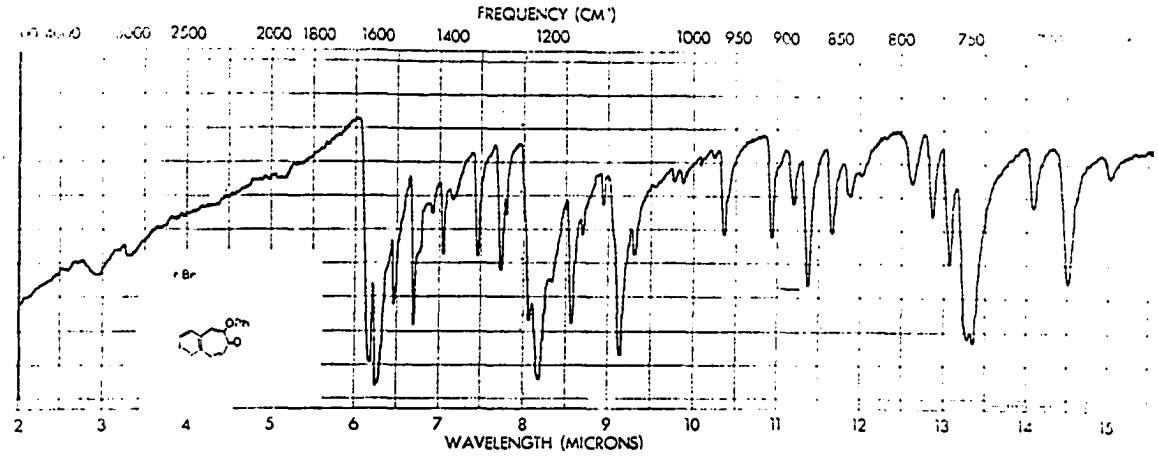
The curious M - 17 ion is due to the loss of an -OH

Figure 12. Infrared spectra

Top - 2-Phenoxy-4,5-benztropone (XXV)

Middle - 2-Phenoxy-4,5-benztropone-3,6-d_2 (XXX)

Bottom - 2-Phenoxy-4,5-benztropone-7-d (XXXI)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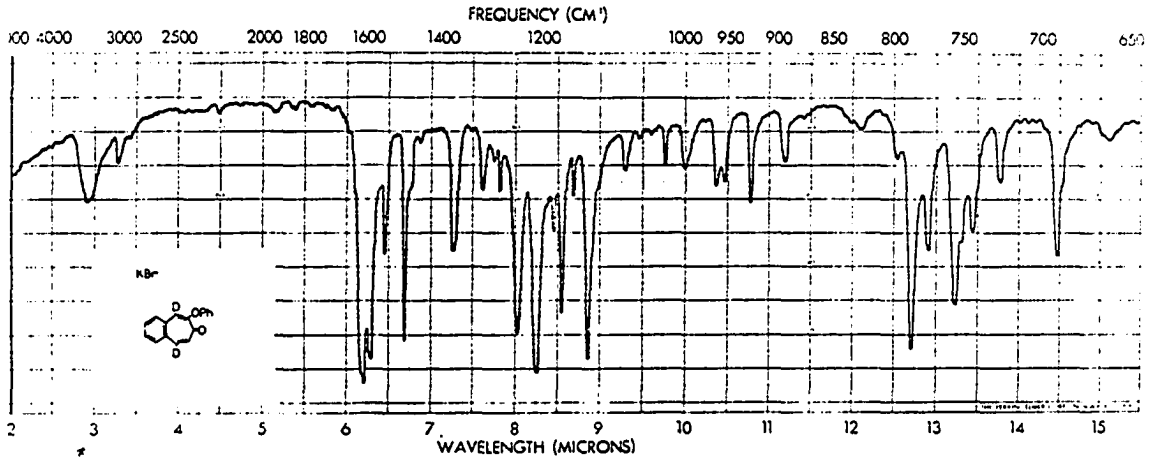
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

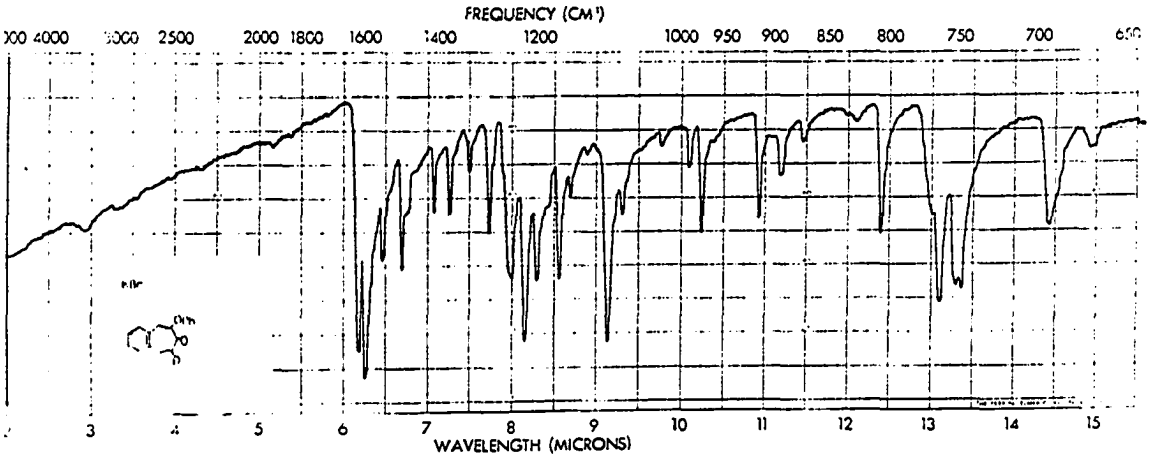
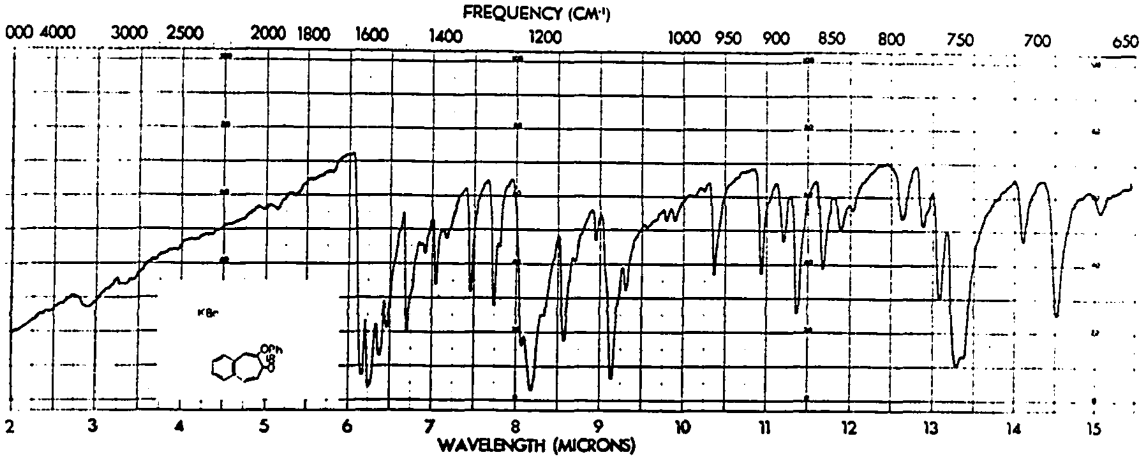

FREQUENCY (CM⁻¹)
4000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 13. Infrared spectra

Top - Carbonyl-^{18}O-labelled 2-phenoxy-4,5-benztropone (XXXIII)

Middle - 2-(^{18}O-Phenoxy)-4,5-benztropone (XXXIV)

Bittom - 2-Phenoxy-4,5-benztropone-1-^{13}C (XXXV)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KBr
OPh
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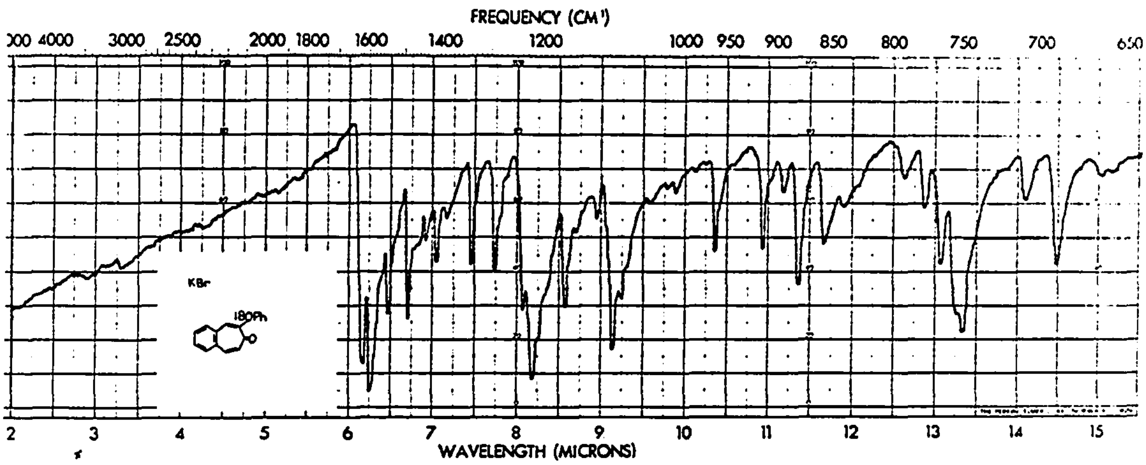
WAVELENGTH (MICRONS)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18OPh
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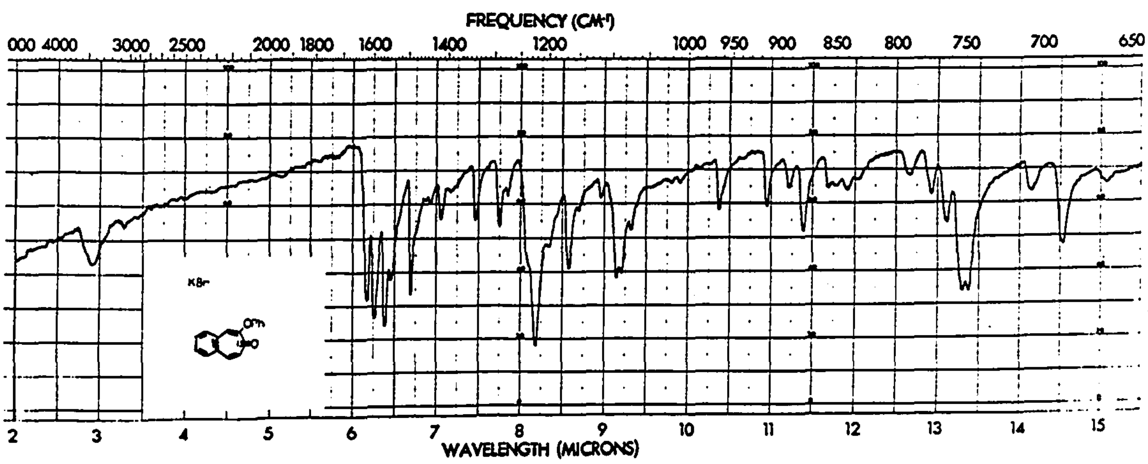
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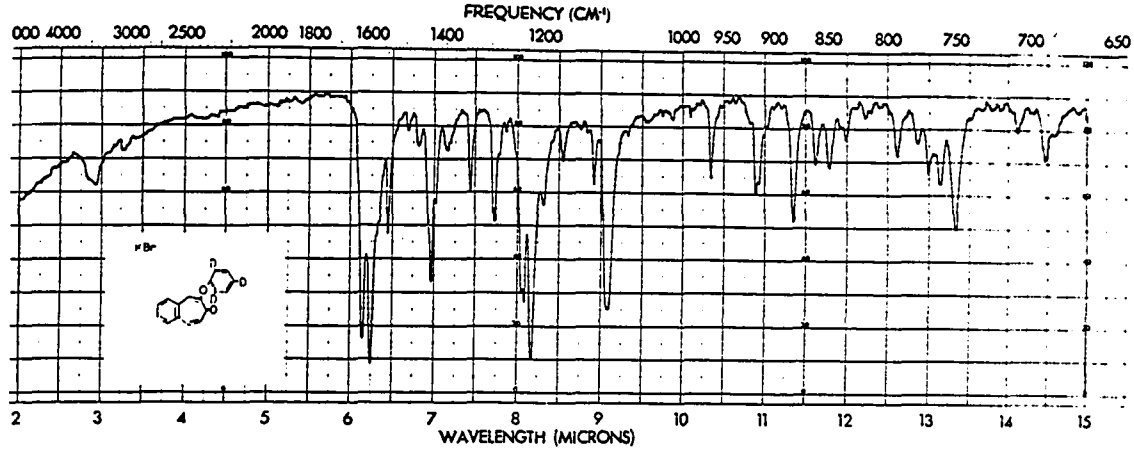
KBr
OPh
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 14. Infrared spectra

Top - 2-(2,4,6-Trideuteriophenoxy)-4,5-benztropone (XXXII)

Middle - 2-Thiophenoxy-4,5-benztropone (XXXVI)

Bottom - 2-(N-Methylanilino)-4,5-benztropone (XXXVII)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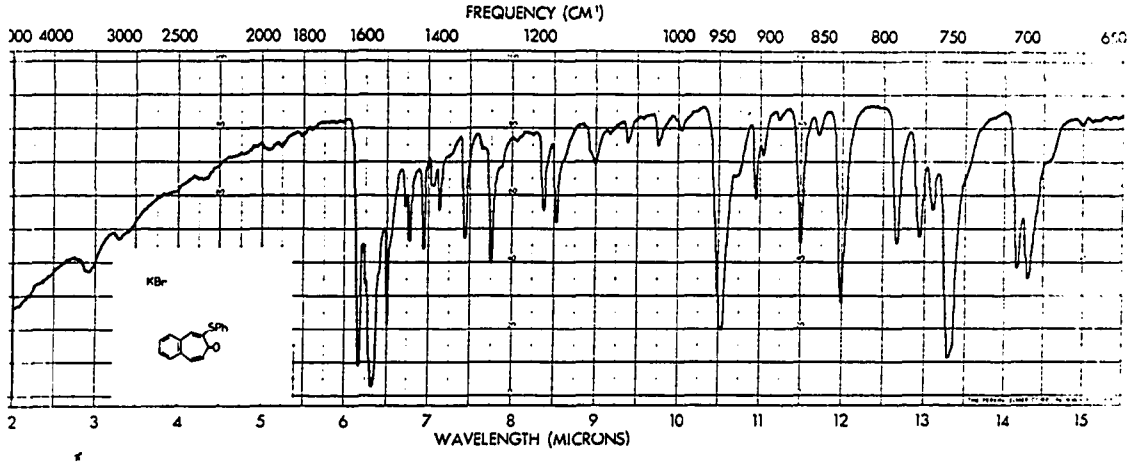
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

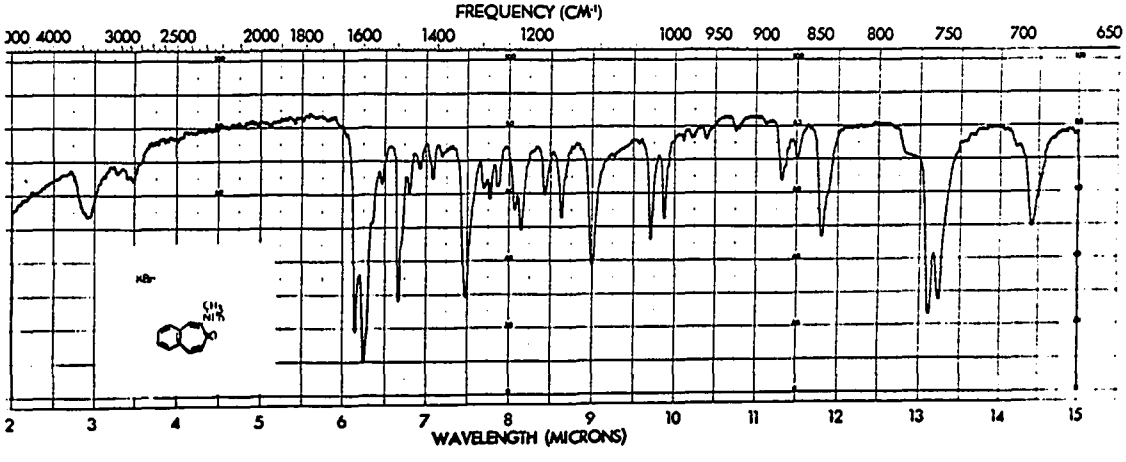
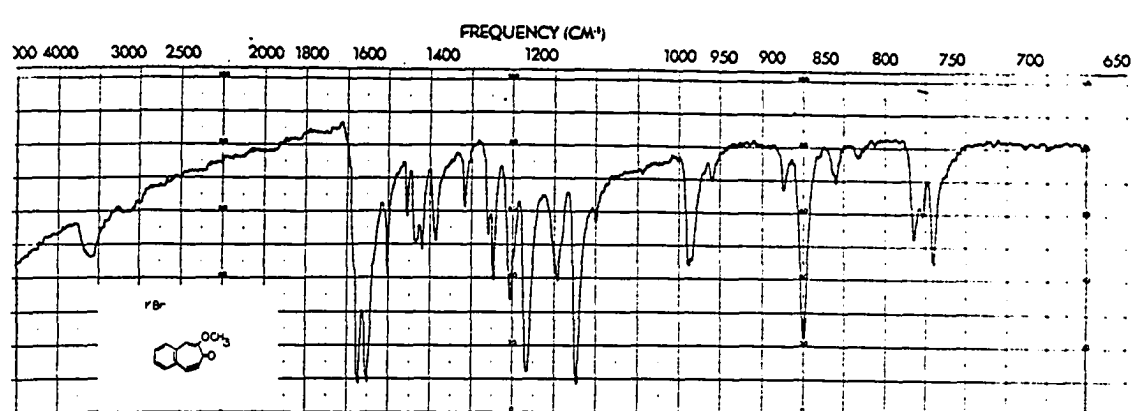

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

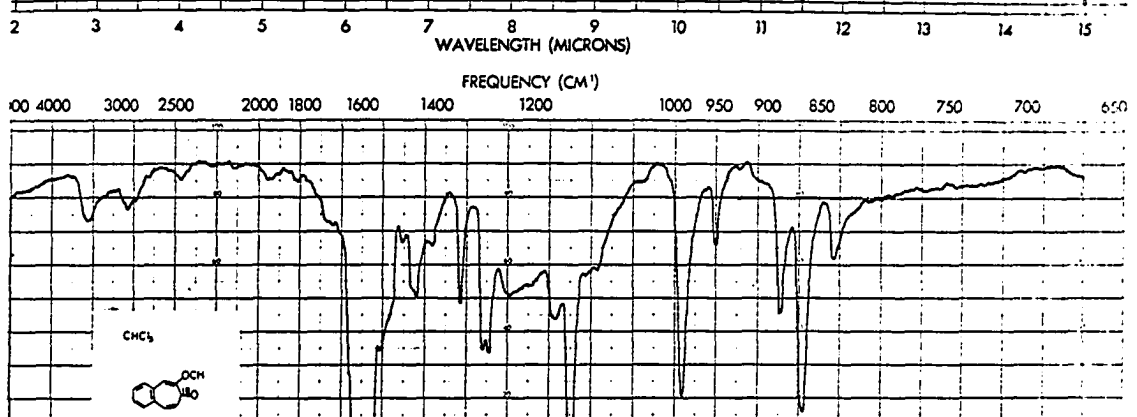
Figure 15. Infrared spectra

Top - 2-Methoxy-4,5-benztropone (XXXVIII)

Middle - Carbonyl-^{18}O-labelled 2-methoxy-4,5-benztropone (XXXIX)

Bottom - 2-(Methoxy-^{13}C)-4,5-benztropone (XL)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
CHCl₃
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

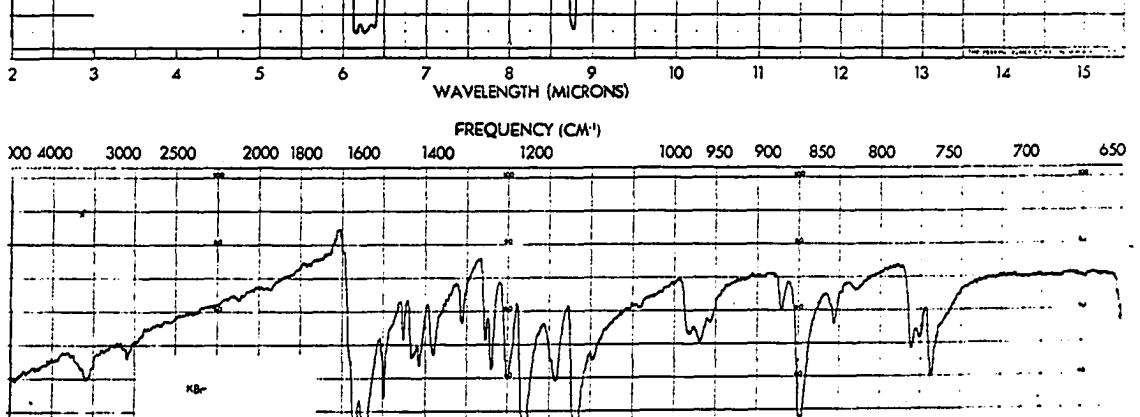
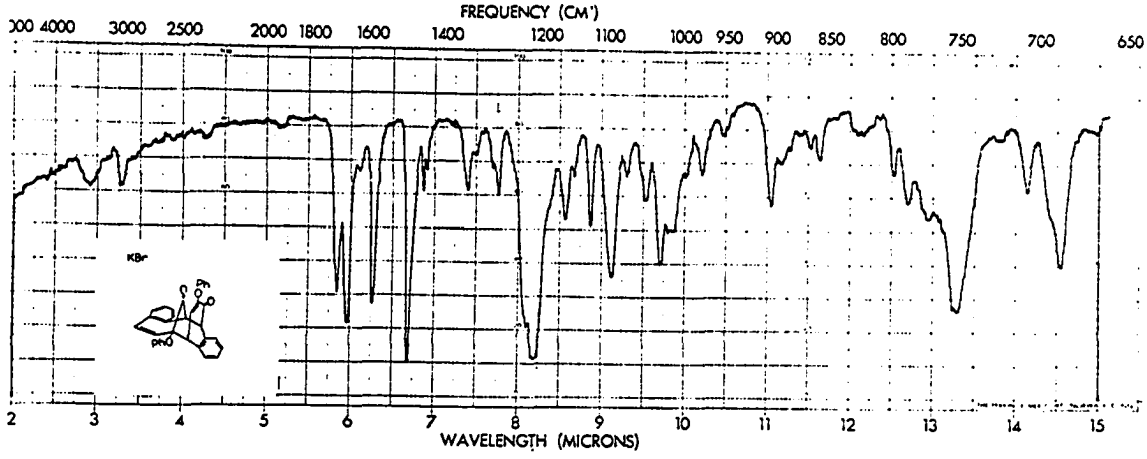

FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

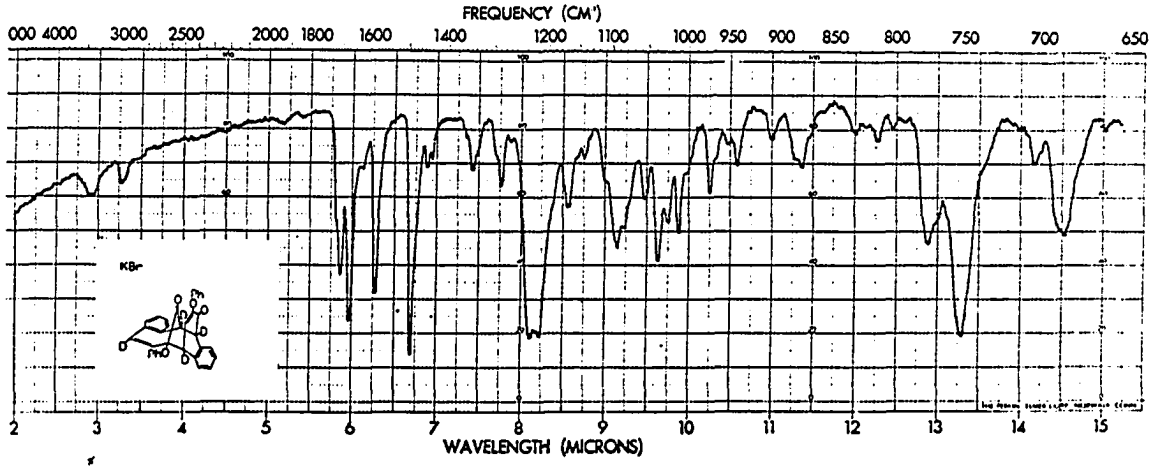
Figure 16. Infrared spectra

Top - Dimer A (XLIII)

Middle - Dimer A-1,2,5,8-d_4 (LIII)

Bottom - Dimer A-6,9-d_2 (LVI)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

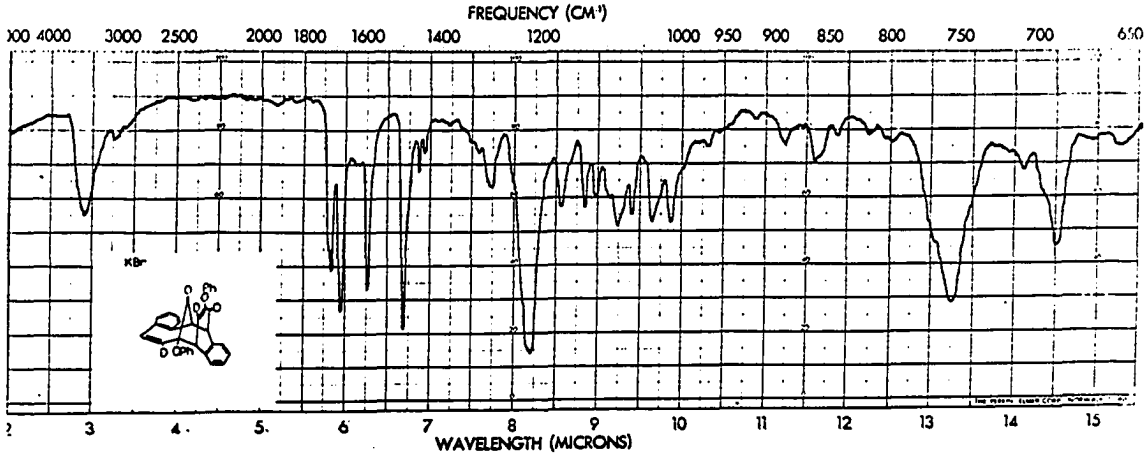
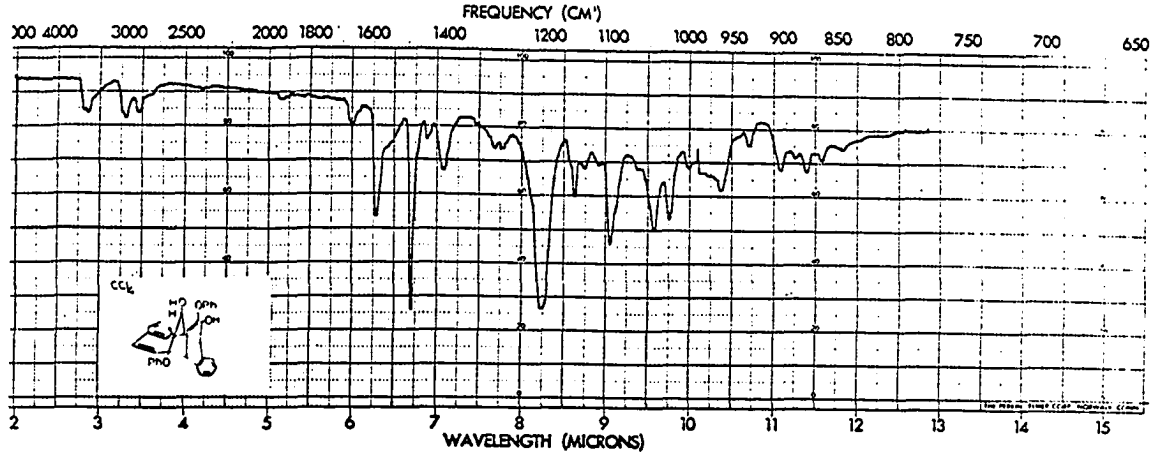

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

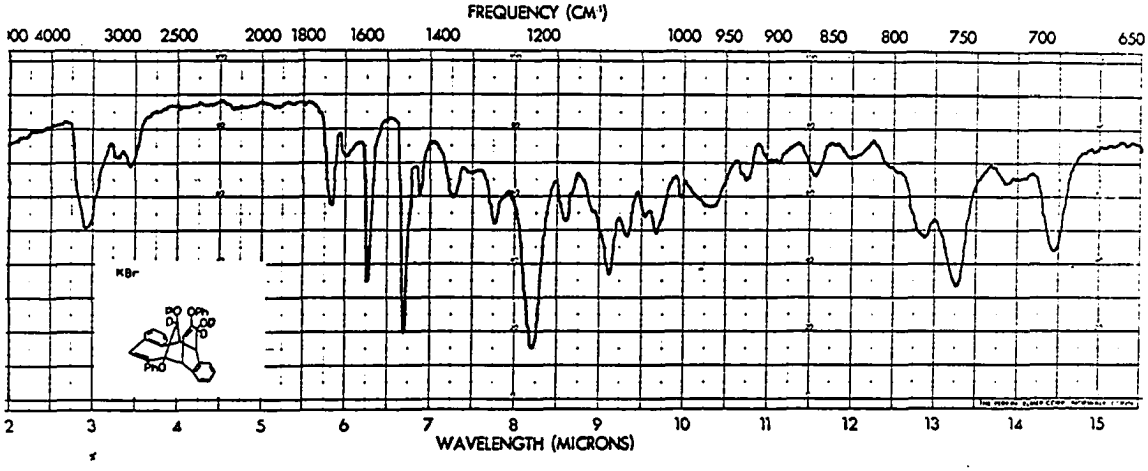
Figure 17. Infrared spectra

Top - Dimer A diol (XLIX)

Middle - Dimer A diol-11,14,O-d_4 (LVIIa)

Bottom - Dimer A diol-6,9,O-d_4 (LVIIIa)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
CCl4
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

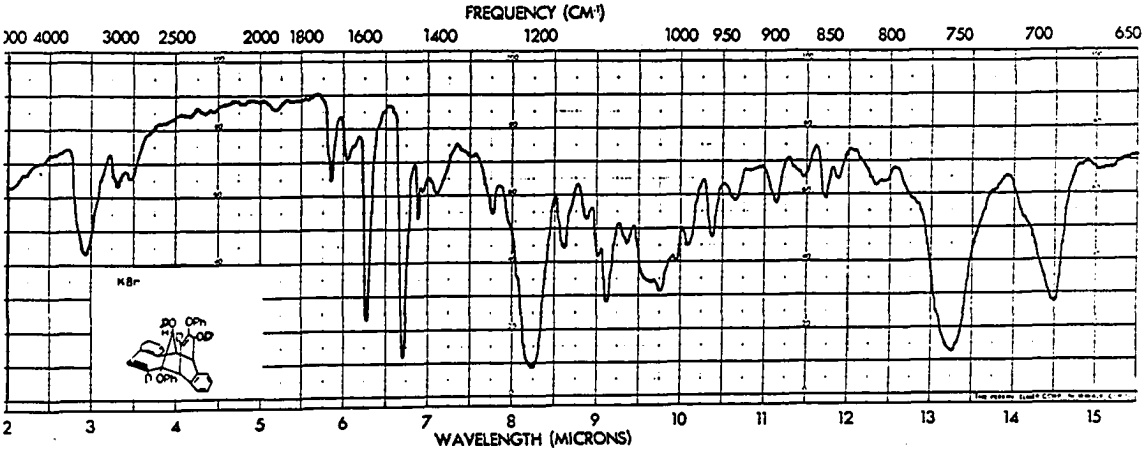
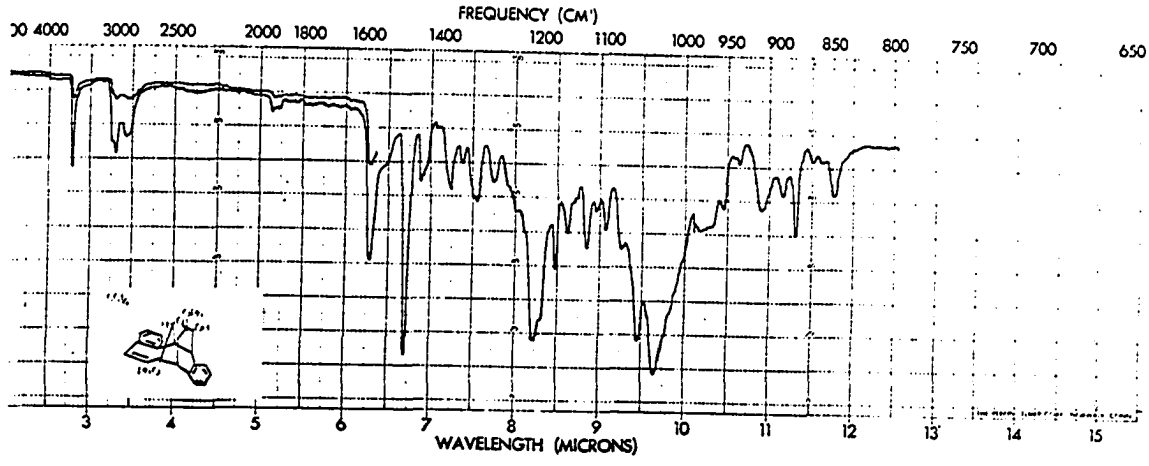

FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

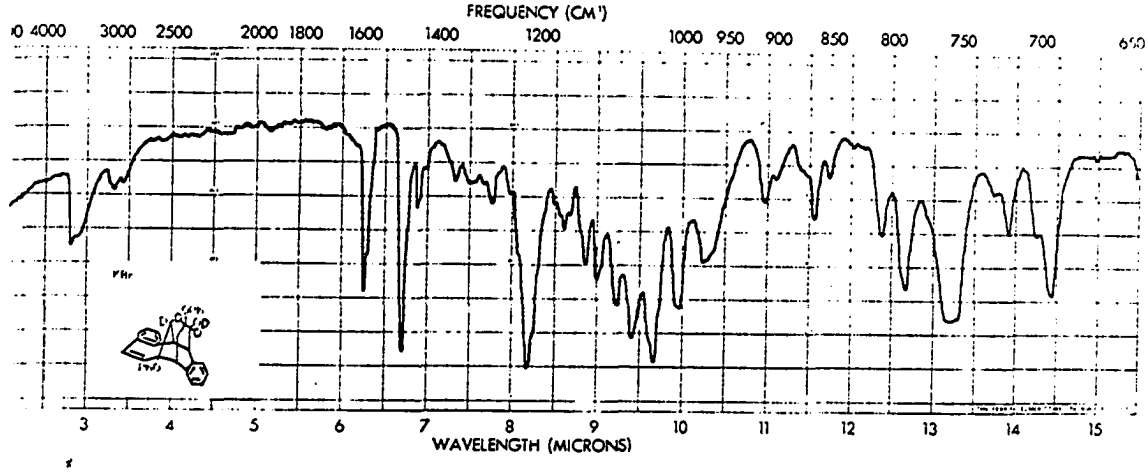
Figure 18. Infrared spectra

Top - Dimer A alcohol ether (L)

Middle - Dimer A alcohol ether-11,14,O-d_3 (LIXa)

Bottom - Dimer A alcohol ether-6,9a,O-d_3 (LXa)


FREQUENCY (CM')
00 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM')
0 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

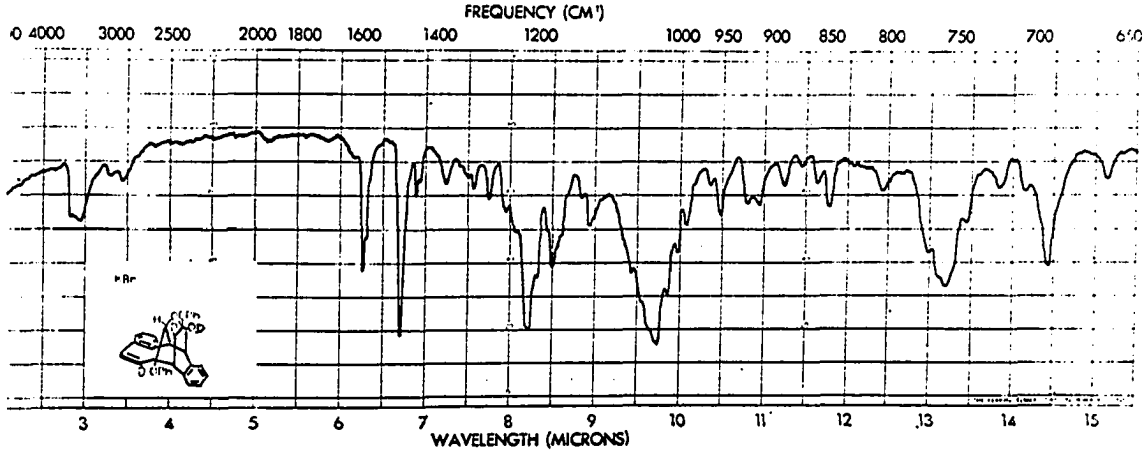
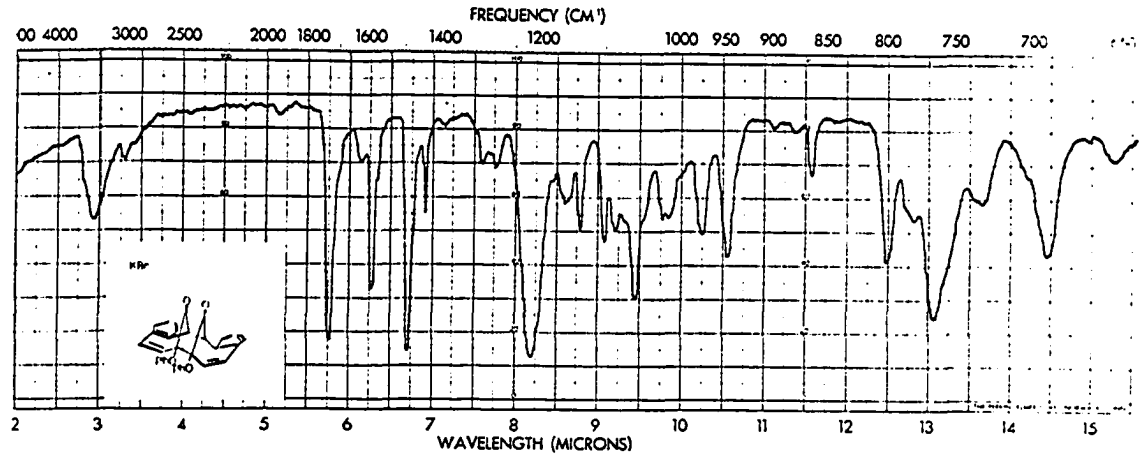

FREQUENCY (CM')
0 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

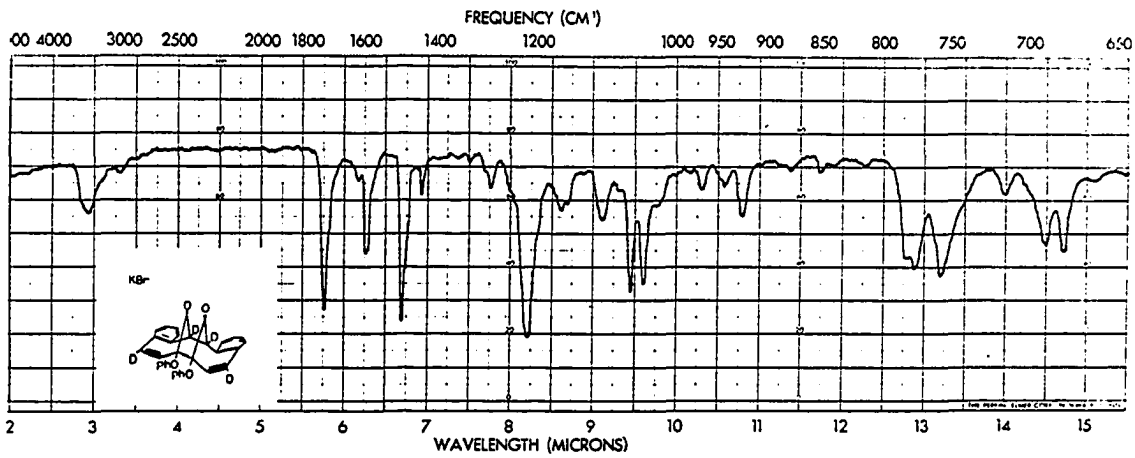
Figure 19. Infrared spectra

Top - Dimer B (XLIV)

Middle - Dimer B-1,2,5,10-d_4 (LI)

Bottom - Dimer B-6,9-d_2 (LIV)


FREQUENCY (CM⁻¹)
00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

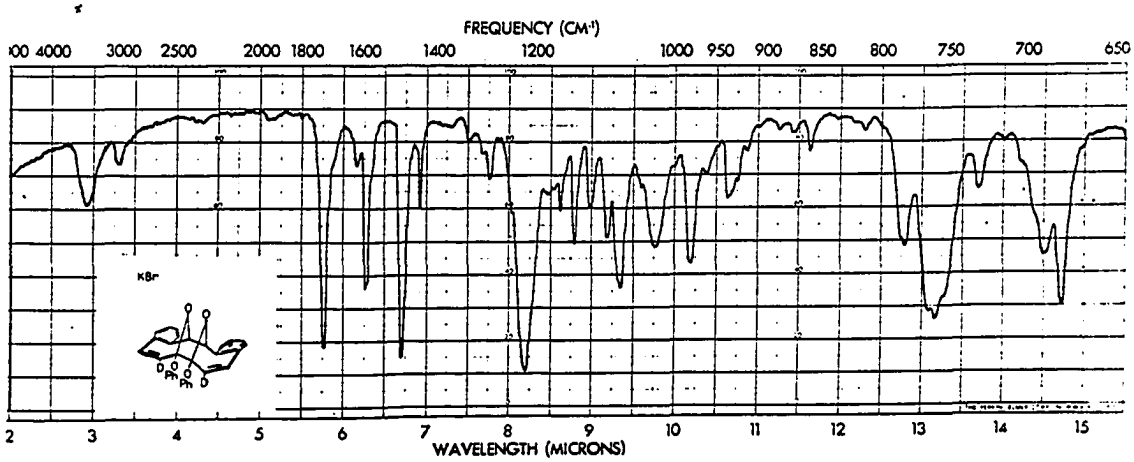
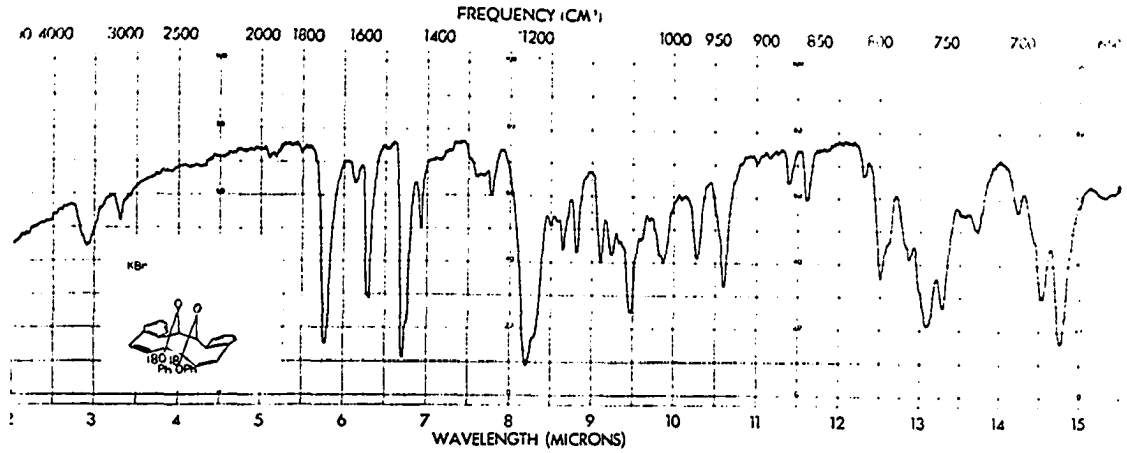

FREQUENCY (CM⁻¹)
00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

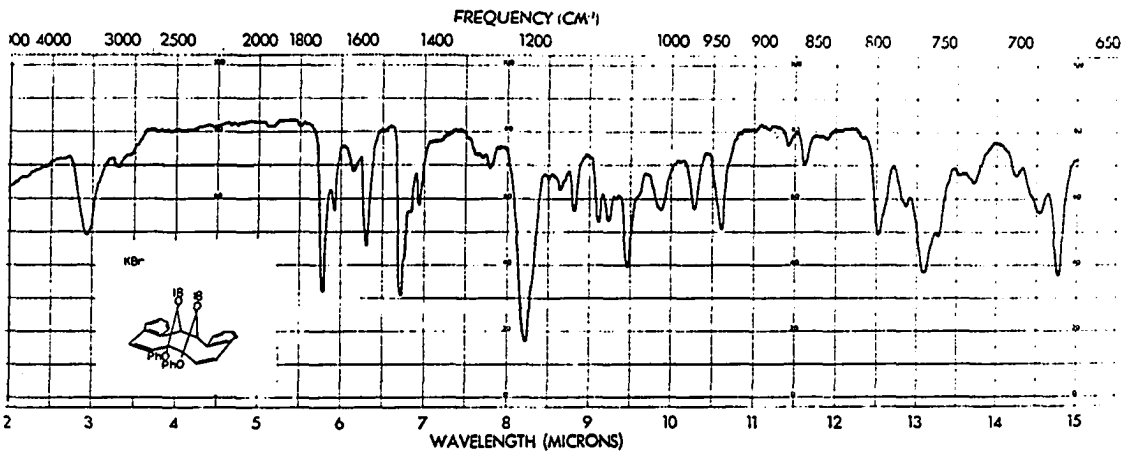
Figure 20. Infrared spectra

Top - Carbonyl-^{18}O-labelled Dimer B (LXXIV)

Middle - Ether-^{18}O-labelled Dimer B (LXXIII)

Bottom - Dimer B-7,8-^{13}C (LXXV)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750
KBr
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
WAVELENGTH (MICRONS)

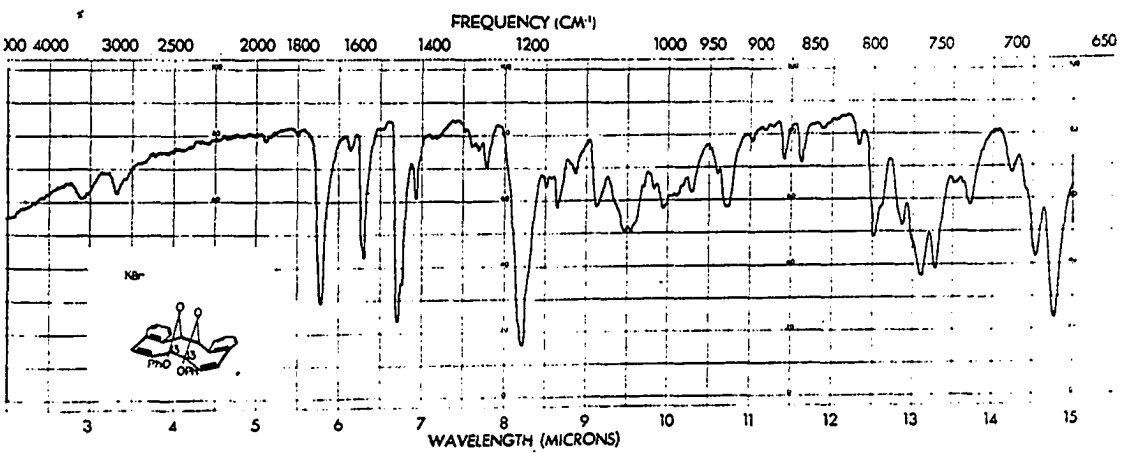
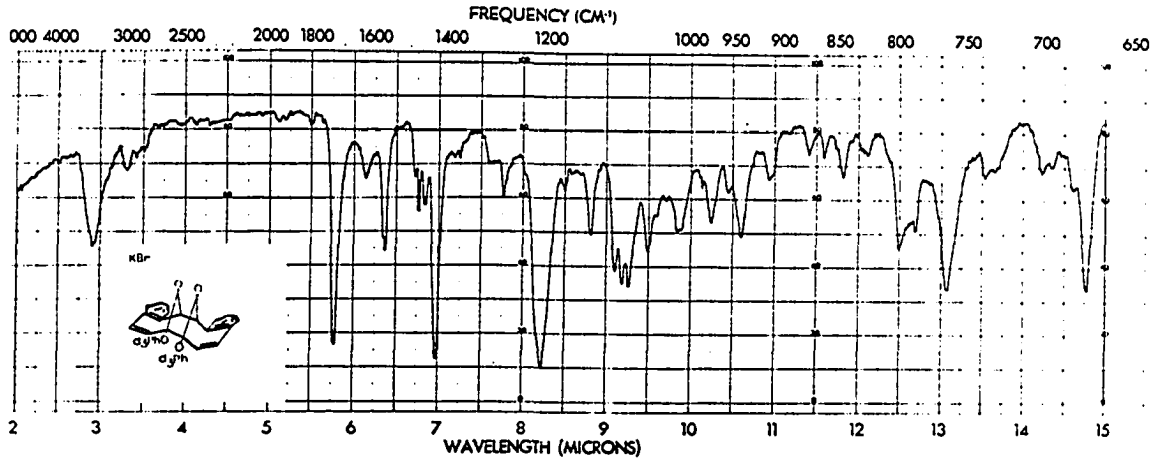

FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
WAVELENGTH (MICRONS)

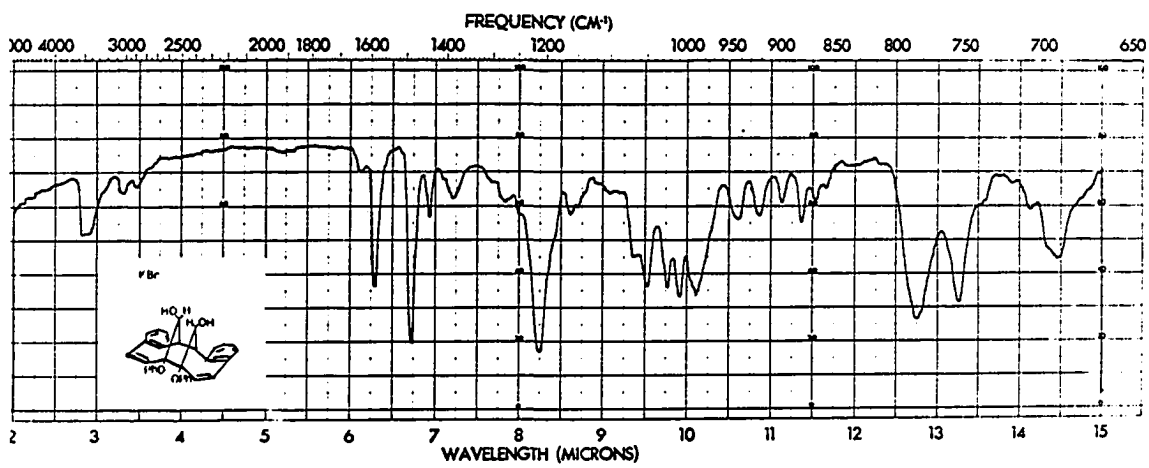
Figure 21. Infrared spectra

Top - 2,4,6-Trideuteriophenoxy Dimer B (XLVII)

Middle - Dimer B diol (LXI)

Bottom - Dimer B diol-13,14-d_2 (LXII)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

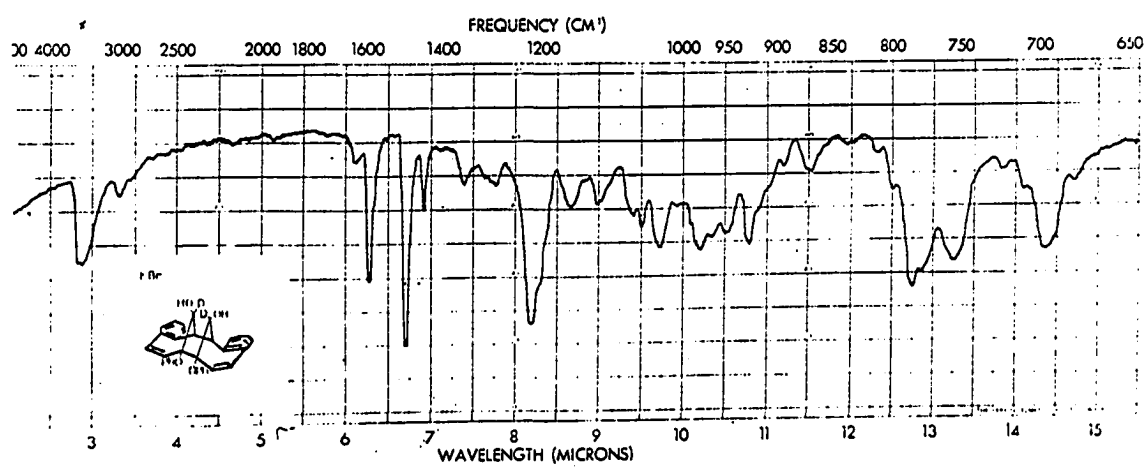
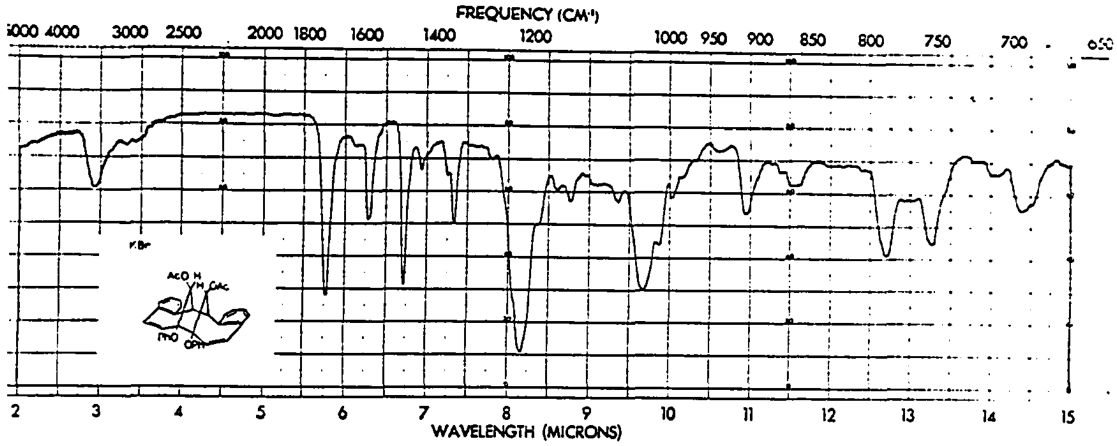

FREQUENCY (CM⁻¹)
00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

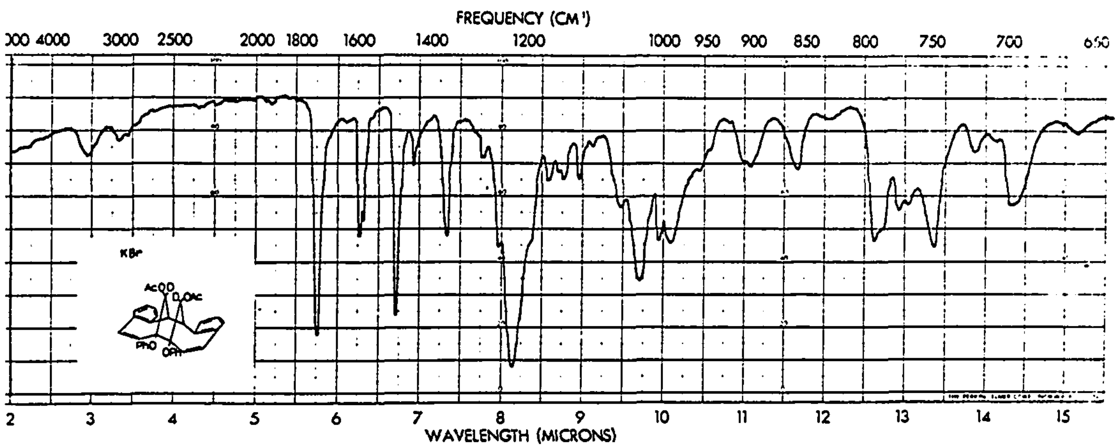
Figure 22. Infrared spectra

Top - Dimer B diol diacetate (LXIII)

Middle - Dimer B diol diacetate-13,14-d_2 (LXIV)

Bottom - Dimer B diol diacetate-d_6 (XCI)


FREQUENCY (CM-1)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
KBr


FREQUENCY (CM-1)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
KBr

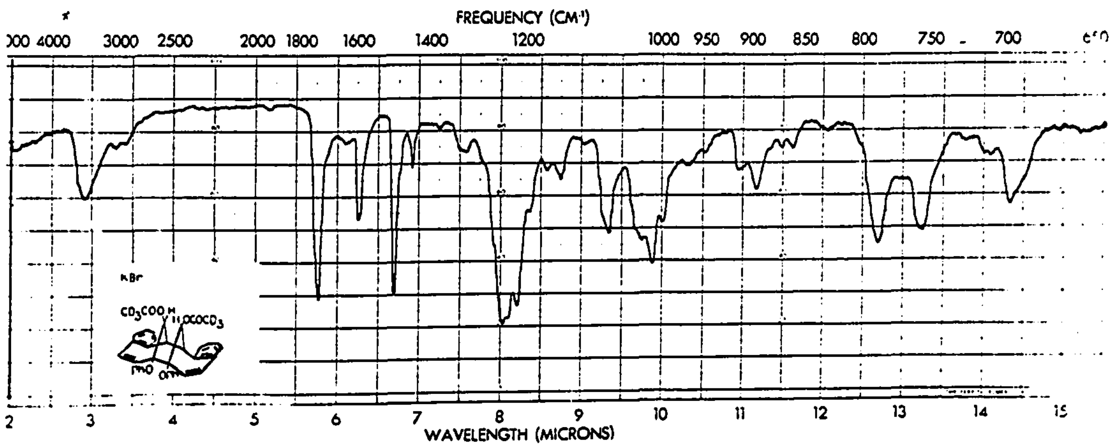
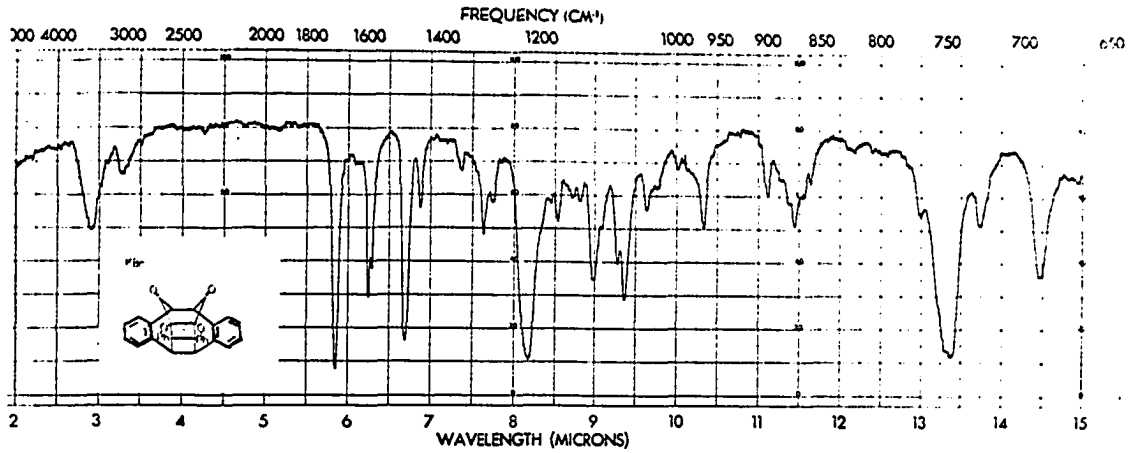

FREQUENCY (CM-1)
4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
KBr

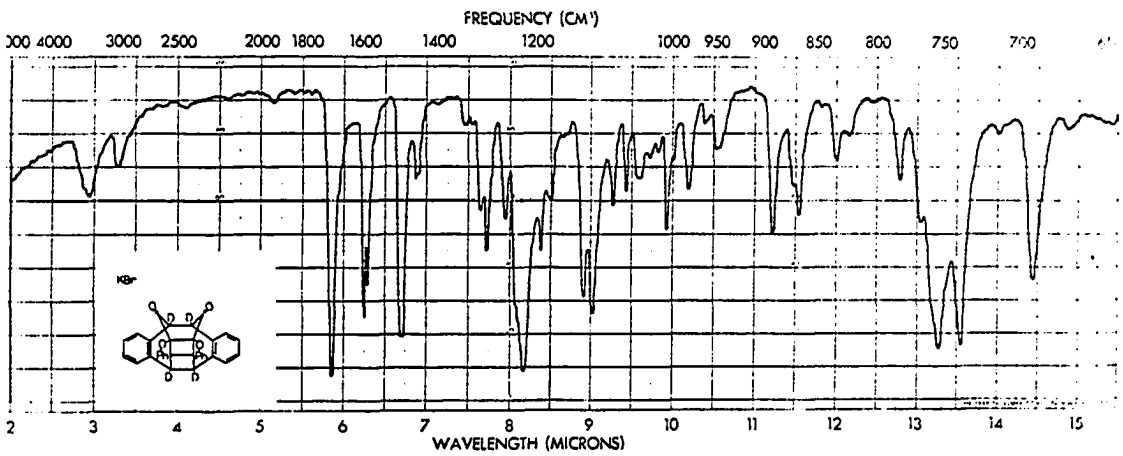
Figure 23. Infrared spectra

Top - Dimer C (XLV)

Middle - Dimer C-1,2,5,10-d_4 (LII)

Bottom - Dimer C-6,9-d_2 (LV)


FREQUENCY (CM⁻¹)
3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

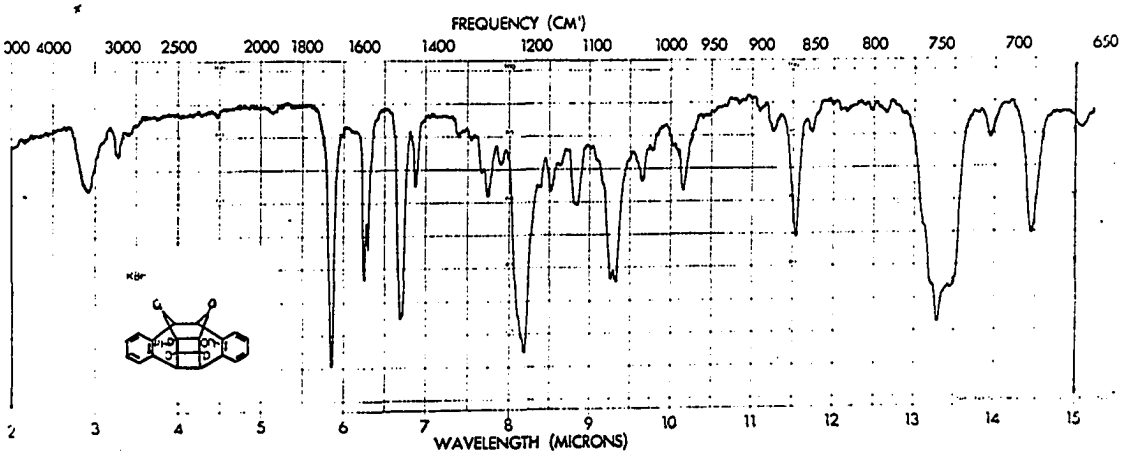
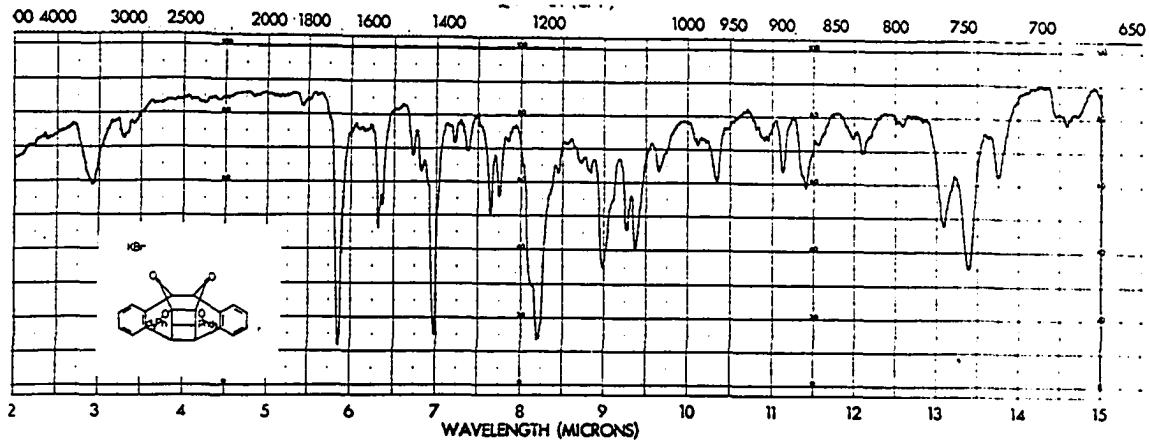

FREQUENCY (CM⁻¹)
3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

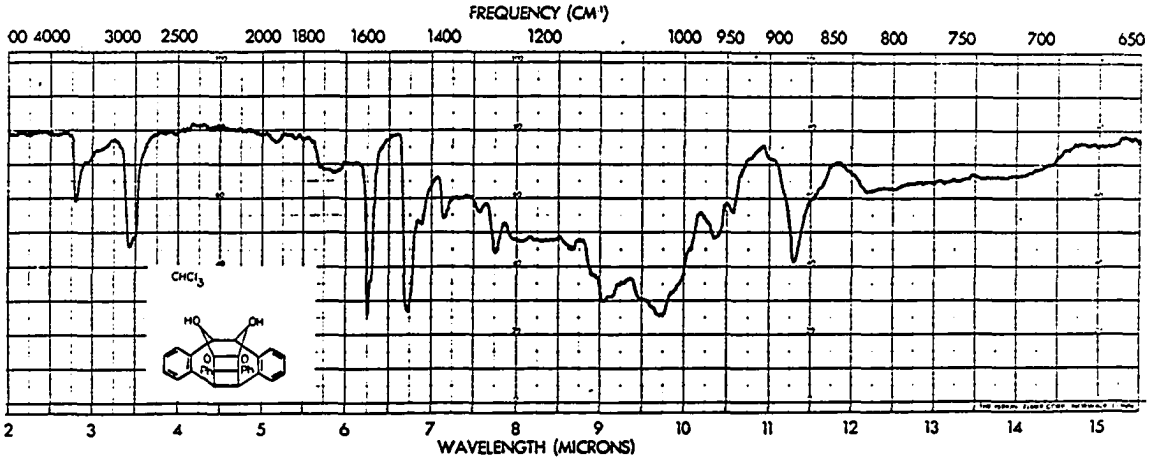
Figure 24. Infrared spectra

Top - 2,4,6-Trideuteriophenoxy Dimer C (XLVIII)

Middle - Dimer C diol (LXV)

Bottom - 2,4,6-Trideuteriophenoxy Dimer B diol diacetate (XCII)


00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
FREQUENCY (CM⁻¹)


00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
CHCl3
HO
OH
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
FREQUENCY (CM⁻¹)

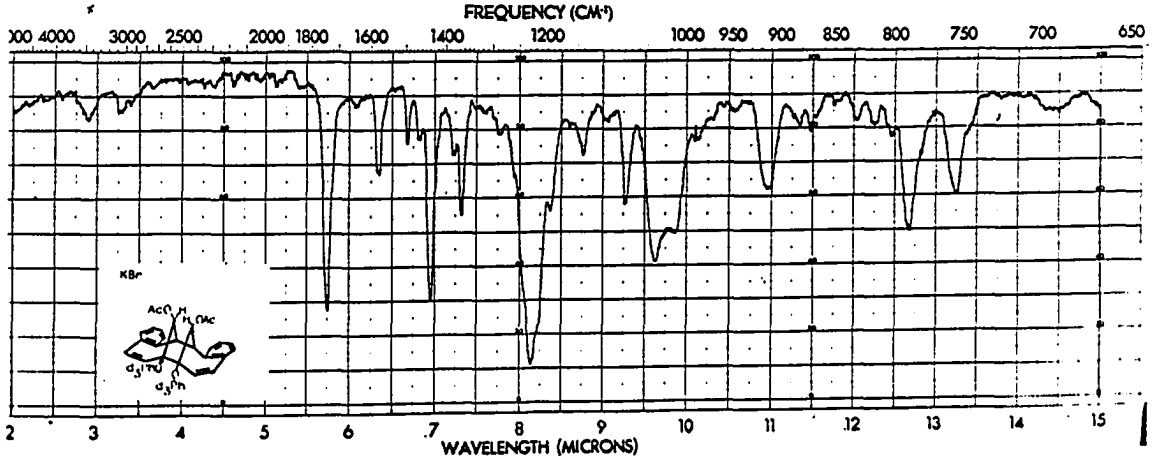

X00 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
KBr
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 25. Nuclear magnetic resonance spectra

Top - 2-Phenoxy-4,5-benztropone (XXV)

Middle - 2-Phenoxy-4,5-benztropone -1-^{13}C (XXXV)

Bottom - 2-(2,4,6-Trideuteriophenoxy)-4,5-benztropone (XXXII)

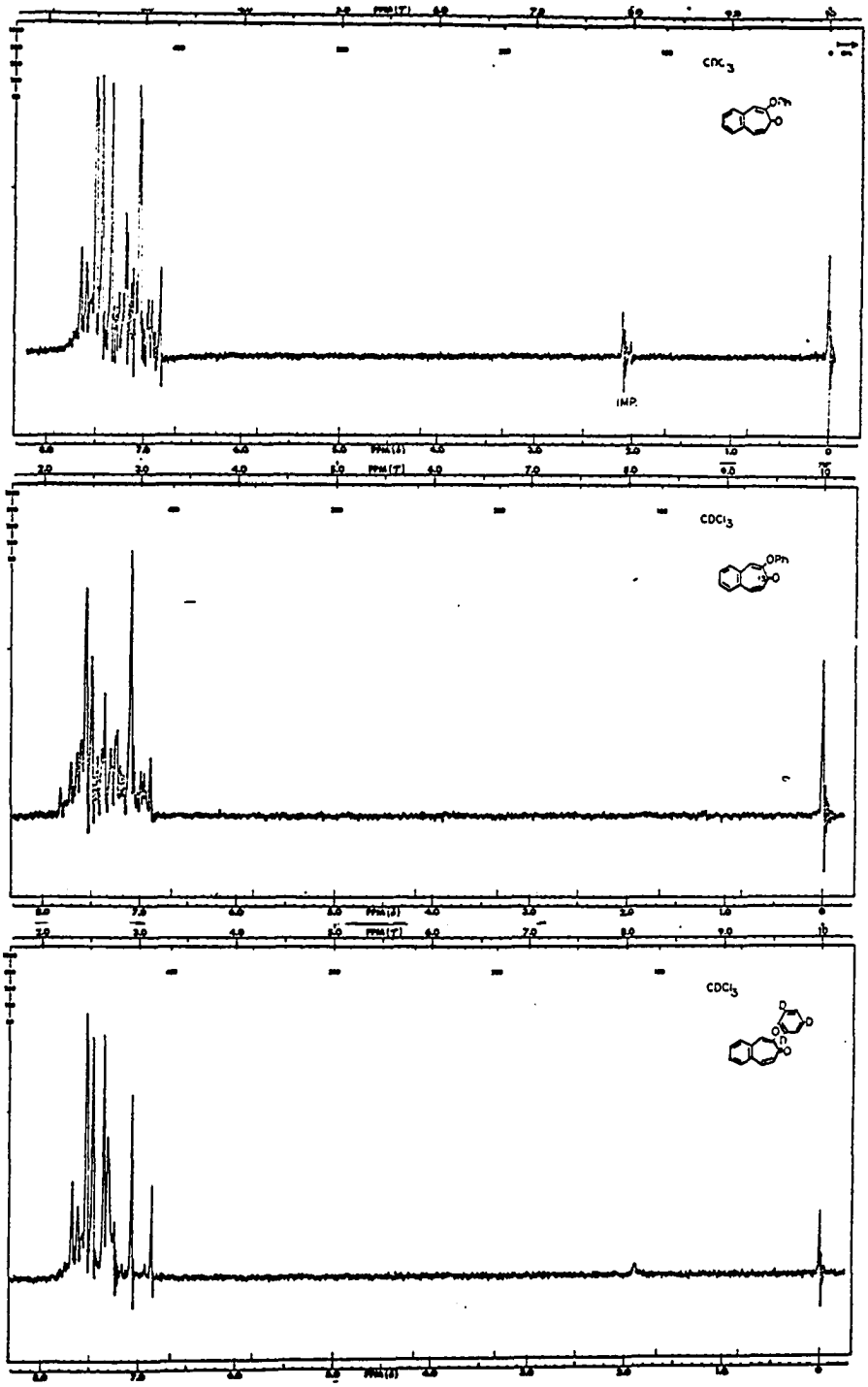
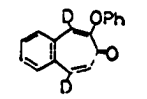

CDCl3
OPh
IMP.
CDCl3
OPh
CDCl3

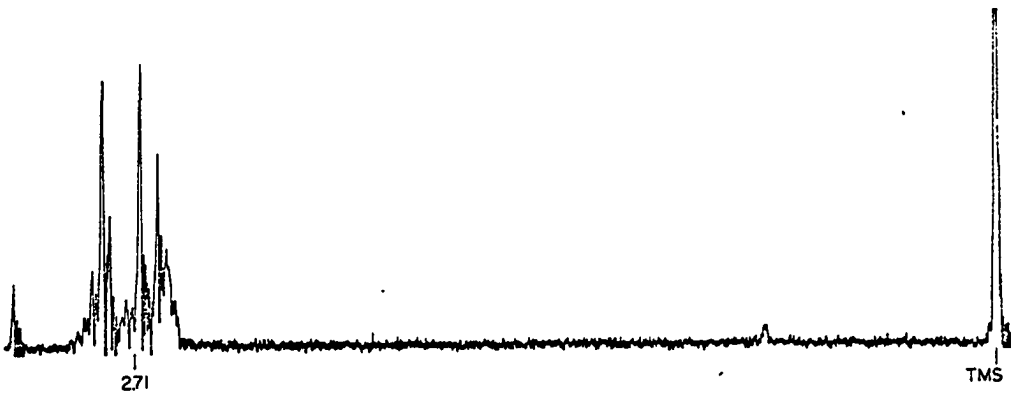
Figure 26. Nuclear magnetic resonance spectra

Top - 2-Phenoxy-4,5-benztropone-3,6-d_2 (XXX)

Bottom - 2-Phenoxy-4,5-benztropone-7-d (XXXI)

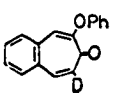
$CDCl_3$

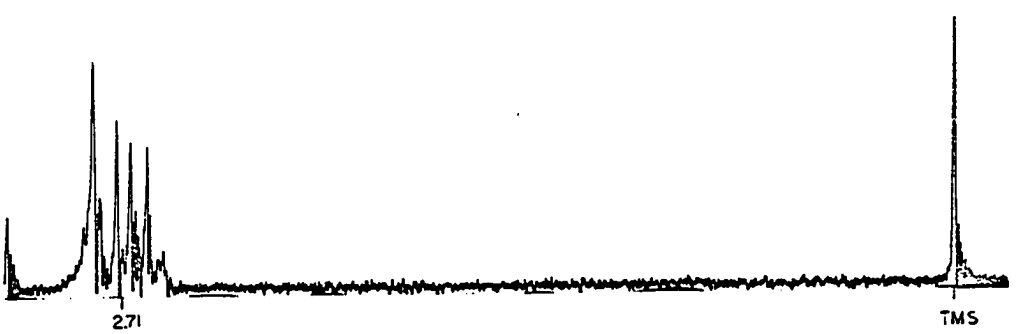




TAU

$CDCl_3$



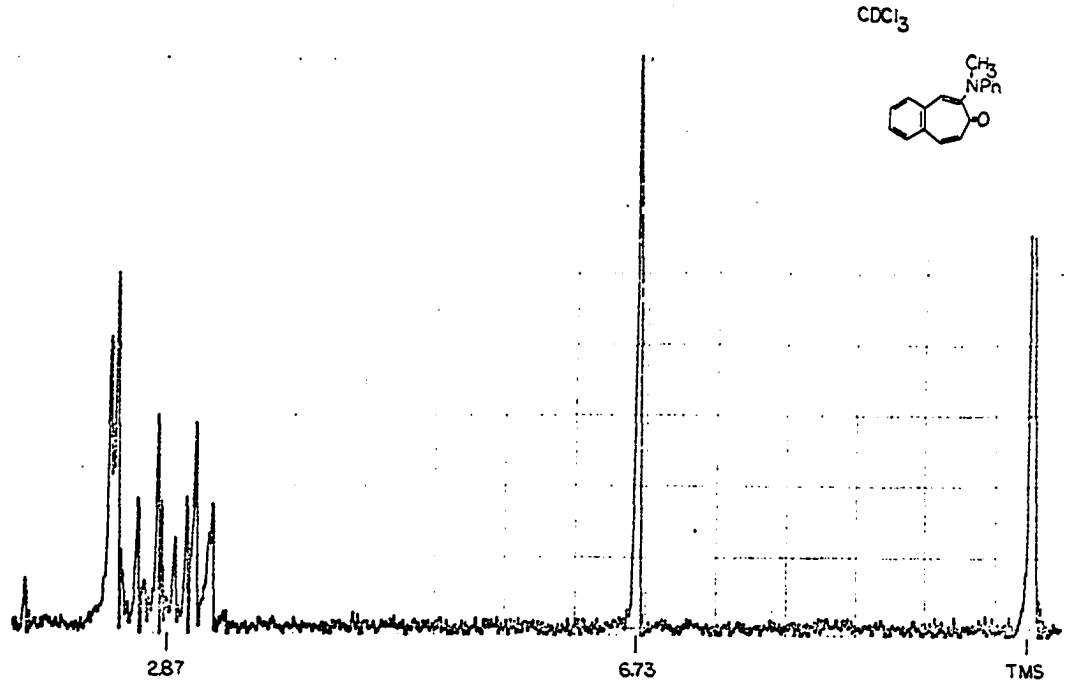


TAU.

Figure 27. Nuclear magnetic resonance spectra

Top - 2-(N-Methylanilino)-4,5-benztropone (XXXVII)

Bottom - 2-(Methoxy-^{13}C)-4,5-benztropone (XL)



TAU

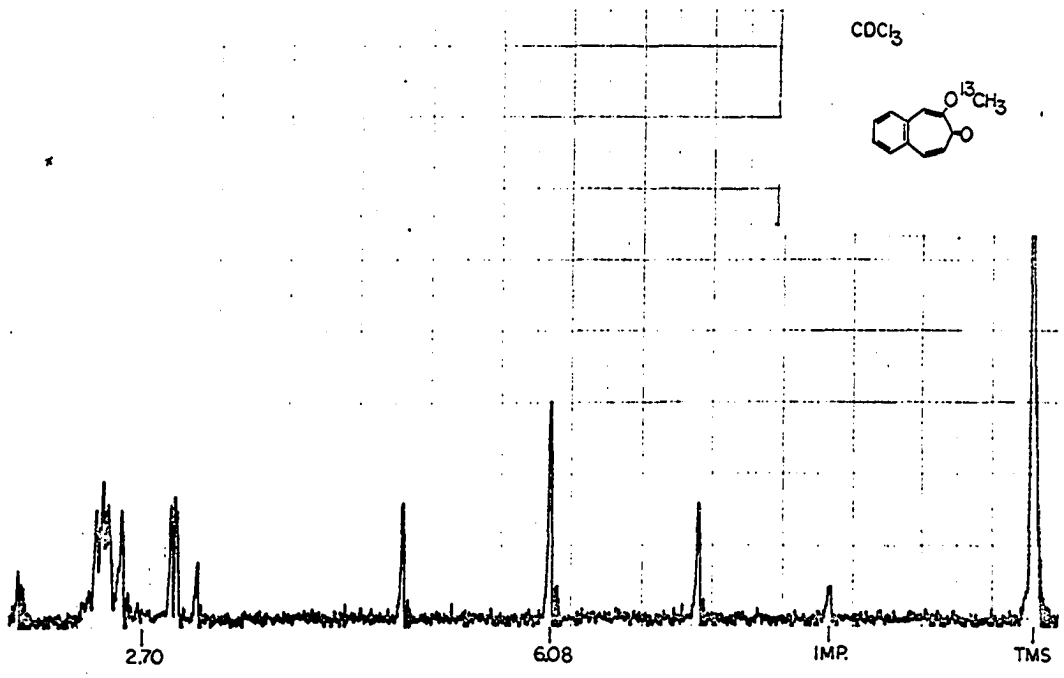


Figure 28. Nuclear magnetic resonance spectra

Top - 2-Thiophenoxy-4,5-benztropone (XXXVI)

Middle - 2-Methoxy-4,5-benztropone (XXXVIII)

Bottom - Dimer B (XLIV)

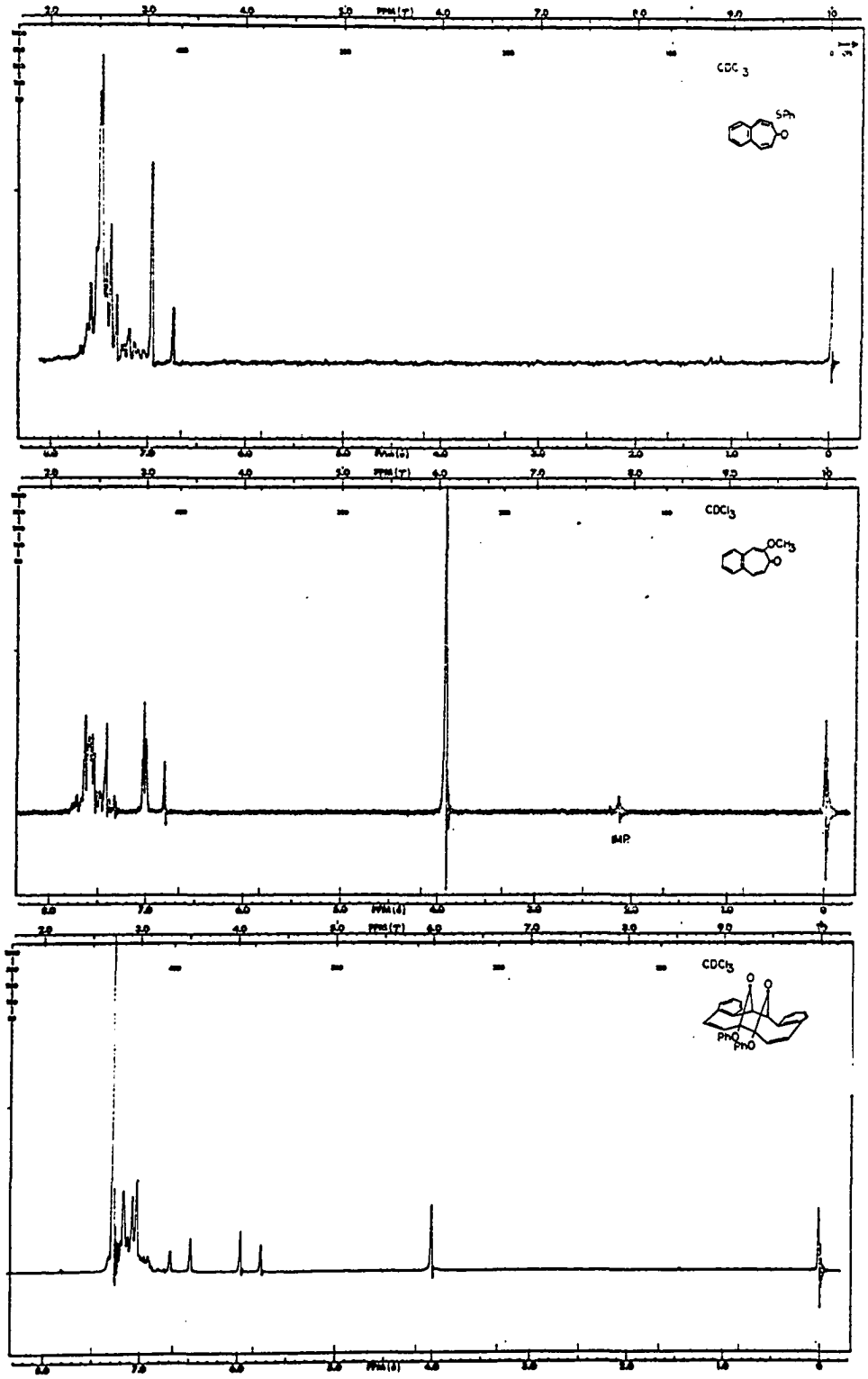
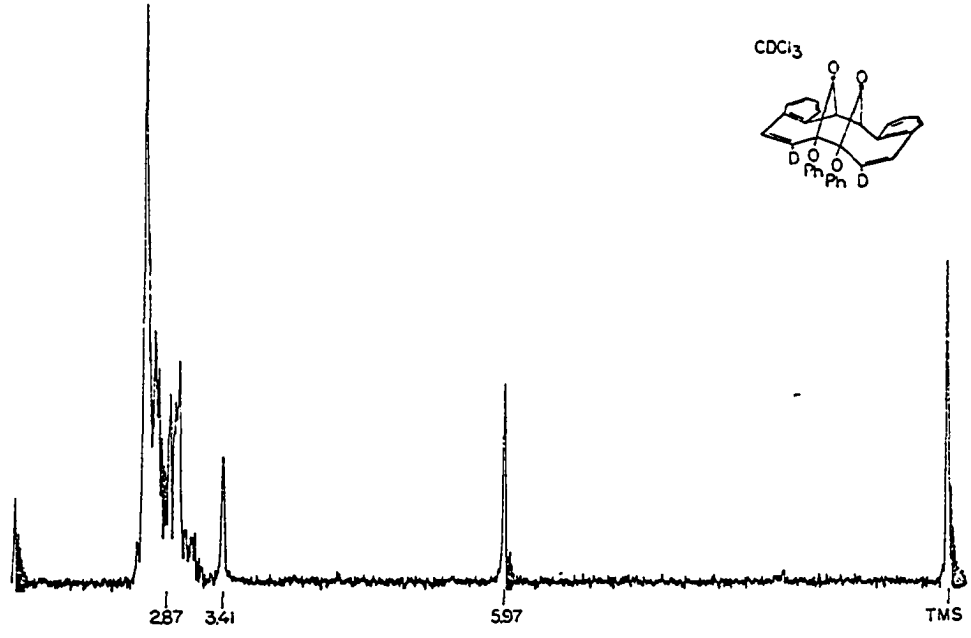

CDCl3
CDCl3
OCH3
BHP
CDCl3
PhO
PhO

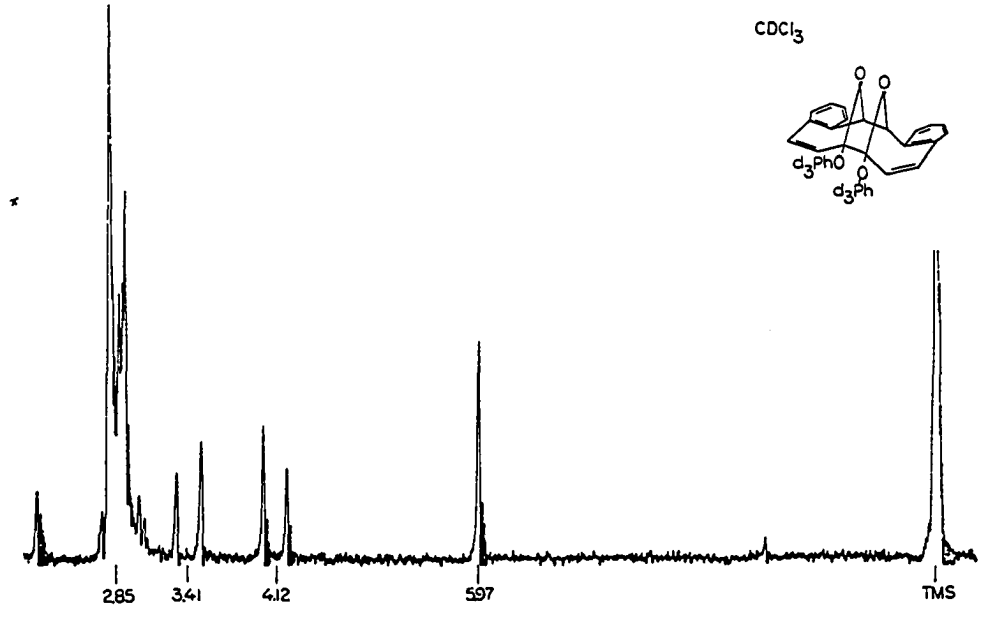
Figure 29. Nuclear magnetic resonance spectra

Top - Dimer B-6,9-d_2 (LIV)

Bottom - 2,4,6-Trideuteriophenoxy Dimer B (XLVII)


CDCl3
D
O
Ph
O
Ph
D
2.87
3.41
5.97
TMS

TAU

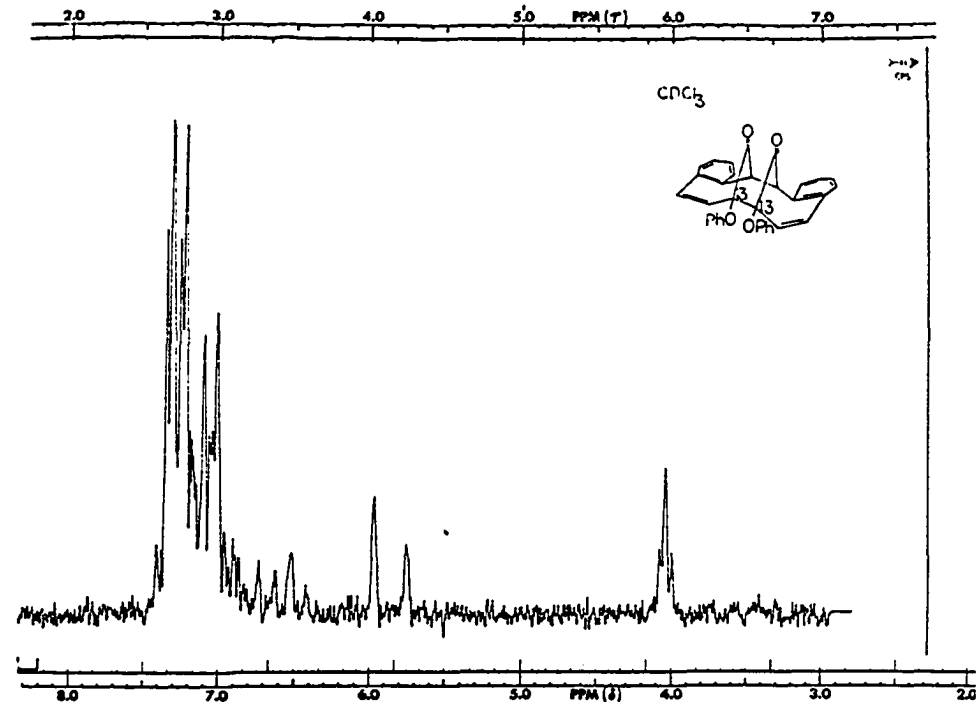

CDCl3
d3PhO
O
d3Ph
2.85
3.41
4.12
5.97
TMS

TAU

Figure 30. Nuclear magnetic resonance spectra

Top - Dimer B-7,8-^{13}C (LXXV)

Bottom - Dimer B diol (LXI)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
CDCl3
PhO
OPh
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0

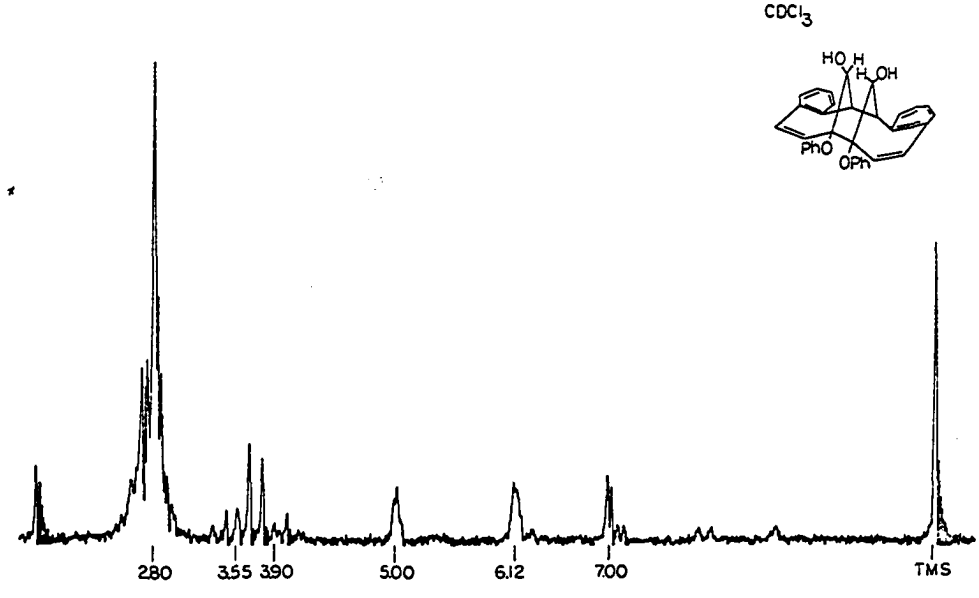
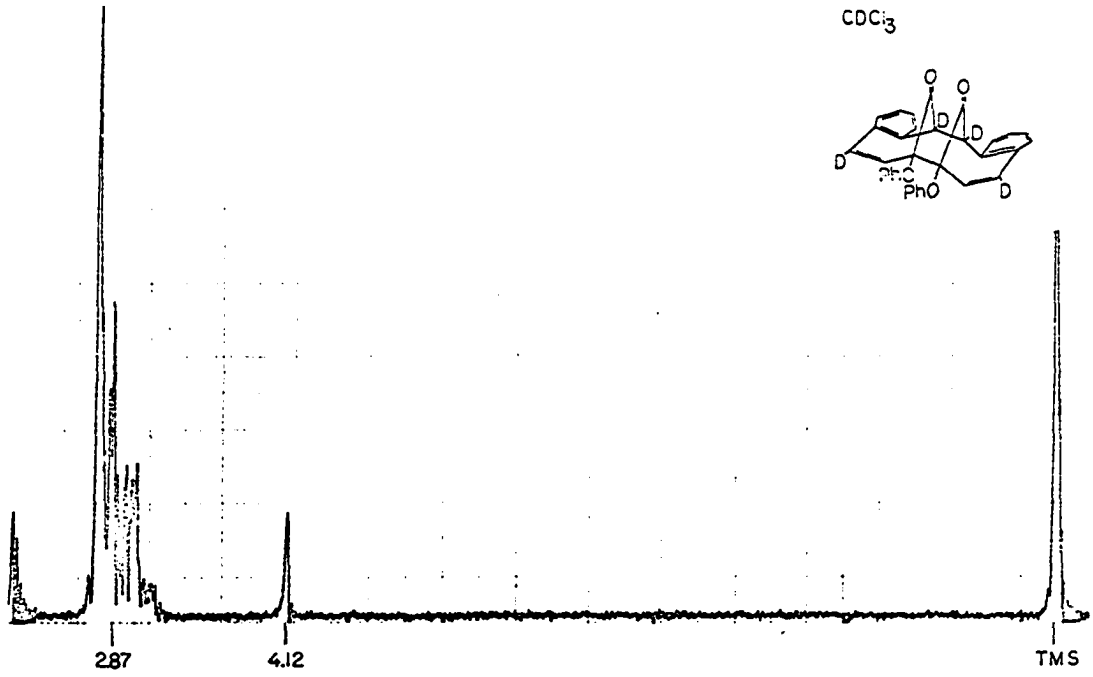

CDCl3
HO
H
H
OH
PhO
OPh
2.80
3.55
3.90
5.00
6.12
7.00
TMS
TAU

Figure 31. Nuclear magnetic resonance spectra

Top - Dimer B-1,2,5,10-d_4 (LI)

Bottom - Dimer B diol diacetate (LXIII)


CDCl3
O
O
D
D
D
PhO
D
2.87
4.12
TMS
TAU

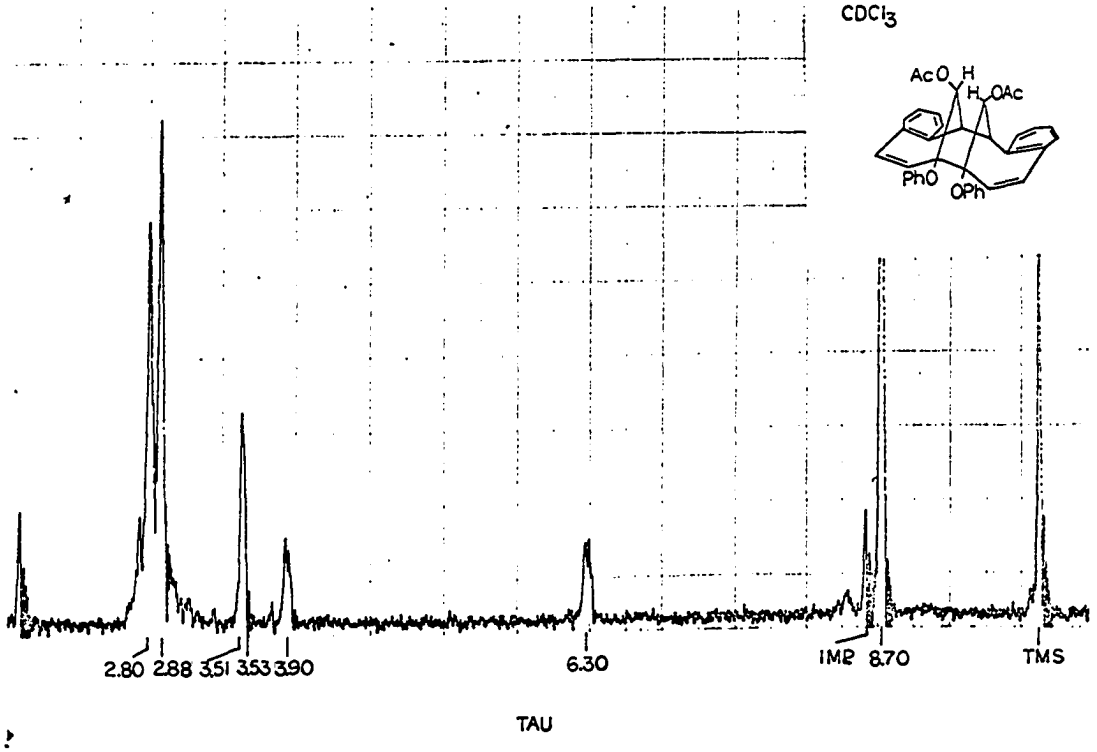
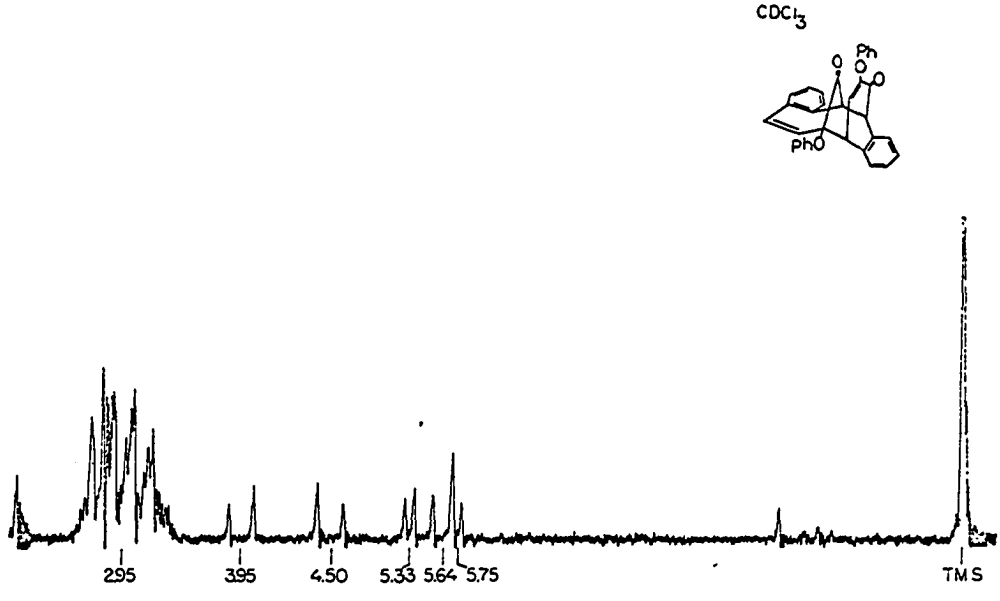
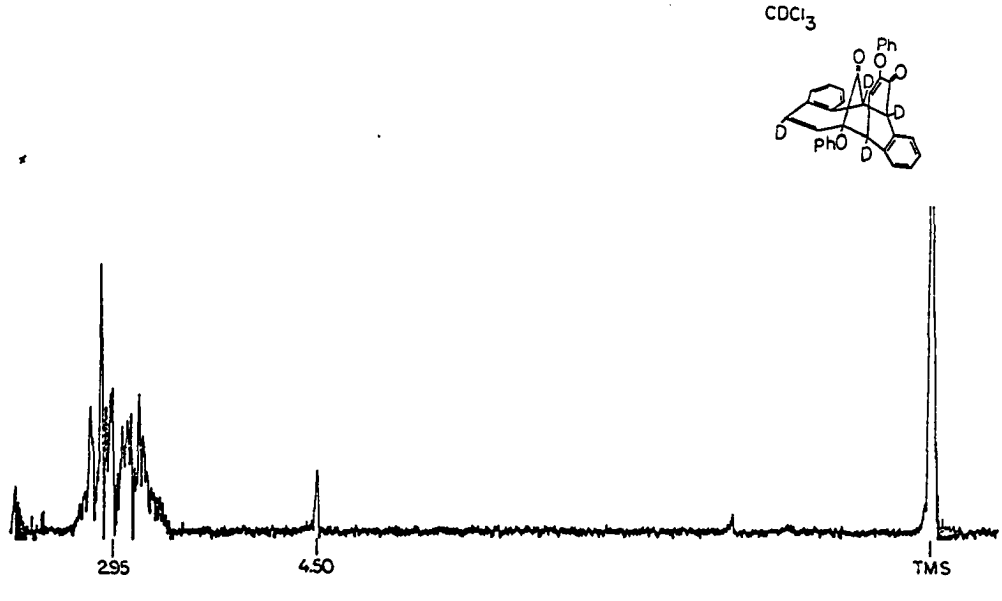

CDCl3
AcO
H
H
OAc
PhO
OPh
2.80
2.88
3.51
3.53
3.90
6.30
IMP
8.70
TMS
TAU

Figure 32. Nuclear magnetic resonance spectra

Top - Dimer A (XLIII)

Bottom - Dimer A-1,2,5,8-d_4 (LIII)

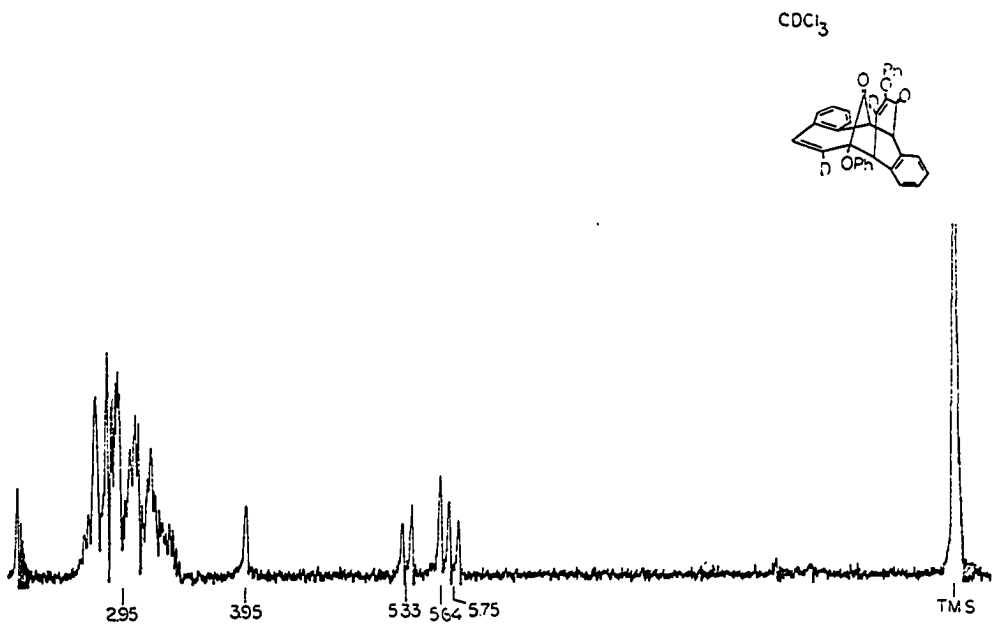

CDCl3
Ph
O
O
O
PhO
2.95
3.95
4.50
5.33
5.64
5.75
TMS
TAU


CDCl3
Ph
O
O
O
D
D
D
PhO
2.95
4.50
TMS
TAU

Firuge 33. Nuclear magnetic resonance spectra

Top - Dimer A-6,9-d_2 (LVI)

Bottom - Dimer A diol (XLIX)

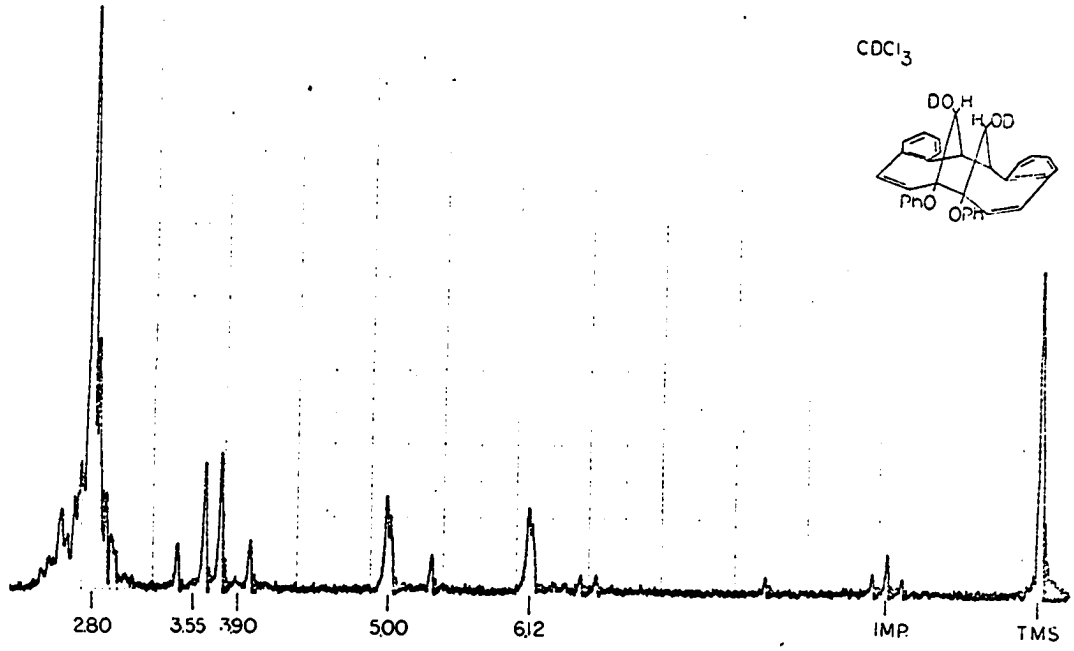

CDCl3
OPh
2.95
3.95
5.33
5.64
5.75
TMS
TAU


CDCl3
HO
OPh
OH
PhO
2.91
4.16
4.52
4.90
5.33
5.64
5.70
6.34
6.36
TMS
TAU

Figure 34. Nuclear magnetic resonance spectra

Top - Dimer B diol-O-d (LXIa)

Bottom - Dimer A diol-O-d (XLIXa)


CDCl3
DO H
H OD
PhO
OPh
2.80
3.55
3.90
5.00
6.12
IMP.
TMS
TAU

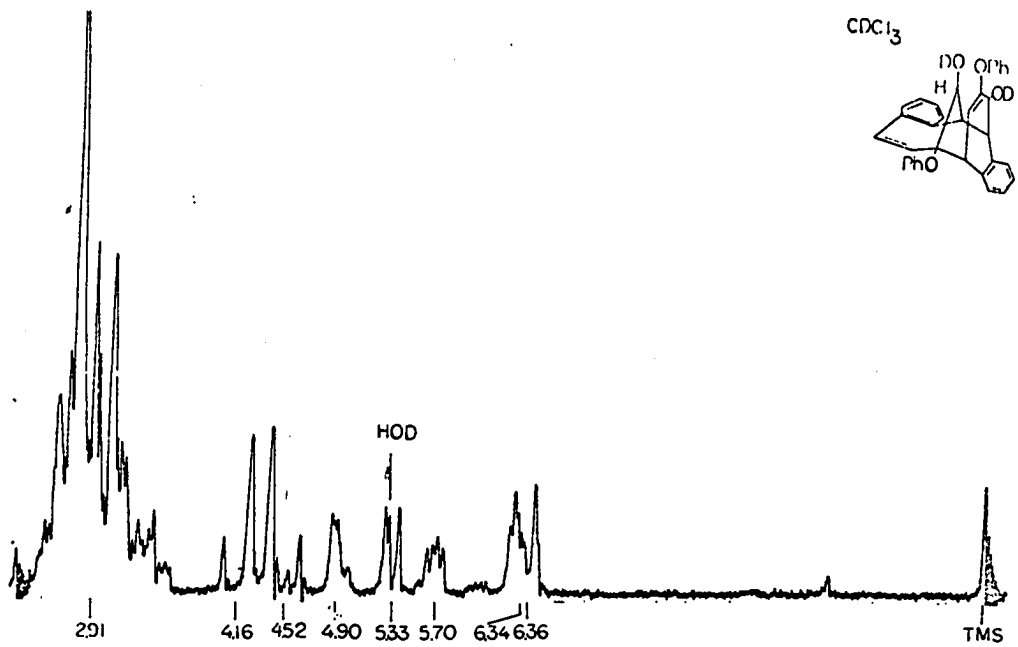

CDCl3
DO OPh
H
OD
PhO
HOD
2.91
4.16
4.52
4.90
5.33
5.70
6.34
6.36
TMS
TAU

Figure 35. Nuclear magnetic resonance spectra

Top - Dimer B diol-13,14-d_2 (LXII)

Middle - Dimer A diol-11,14,0-d_4 (LVIIa)

Bottom - Dimer B diol diacetate-13,14-d_2 (LXIV

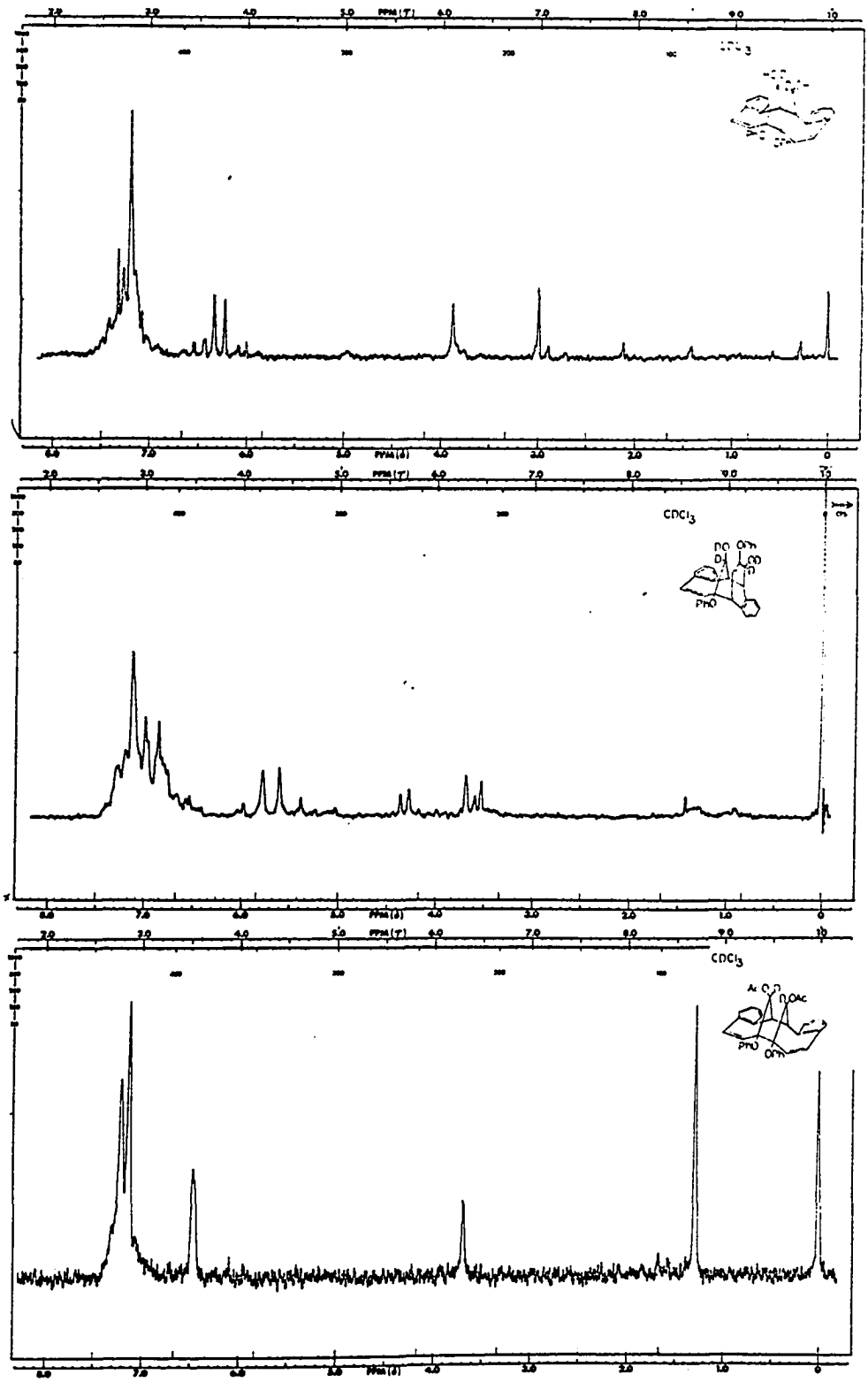

CDCl3
CDCl3
CDCl3

Figure 36. Nuclear magnetic resonance spectra

Top - Dimer A diol-6,9-d_2 (LVIII)

Bottom - Dimer A diol-6,9,0-d_4 (LVIIIa)

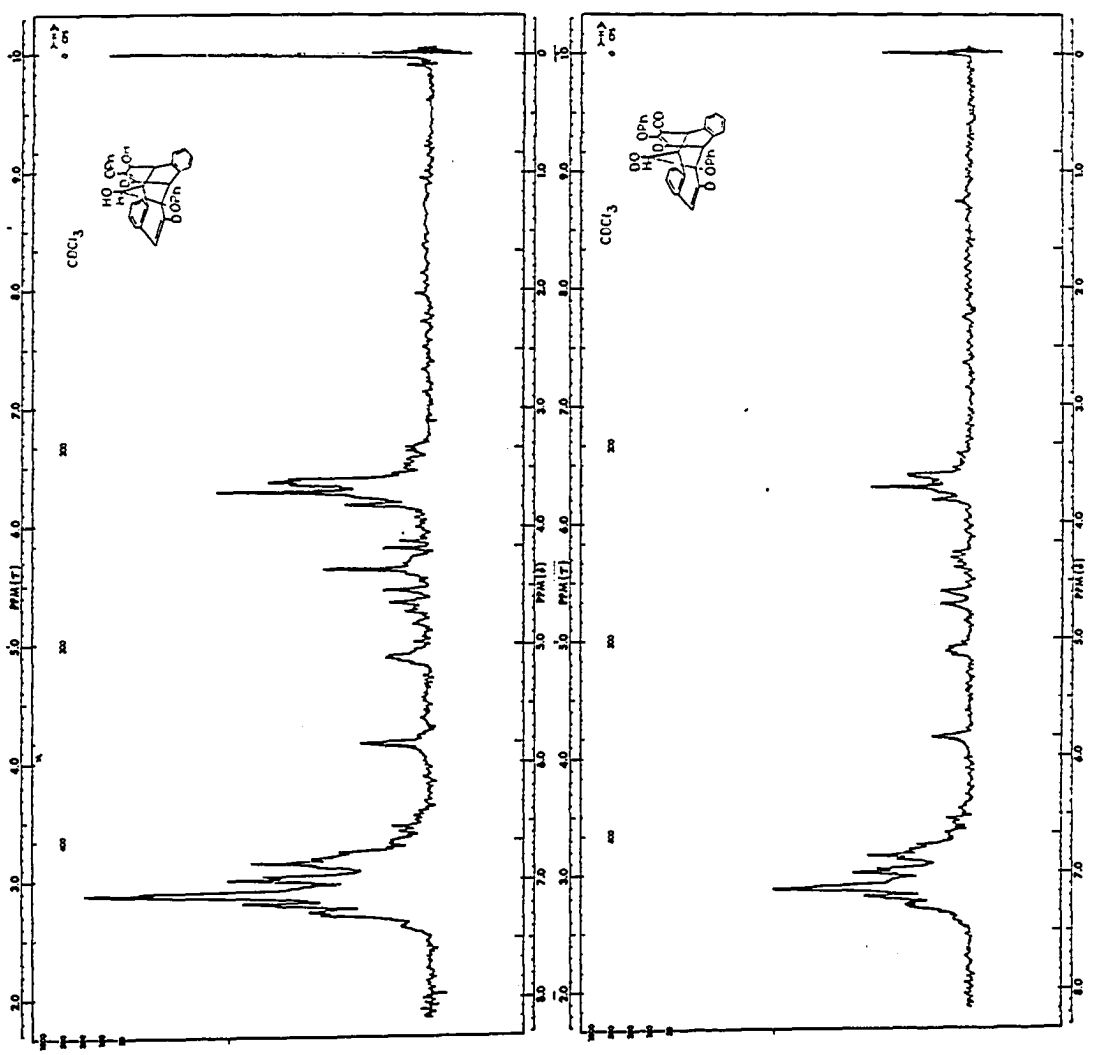
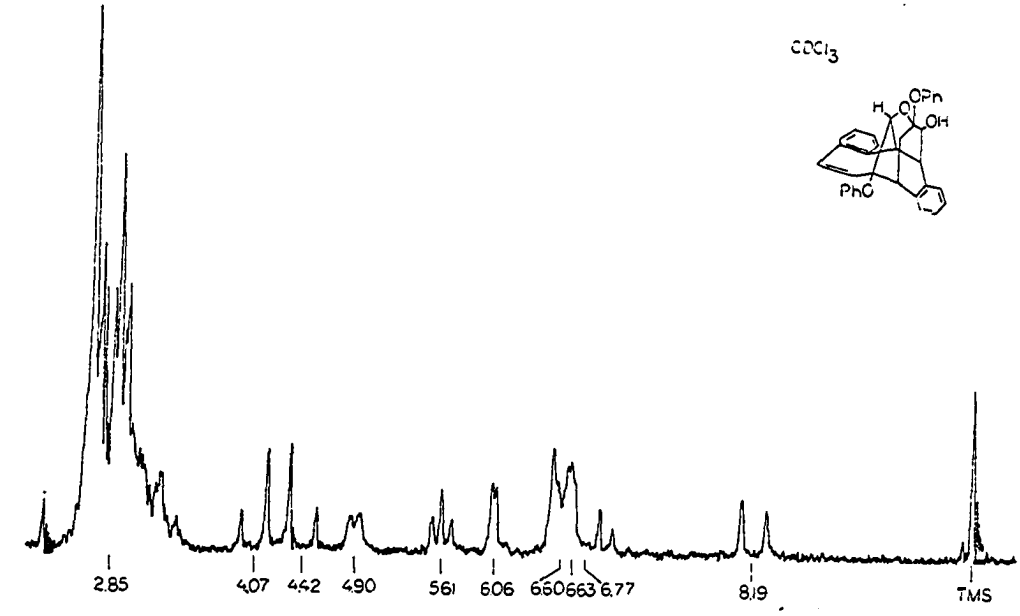

CDCl3
CDCl3
PPM (τ)
PPM (τ)

Figure 37. Nuclear magnetic resonance spectra

Top - Dimer A alcohol ether (L)

Bottom - Dimer A alcohol ether-C-d (La)


CDCl3
OPh
H
O
OH
PhO
2.85
4.07
4.42
4.90
5.61
6.06
6.60
6.63
6.77
8.19
TMS
TAU

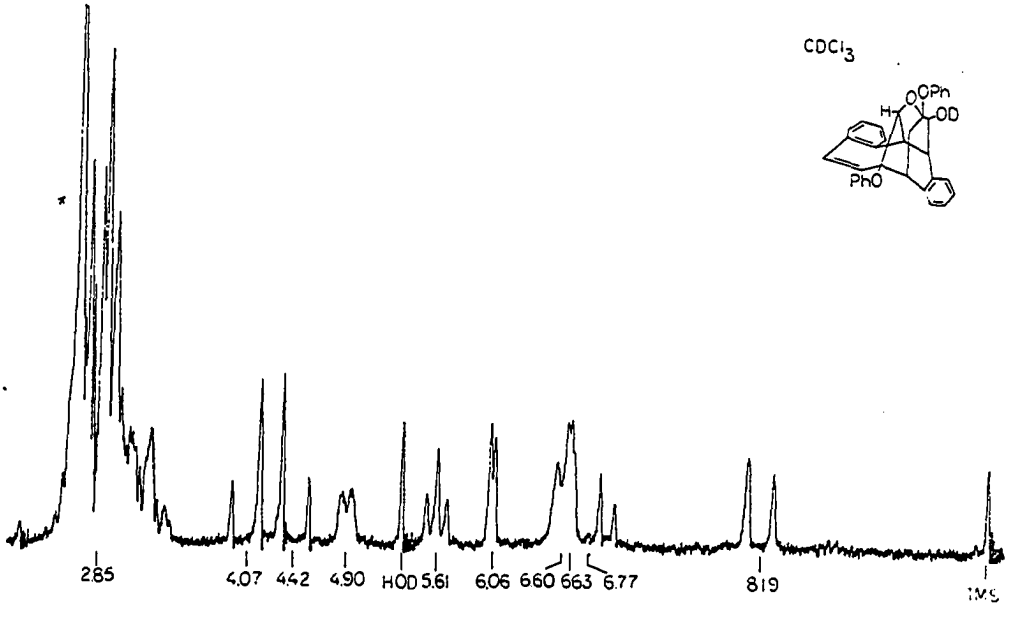

CDCl3
OPh
H
O
OD
PhO
2.85
4.07
4.42
4.90
HOD
5.61
6.06
6.60
6.63
6.77
8.19
TMS
TAU

Figure 38. Nuclear magnetic resonance spectra

Top - Dimer A alcohol ether-11,14,0-d_3 (LIXa)

Bottom - Dimer A alcohol ether-6,9a,0-d_3 (LXa)

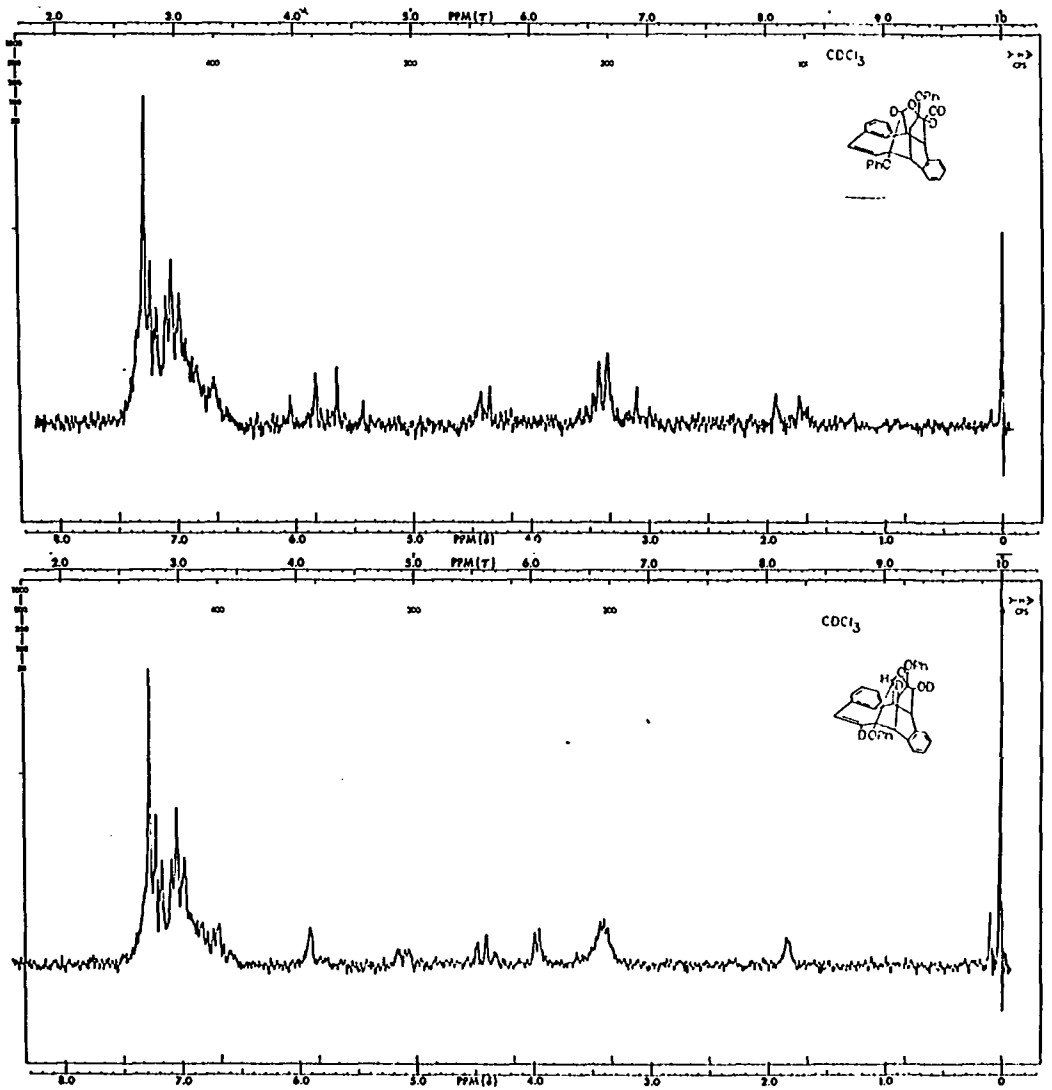
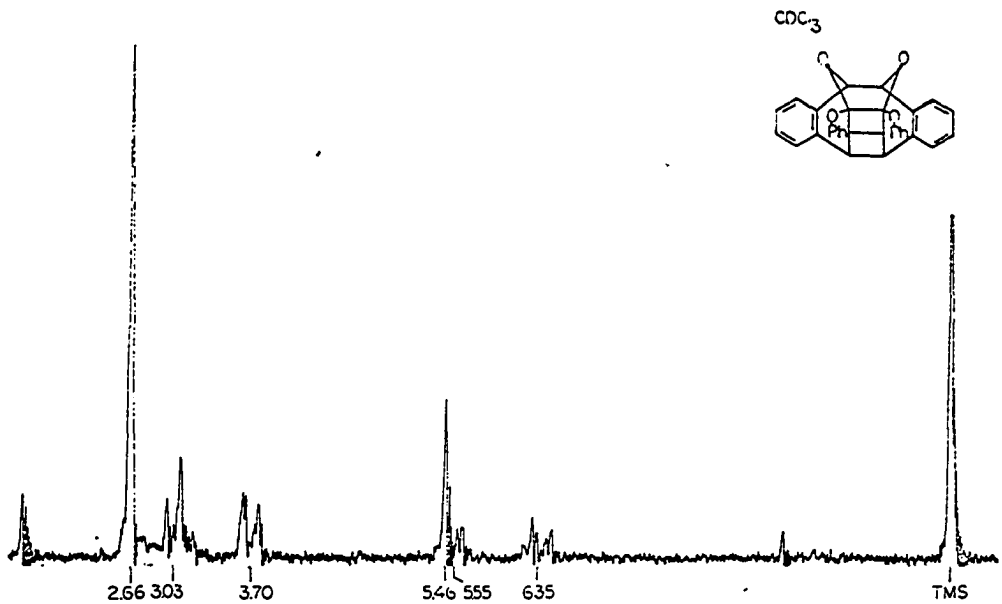

PPM(τ)
CDCl3
PPM(δ)
PPM(τ)
CDCl3
PPM(δ)

Figure 39. Nuclear magnetic resonance spectra

Top - Dimer C (XLV)

Bottom - Dimer C-1,2,5,10-d_4 (LII)


CDCl3
2.66 3.03
3.70
5.46 5.55
6.35
TMS
TAU

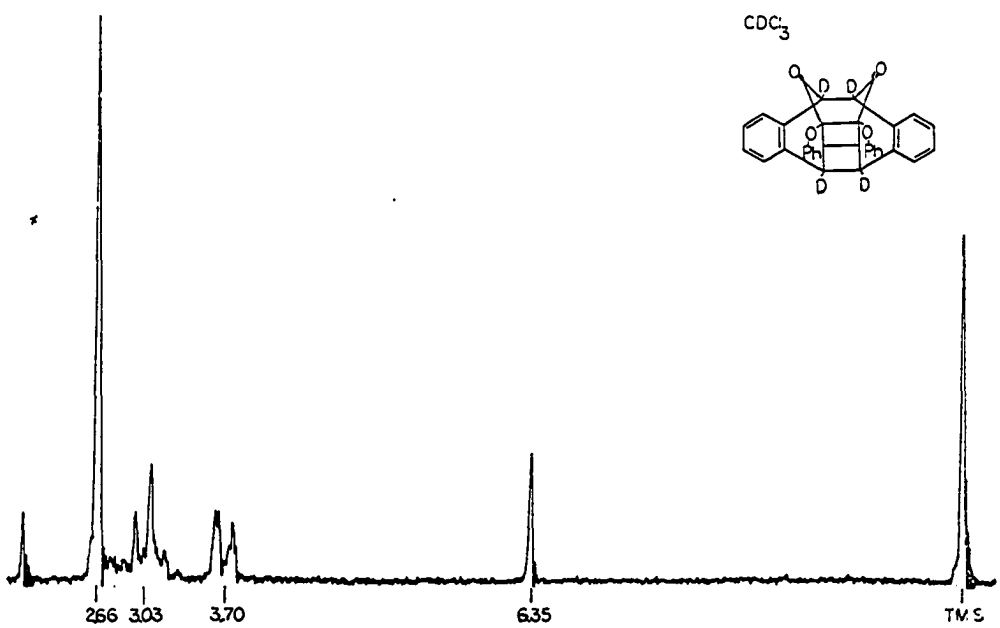

CDCl3
D D
D D
2.66 3.03
3.70
6.35
TMS
TAU

Figure 40. Nuclear magnetic resonance spectra

Top - Dimer C-6,9-d_2 (LV)

Bottom - 2,4,6-Trideuteriophenoxy Dimer C (XLVIII)

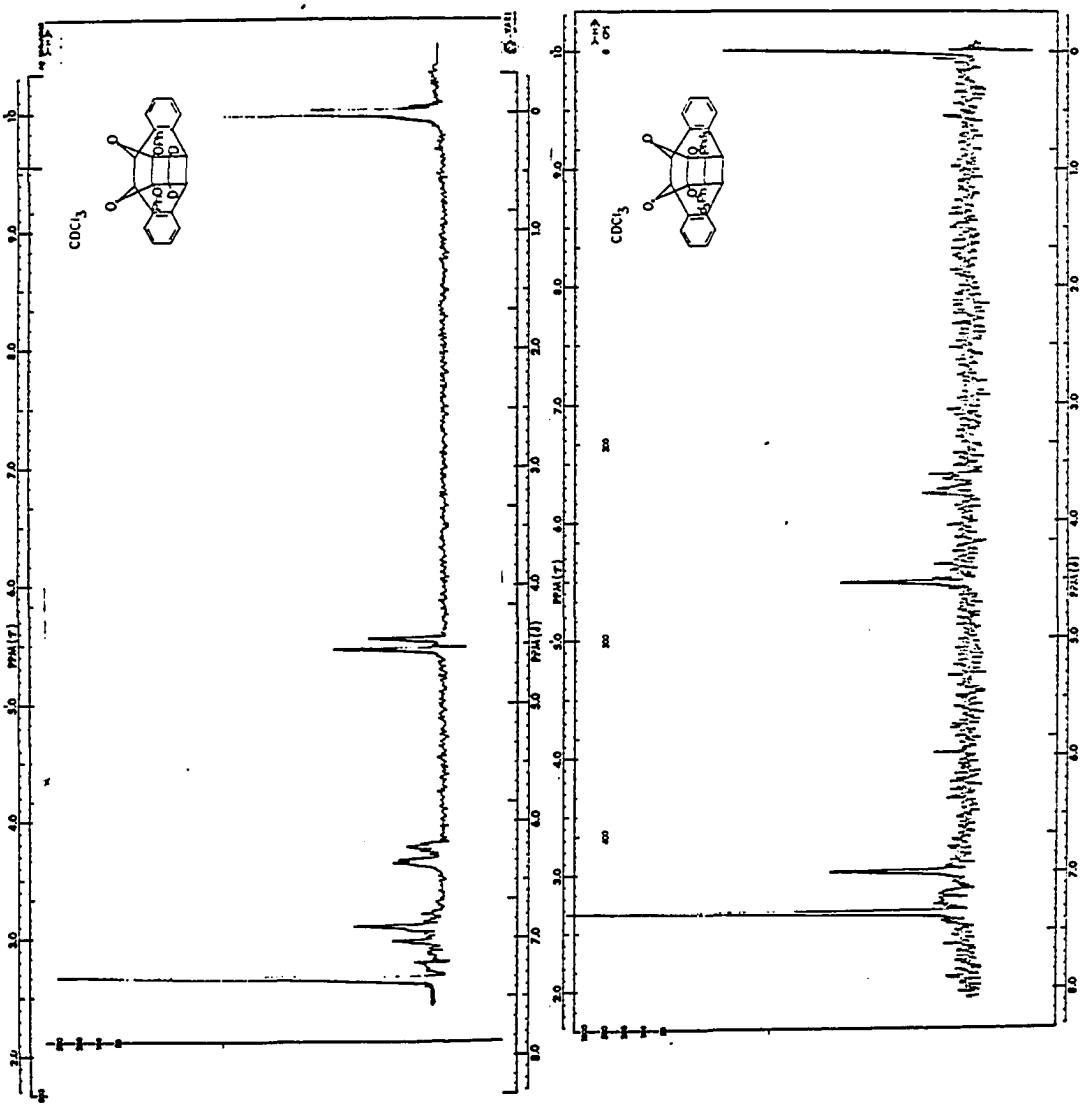

CDCl3
PPM(T)
CDCl3
PPM(T)

Figure 41. Nuclear magnetic resonance spectrum of Dimer C diol (LXV)

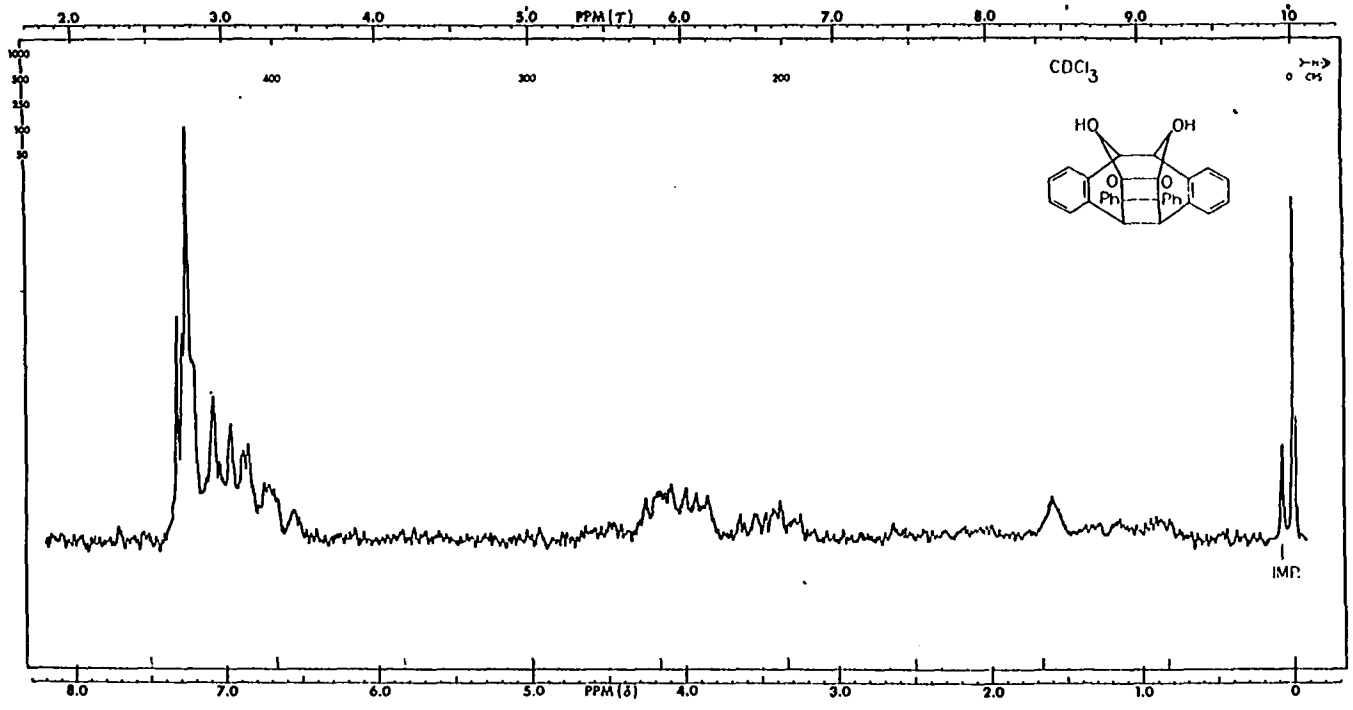
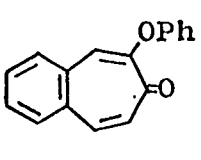
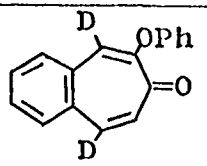
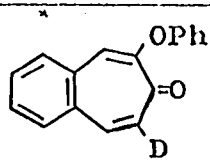
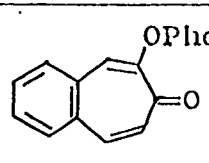
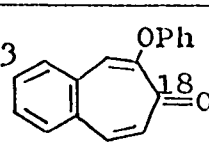
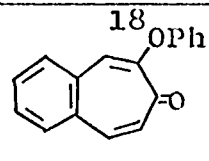
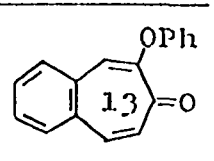

2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
CDCl3
HO
OH
O
Ph
O
Ph
IMΩ
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0

Table 7. Mass spectra of the principle ions of 2-phenoxy-4,5-benztropone and derivatives at 70 ev[a]

m/e	 XXV	 XXX	 XXXI	 XXXII	 XXXIII	 XXXIV	 XXXV
251				100			
250		100		34	42	22.8	
249			100				100
248	100				100	100	91.8
233		27		27	6.0	2.4	
232			28				21.4
231	25				32.8	24.6	16.3
223				64			
222		60		20	21.5	3.4	5.9
221			61				60
220	58				75.3	68.5	52.3
219							8.1
195				20			
194		18					
193		20	19	14			4.4
192	18		23		31.2	19.6	25.6

[a]Intensity expressed as per cent of base peak

Table 7. (continued)

m/e	XXV	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV
191	26				40.8	25.2	28
190							7.0
189							7.0
167		4.4		8.4			
166		2.2	4.7				2.3
165	7.1	1.1	1.8		12.4	7.0	5.9
149							15.1
146		3.3			1.5		
145			3.5	3.2			2.0
144	4.6				5.4	4.0	3.1
129		19					
128			18				7.0
127	23			24.6	34.4	22.6	20.9
126							8.1
125.5				15.4			
125		18			10.8	3.0	
124.5			16				13.2
124 (M^{++})	15				19.3	16.8	12.8
117		23					
116			23				
115	33			31.0	48.3	28.2	28

Table 7. (continued)

m/e	XXV	XXX	XXXI	XXXII	XXXIII	XXXIV	XXXV
103		4.8					
101	7		4.8	5.6	8.6	7.1	5.9
90		7.0	3.1				
89	8.0		3.1	6.6	10.7	6.5	
80				16.0			
77	25	12	13	9.4	33.4	22.6	20
53				9.4			
52				8.0			14
51	20	14	15	9.0	28	12.1	3.5

Metastable ions in the spectrum of XXV[a]

Process	m_c*	m_f*	Process	m_c*	m_f*
248 - 231	215.5	215.1	192 - 191	190.1	190.1
248 - 220	195.0	195.5	127 - 126	125.1	125.1
220 - 192	167.5	167.6	127 - 101	80.4	80.4
191 - 165	142.5	142.7	115 - 89	68.8	68.5

[a]Each of the isotopically labelled derivatives of XXV exhibited all these metastable ions appropriately shifted.

group from the molecular ion(metastable ion at 215.0) in which the hydrogen atom is derived from an ortho-hydrogen of the phenoxy group. This is clearly demonstrated by the loss of -OD from the 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone (XXXII). Confirmation of the ortho-hydrogen atom involvement (as opposed to the para) comes from the observed equal intensity loss of -OH from 2-(4-chlorophenoxy)-4,5-benztropone. The source of the oxygen atom of the hydroxyl radical was, surprisingly, not unique. Comparison of the mass spectrum of either carbonyl-^{18}O-labelled 2-phenoxy-4,5-benztropone (XXXIII) or 2-(^{18}O-phenoxy)-4,5-benztropone (XXXIV) with that of unlabelled compound (XXV) shows that the oxygen atom is derived about equally from ether and carbonyl oxygen atoms of XXV.

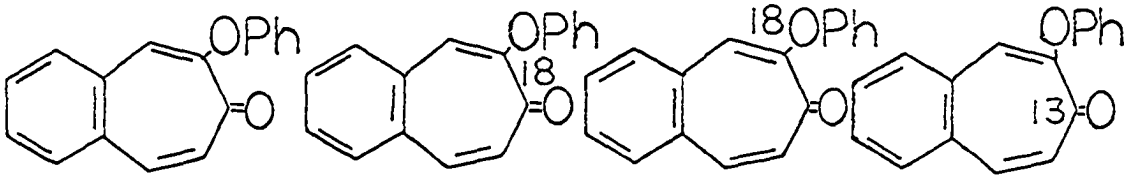
The quantitative agreement between the experiments in which the ether oxygen and the carbonyl oxygen, respectively, were labelled is quite good. The mass spectra of 2-phenoxy-4,5-benztropone and its labelled derivatives at low ev (12 ev) are shown in Table 8, page 117. At the lowest ionizing voltage the isotope incorporation can be accurately measured. The calculation is shown below by using the data in Table 8.

The ^{18}O incorporation for XXXIII is:

$$\frac{44 - 2.2}{100 + 44 - 2.2} = 29.4\%$$

Loss of -OH from XXXIII gives $\frac{19.7 - 1.1}{100 + 19.7 - 1.1} = 15.58\%\ ^{18}O$

Table 8. Mass spectra of 2-phenoxy-4,5-benztropone and its derivatives at 12 ev[a]



m/e	XXV	XXXIII	XXXIV	XXXV
250	17.5 (2.2)	16.5 (44)	16.0 (21)	12.0
249	146.5 (18.9)	7.5 (19.7)	15.0 (19.7)	69.0
248	775.0 (100)	38.0 (100)	76.0((100)	56.5
233	1.0 (1.1)	6.0 (19.7)	2.9 (9.5)	
232	16.0 (17.8)	5.5 (18)	5.5 (18)	
231	90.0 (100)	30.5 (100)	30.5 (100)	
222	0.5 (0.9)	9.0 (33)	1.3 (3.9)	
221	9.5 (17.9)	4.8 (18)	5.7 (17.3)	28.5
220	53.0 (100)	27.0 (100)	3 .1 (100)	31.0

[a]Intensity is the relative intensity

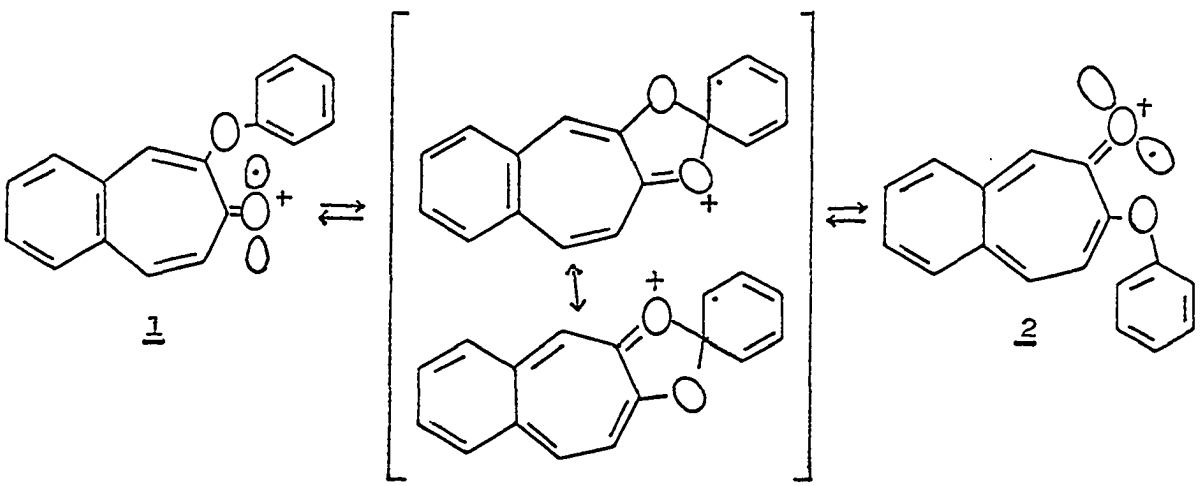
incorporation. That means $\frac{15.58}{29.4}$ = 52.9% ^{18}O retained; i.e. 47.1% carbonyl oxygen is lost.

The ^{18}O incorporation of XXXIV is:

$$\frac{21 - 2.2}{100 + 21 - 2.2} = 15.85\%$$

Loss of -OH from XXXIV gives $\frac{9.5 - 1.1}{100 + 9.5 - 1.1}$ = 7.67% ^{18}O incorporation. That means $\frac{7.67}{15.85}$ = 48.5% ^{18}O retained; i.e. 51.5% ether oxygen is lost.

This fragmentation continues to occur at lowered ionizing voltages, and below 20 ev this M - 17 ion (m/e 231) becomes the most intense fragment ion. Fragmentation is considered to arise from the lowest energy ionization of 2-phenoxy-4,5-benztropone since it is the favored fragment at low ionization voltages. It seems reasonable that this lowest energy ionization involves the removal of an electron from the high energy non-bonding orbital on the carbonyl oxygen atom. The loss of both oxygens with approximately equal facility suggests a rapid equilibration of the isomeric ions 1 and 2. This equilibration does not appear to occur thermally as mentioned previously. A mechanism consistent with these observations is outlined in Figure 42, page 119. The photochemical phenyl shift of 2-phenoxy-4,5-benztropone provides a good model for the phenyl shift in the radical ion. The half-vacant non-bonding orbital is suitably positioned for attack on the phenyl group. The intermediate formed can revert to 1 or go on to 2. Either 1 or 2 can abstract an ortho-hydrogen



1 2

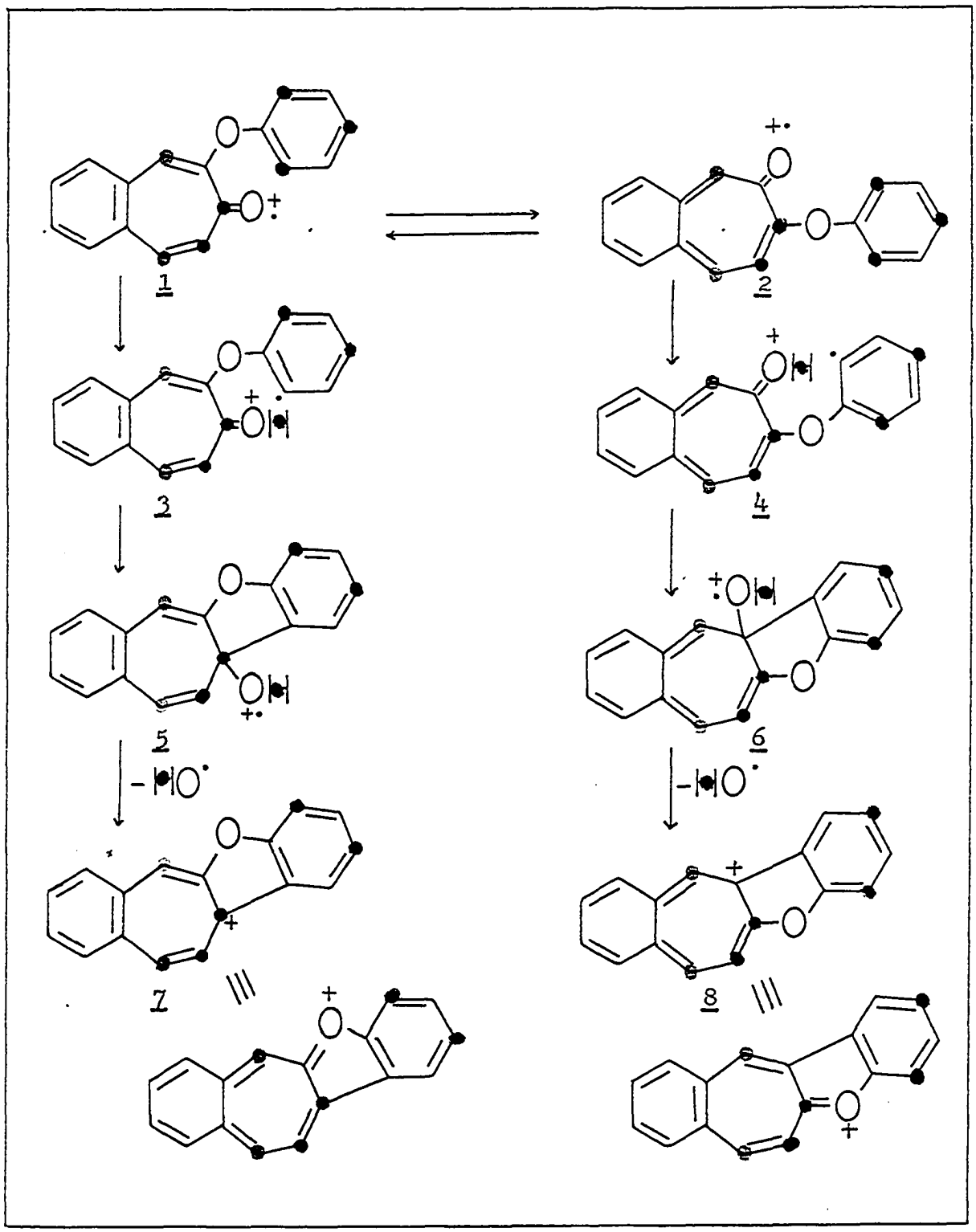
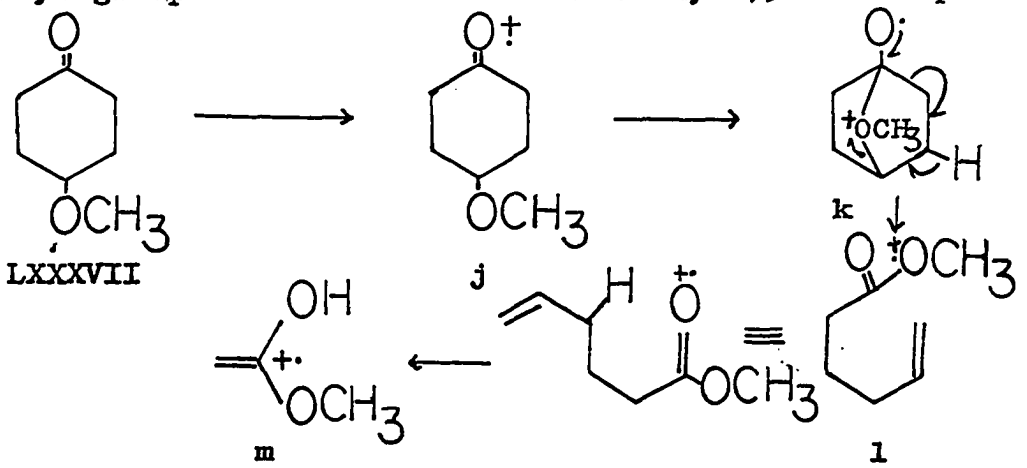


Figure 42. Mechanism of loss OH from 2-phenoxy-4,5-benztropone upon electron impact

from the phenoxy group giving 3 or 4. Cyclization by addition of the aryl radical to the protonated carbonyl group gives 5 and 6 respectively. Loss of hydroxyl radical from 5 and 6 then gives the isomeric ions 7 and 8 which do not appear to undergo further fragmentation.

Recently, increasing attention has been given to the electron impact induced rearrangement of substituents other than hydrogen in mass spectrometric fragmentation reactions. This is due to the intrinsic mechanistic interest that such rearrangements possess and the possible limitation that their occurrence may impose on the use of the "element mapping" technique (50,51). Examples of aryl (52) and alkyl (53) group rearrangements are shown in Figure 43, page 121.

Recently Djerassi et al.(54) reported an example of interaction of a remote functional group with an ionized carbonyl group as shown below. 2-Phenoxy-4,5-benztropone is



the first example of an aryl migration from one oxygen atom to another upon electron impact.

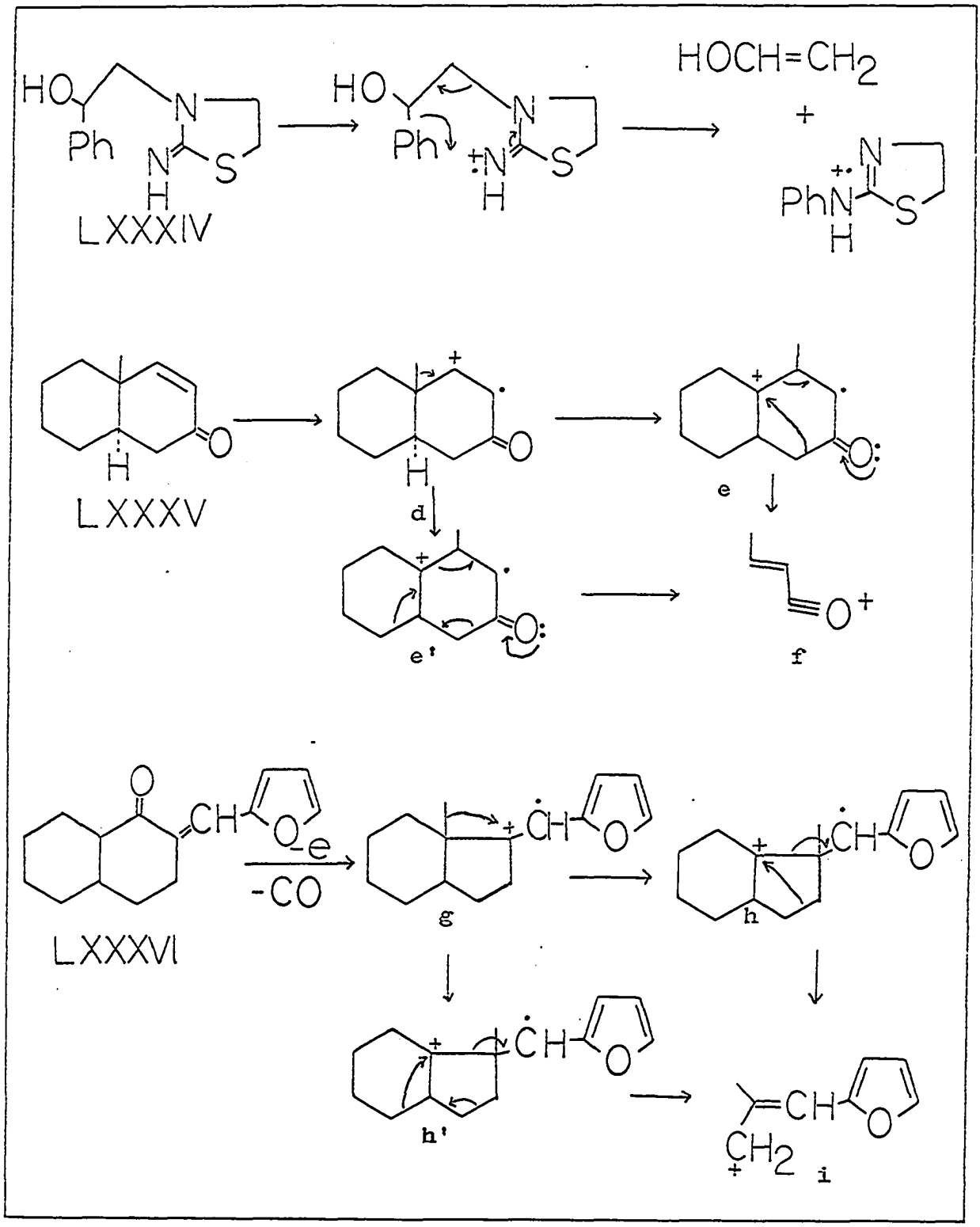


Figure 43. Examples of aryl and alkyl migration upon electron impact

It was thought probable that further evidence for this phenyl migration would be found in the ions derived from loss of carbon monoxide, and this was indeed found to be the case. In the fragmentation sequence 248 → 220 → 192 → 191 → 165, the first and second processes involve loss of carbon monoxide. Loss of carbon monoxide from the parent ion involves both oxygen atoms. Loss of the ether oxygen is favored over loss of the carbonyl oxygen in 2-phenoxy-4,5-benztropone. The ratio is about 4:1 at 12 ev shown by following calculation from the data in Table 8.

Loss of CO from XXXIII gives $\frac{33 - 0.9}{100 + 33 - 0.9} = 24.2\%$ ^{18}O incorporation. That means $\frac{24.2}{29.4} = 82.4\%$ ^{18}O retained; i.e. 17.6% carbonyl oxygen is lost. Loss of CO from XXXIV gives $\frac{3.9 - 0.9}{100 + 3.9 - 0.9} = 2.91\%$ ^{18}O incorporation. That means $\frac{2.91}{15.85} = 18.4\%$ ^{18}O retained; i.e. 81.6% ether oxygen is lost. This ratio agrees well with the observations on 2-phenoxy-4,5-benztropone-1-^{13}C (XXXV) which contains 52% ^{13}C. Loss of CO from XXXV gives $\frac{28.5 - 31 \times 0.179}{31 + 28.5 - 31 \times 0.179} = 42.7\%$ ^{13}C incorporation. That means $\frac{42.7}{52} = 82.1\%$ ^{13}C retained; i.e. 17.9% ^{13}CO is lost in the first loss of carbon monoxide. The loss of both oxygen atoms as carbon monoxide clearly shows that the oxygen to oxygen phenyl shift is also important in this process. The loss of carbon monoxide from the parent ion is a relatively low energy process and is an important

fragmentation mode at low ionizing voltage. The loss of OH is the only process which is more favorable at low ionizing voltage. It thus seems likely that carbon monoxide loss also occurs from the n+ ions (1 and 2). If one assumes that the loss of carbon monoxide involves prior isomerization to the norcaradienone type structures (9 and 10), it is possible to rationalize why loss of carbon monoxide from 2 is favored over 1. The isomerization of 2 to 10 is clearly a lower energy process than 1 to 9. The former process produces a benzene ring while the latter destroys one (Figure 44, page 124). In principle, loss of CO from XXV might involve the ether portion of the molecule rather than the carbonyl group. This is most unlikely because of the observed efficiency of the loss of CO at low ionizing voltages. The loss of CO from diphenyl ether has an appearance potential at 12.56 ev (55), in sharp contrast to the efficient loss of CO from XXV at 11 ev. The equilibrium between 1 and 2 is rapid under all conditions in which fragmentation can be observed. The ratio (1:1) of the loss of ether oxygen to the loss of carbonyl oxygen is constant in the loss of OH between 70 and 12 ev. The ratio in the loss of carbon monoxide at 12 ev is 4:1,but the ratio at 70ev changes to 3:1. The calculation at 70 ev is shown below by using the data in Table 7. Loss of OH from XXXIII gives $\frac{6}{32.8+6}$ =15.5% ^{18}O incorporation; that means $\frac{15.5}{29.4}$ =53.2% ^{18}O retained. Loss of OH from XXXIV gives $\frac{2.4}{24.6+2.4}$ = 9% ^{18}O

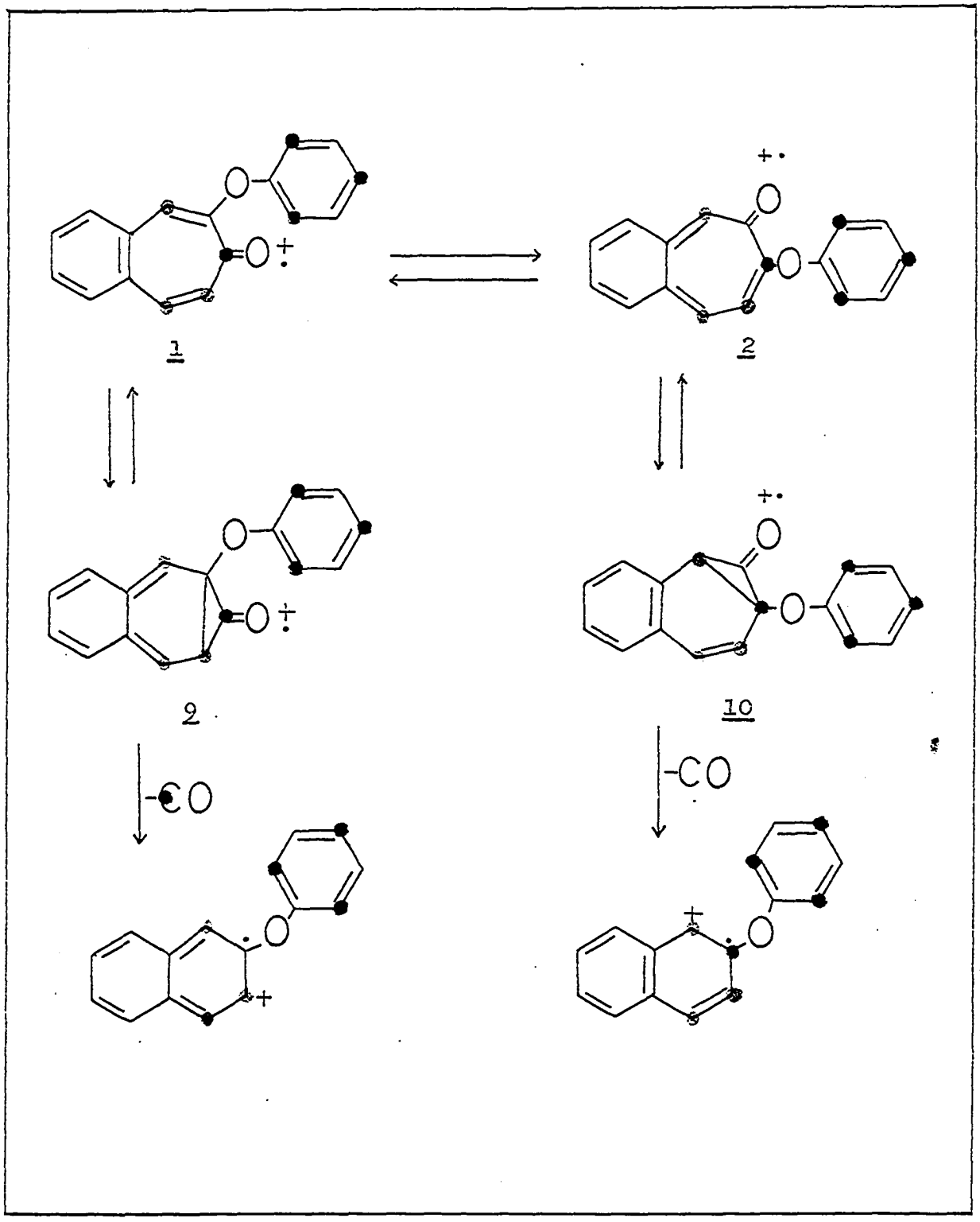


Figure 44. Mechanism of loss CO from 2-phenoxy-4,5-benztropone upon electron impact

incorporation; that means $\frac{9}{15.85}$ = 56.7% ^{18}O retained. Loss of CO from XXXIII gives $\frac{21.5}{75.3 + 21.5}$ = 22% ^{18}O incorporation; that means $\frac{22}{29.4}$ = 77.8% ^{18}O retained. Loss of CO from XXXIV gives $\frac{3.4}{68.5 + 3.4}$ = 4.7% ^{18}O incorporation; that means $\frac{4.7}{15.85}$ = 29% ^{18}O retained.

Since so many labelled compounds were synthesized in this study, it is possible to suggest resonable mechanism for subsequent fragmentations and proposed structures of the fragment ions (Figure 45, page 126). There can be no doubt that 2-naphthyl phenyl ether cation radical is produced in the decomposition of 1. The subsequent fragmentations (220 → 192→ 191 → 165, 220 → 144, 220 → 127 and 220 → 77) are all observed in the mass spectrum of 2-naphthyl phenyl ether (LXXXVIII) (Table 9, page 127). Furthermore, loss of carbon monoxide from the 220 ion in each case involves only the 2-carbon of the naphthalene ring as shown by the spectrum of 2-phenoxy-naphthalene-2-^{13}C (XLI), which contains 55% ^{13}C. From the data in Table 9, the percentage of loss ^{13}CO can be calculated. Loss of CO from XLI gives $\frac{4 - 22.5x1.7/11.2}{22.5 + 4 - 22.5x1.7/11.2}$ = 2.6% ^{13}C incorporation. That means $\frac{2.6}{55}$ = 5% ^{13}C retained; i.e. 95% of ^{13}C is lost. The fragmentation sequence 220 → 192 → 191 → 165 can be delineated in a structural sense by noting the loss or retention of the various labels in each fragment ion. Loss of carbon monoxide from 220 requires bonding

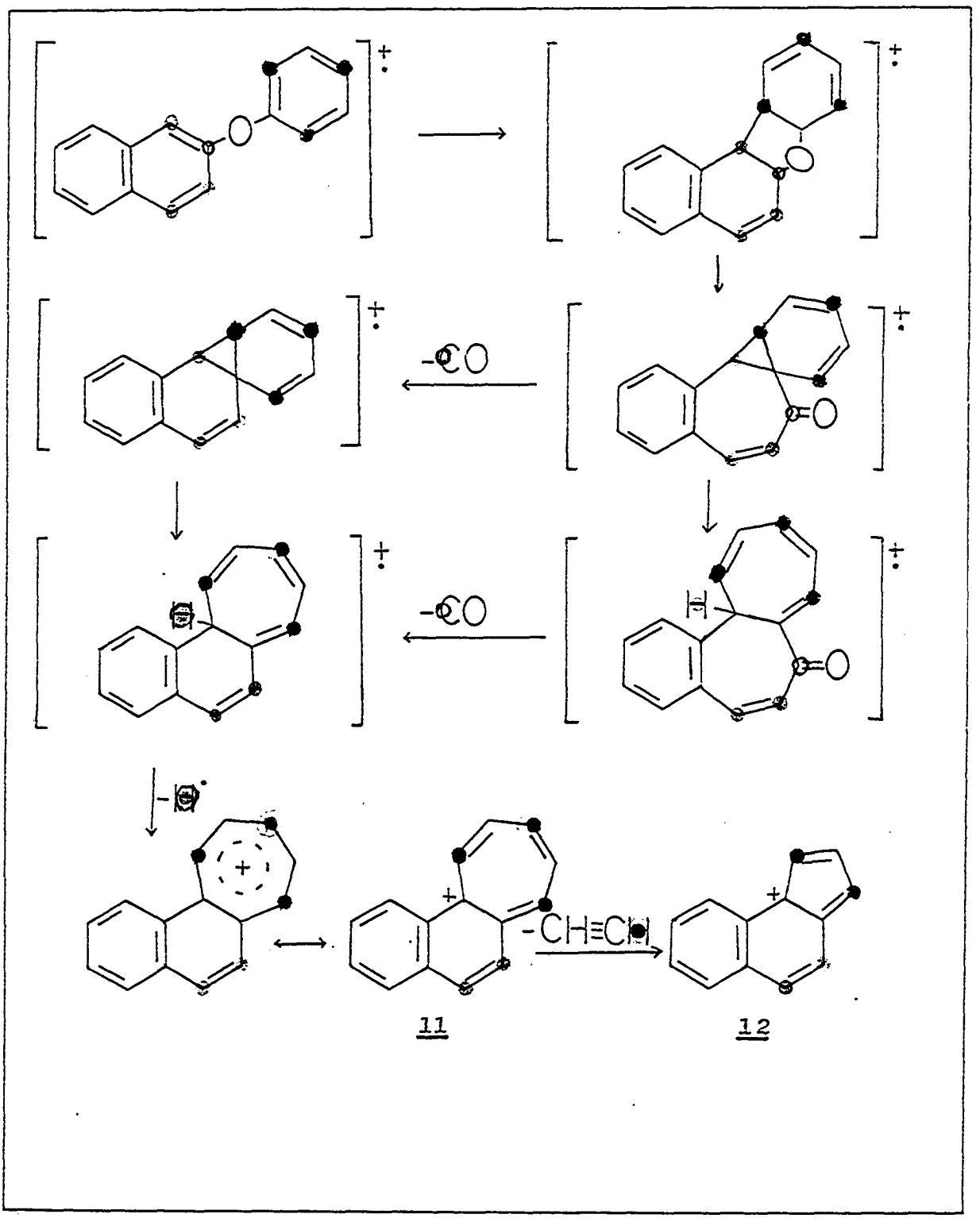
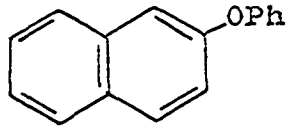
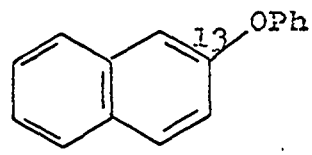
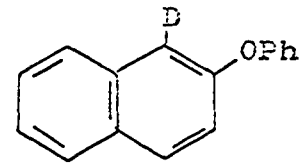


Figure 45. Mechanism for subsequent fragmentations of 2-phenoxy-4,5-benztropone after loss of CO

Table 9. Mass spectra of 2-phenoxynaphthalene and its derivatives at 70 ev[a]

			
m/e	LXXXVIII	XLI	XLII
221	17.0	100	89.8
220	100	82.5	100
193	1.7	4.0	
192	11.2	22.5	19.2
191	15.1	22.5	17.0
166		2.5	3.1
165	3.6	5.8	4.3
145		2.5	2.8
144	2.8	2.0	3.9
128		10.2	7.3
127	9.2	12.0	11.6
126	3.9	3.0	4.3
115	8.3	17.5	8.6
102		2.0	
101	3.0	3.3	3.1
77	6.4	12.0	9.5

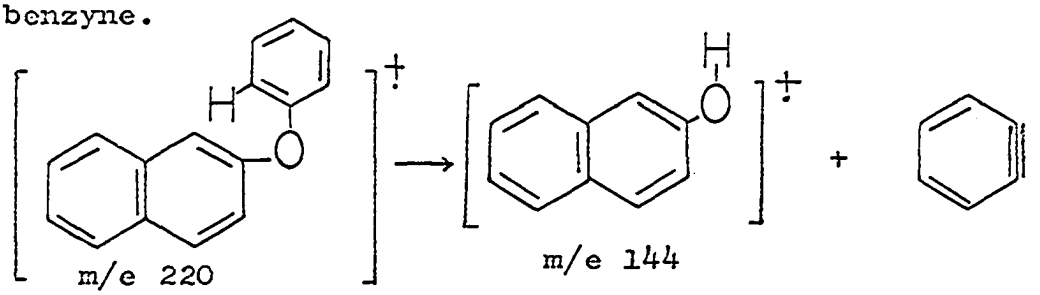
[a]Intensity expressed as per cent of base peak

between the naphthalene nucleus and the phenyl ring at some stage prior to expulsion of carbon monoxide. This mechanism is consistent with the highly specific loss of the 2-carbon of

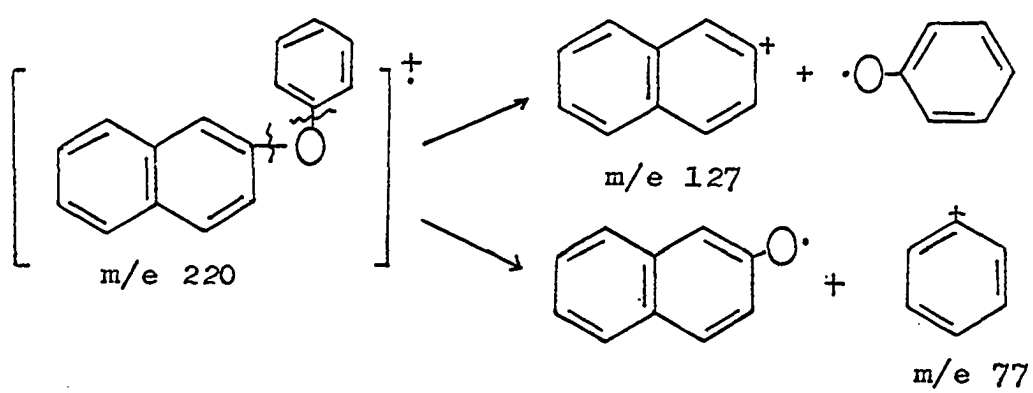
the 2-naphthyl phenyl ether and suggests that the 192 ion thus formed should easily lose a hydrogen atom to give the 191 ion. This conversion of the 192 ion to the 191 ion is an interesting process. One would expect the cycloheptatriene derivative (11) to exhibit a low specificity of loss of hydrogen vs deuterium in the 192 → 191 transformation due to equilibration of hydrogen and deuterium (by a sequence of 1,5 hydrogen transfers) prior to tropylium ion formation. This is the case. Some deuterium is lost from the 2-phenoxy-4,5-benztropone-3,6-d_2 (XXX) and 2-(2,4,6-trideuteriophenoxy)4,5-benztropone (XXXII). Deuterium is not lost from 2-phenoxy-4,5-benztropone-7-d (XXXI). The source of the hydrogen atoms in the acetylene lost from 11 is somewhat difficult to follow because of the scrambling in the cycloheptatriene derivative. In the 3,6-dideuterio and trideuteriophenyl derivatives loss of acetylene is primarily C_2HD. In the 7-deuterio derivative loss of acetylene is primarily (90%) C_2H_2. These results clearly show that loss of acetylene in the 191 → 165 process involves primarily the seven-membered ring of 11. The 165 ion then may be assigned the structure 12.

The m/e 220 ion also gives rise to fragments ions of m/e 144,127,77 and 51. The 144 ion retains both deuterium atoms in the 3,6-dideuterio derivative and the single deuterium atom in the 7-deuterio derivative. It clearly retains one deuterium atom in the trideuteriophenyl derivative.

The ^{18}O-label (from either carbonyl (XXXIII) or ether (XXXIV) labelled 2-phenoxy-4,5-benztropone) and ^{13}C-label(XXXV) are partially retained (Table 7, page 114). These observations are sensibly accounted for by fragmentation of the 2-naphthyl phenyl ether cation radical to 2-naphthol cation radical and benzyne.



In the fragmentation of the 2-naphthyl phenyl ether cation radical to the m/e 127 ion all deuterium atoms in the 3,6-dideuterio derivative (XXX) and the 7-deuterio derivative (XXXI) are retained. All deuterium atoms in the trideuteriophenyl derivative (XXXII) are lost. The ^{13}C-label is retained, but all ^{18}O-label from either precursor is lost. The m/e 127 ion thus is the 2-naphthyl cation and the other fragment is the phenoxy radical (56). The alternate fission leads to phenyl cation (m/e 77) and 2-naphthoxy radical. The m/e 77

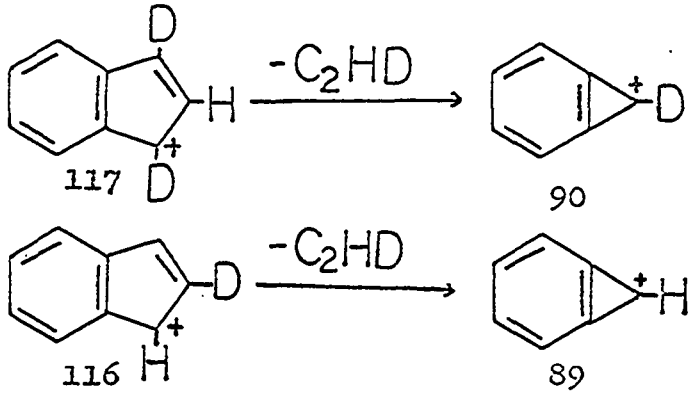


ion shifts to m/e 80 in the trideuteriophenyl derivative as expected. No other label affects the mass of this fragment. The fragment at m/e 51 is produced in a previously recognized fragmentation of phenyl cation (57).

The proposed fragmentations from the m/e 220 ion produced from XXV are in very good agreement with the fragmentations observed for 2-phenoxynaphthalene itself. The spectrum of 2-phenoxynaphthalene-2-^{13}C (XLI) is in total agreement with the previously outlined fragmentation mechanisms and the spectrum of XLI excludes the possibility of carbon monoxide loss occurring from the phenyl ring. The mass spectrum of 1-deuterio-2-phenoxynaphthalene (XLII) was studied in an attempt to pinpoint the source of the hydrogen atom loss in the m/e 192 → 191 fragmentation in XXV. From the data in Table 9, XLII has $\frac{89.8 - 100x17\%}{100 + 89.8 - 100x17\%}$ =39% deuterium incorporation. The hydrogen atom loss in the m/e 192 → 191 fragmentation in XLII shows $\frac{19.2 - 17x11.2/15.1}{17 + 19.2 - 17x11.2/15.1}$ =27.8% deuterium incorporation. That means $\frac{27.8}{39}$ = 71.1% deuterium retained; i.e. 28.9% deuterium is lost, a value consistent with that found for the corresponding process in 3,6-dideuterio derivative.

The mode of formation of the fragment at m/e 115 is uncertain because it is not related to any ion of higher mass by a metastable ion. The m/e 115 ion clearly retains all deuterium atoms from the 3,6-dideuterio and 7-deuterio

derivatives and all other labels are all lost in its formation. The m/e 89 ion is formed from the m/e 115 cation by loss of C_2H_2 (metastable ion at m/e 68.5). This information clearly marks the m/e 115 ion as the indenyl cation. In accord with this assignment C_2HD is lost from the m/e 117 and m/e 116 ions formed from the 3,6-dideuterio and 7-deuterio derivatives respectively. This ion may be formed in part directly from an



excited state of the molecule ion, although another likely precursor ion is m/e 144 since the indenyl ion is intense in the spectrum of 2-phenoxynaphthalene itself. The m/e 191 and 165 ions are unsuitable precursors on the basis of the total deuterium retention from XXX and XXXI in this ion. In agreement with a sequence fragmentation origin, the intensity of this ion drops rapidly relative to that of other ions, including m/e 144, with decreased electron energies.

The only remaining ions of sufficient intensity to be of interest are m/e 124 and 101. The ion at m/e 124 is the doubly charged parent ion. This identification is secure because it shifts to a non-integral mass (124.5) in the mono-

deuterio derivative. The ion at m/e 101 does not retain any deuterium label and is related to the m/e 127 ion by a metastable ion. Its composition is C_8H_4, and its structure is probably $C_6H_4C{\equiv}C^+$.

Mass spectrometry of 2-thiophenoxy-4,5-benztropone and 2-(N-methylanilino)-4,5-benztropone

The possibility of phenyl shifts from a sulfur to an oxygen atom and from nitrogen to an oxygen atom upon electron impact in the analogous compounds was of interest, and consequently the mass spectra of 2-thiophenoxy-4,5-benztropone and 2-(N-methylanilino)-4,5-benztropone were studied.

The mass spectrum of 2-thiophenoxy-4,5-benztropone (XXXVI) (Table 10, page 133) exhibits, in addition to the losses of 17 mass units (-OH) and 28 mass units (-CO), a loss of 33 mass units (-SH), with metastable ions present at m/e 231.2, 211 and 202 respectively. These three fragments are produced by the lowest energy decompositions of the molecule ion and at 16 ev and lower are the only fragment ions observed. At these lowered ionizing potentials, the M - SH ion becomes relatively more intense than the M - OH ion, and in fact seems to increase slightly relative to M - CO. Recently, the mass spectra of several aromatic sulfides have been reported to exhibit the loss of -SH (58, 59). The spectrum of diphenylsulfide, as remeasured in Dr. Kinstle's group in our

Table 10. Mass spectrum of 2-thiophenoxy-4,5-benztropone (XXXVI)[a]

m/e	Rel. Int.	m/e	Rel. Int.
264	100	191	1.5
247	7.0	189	1.8
237	8.0	165	1.5
236	42.2	158	2.2
231	4.8	155	5.1
221	2.9	132 (M^{++})	8.4
204	2.4	127	17.6
203	5.3	115	13.9
202	7.0	101	5.5
192	0.4	77	7.3

[a]Intensity expressed as per cent of base peak

Department, exhibits M - 32 and M - 34 ions (unlike the behavior of XXXVI) in addition to the M - 33 ion. More importantly, the M - 33 becomes insignificant at 16 ev ionizing potential, very unlike the behavior in XXXVI. For these reasons we propose an equilibration between -SPh and -OPh ions which is initiated by a phenyl migration from sulfur to oxygen. A mechanism analogous to that in Figure 42 would explain the losses of -OH and -SH.

The loss of C=S from the molecule ion does not occur. The loss of C=S does occur to some extent from the M - 17 ion and to a lesser extent from the M - 28 ion, but neither

process occurs at electron energies below 18 ev. It has been shown previously that loss of C=S is more difficult than the analogous loss of carbon monoxide (60).

The mass spectrum of 2-(N-methylanilino)-4,5-benztropone (XXXVII) (Table 11, page 135) exhibits ions at M - 17 and M - 28, with metastable signals at ?28 and ?06 respectively, but does not exhibit M - 30 or M - 41 ions. Therefore we can conclude that if phenyl migration occurs in this system, no fragment ions result from the rearranged ion. Very probably, no rearrangement occurs.

Mass spectrometry of 2-methoxy-4,5-benztropone

The mass spectrum of 2-methoxy-4,5-benztropone was studied to see if 1,4 shifts of alkyl groups analogous to the phenyl shifts occurred. Inspection of the mass spectra of 2-methoxy-4,5-benztropone (XXXVIII) (Table 12, page 136) and its carbonyl-^{18}O-labelled (XXXIX) and ^{13}C-methoxy labelled (XL) derivatives leads to the conclusion that methyl migration analogous to the phenyl migration described above is not important. This conclusion is in agreement with results obtained in purpurogallin tetramethyl ether (26).

The mass spectrum of 2-methoxy-4,5-benztropone exhibits several fragments at M - 18, M - 28, M - 29, M - 30 and M - 31 which are analogous to those found in the spectrum of tropolone methyl ether (IIIa) as mentioned in the Historical

Table 11. Mass spectrum of 2-(N-methylanilino)-4,5-benztropone (XXXVII)[a]

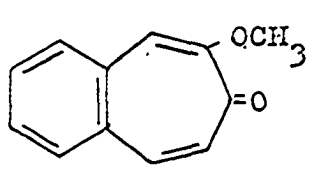
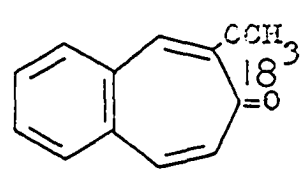
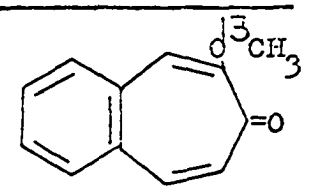
m/e	Rel.Int.	m/e	Rel.Int.
262	19.8	158	10.7
261	100	156	14.4
244	4.8	155	21.4
233	6.4	141	5.9
232	12.8	131 (M^{++})	10.0
217	7.5	128	15.0
192	3.2	127	12.8
184	5.3	115	15.5
169	4.3	106	15.0
168	6.4	77	10.7

[a]Intensity expressed as per cent of base peak

Section (28).

M - 18 peak is the M - H_2O ion which is a relatively weak fragmentation. Loss $H_2{}^{18}O$ in the carbonyl-^{18}O-labelled 2-methoxy-4,5-benztropone (XXXIX) was observed. The loss of carbon monoxide from the parent ion is relatively unimportant compared to the processes which produce M - CHO and M - OCH_3 ions. In the interpretation of the ^{18}O-labelled derivative, it was found about 46% $C^{16}O$ is lost which means about 46% of methyl migration before loss of carbon monoxide. In the processes of the loss of CHO and OCH_3 from the parent ion, the methyl group migration appears to be unimportant.

Table 12. Mass spectra of 2-methoxy-4,5-benztropone and its derivatives[a]

m/e	 XXXVIII	 XXXIX	 XL
189		13.6	
188		100	13.7
187	13.6	16.6	100
186	100	65.2	86.7
169			5.8
168	5.6	8.3	4.9
160		11.9	
159	2.2	50.8	12.3
158	21.4	38.0	29.2
157	50.0	75.0	85.7
156	16.5	11.0	29.2
155	36.5	27.4	66.0
143	3.0		
140	12.1		
129	14.7	28.7	27.7
128	38.2	72.8	64.5
127	19.5	43.5	40.0
115	59.3	98.0	89.0
89	8.5	21.7	18.4

[a]Intensity expressed as per cent of base peak

Metastable ions in the spectrum of XXXVIII

Process	m_c*	m_f*	Process	m_c*	m_f*
186 → 168	151.9	152.0	186 → 158	134.1	134.5
186 → 157	132.6	132.8	155 → 128	105.6	105.5
143 → 115	92.5	92.5	115 → 89	68.8	69.0

From the data in Table 12, carbonyl-^{18}O-labelled 2-methoxy-4,5-benztropone (XXXIX) has $\frac{100}{100 + 65.2} = 60\%$ ^{18}O incorporation. Loss of CHO from XXXIX gives:

$\frac{50.8}{50.8 + 75 - 36.5^a} = 57\%$ ^{18}O incorporation. That means $\frac{57}{60} = 95\%$ ^{18}O retained. 2-(Methoxy-^{13}C)-4,5-benztropone (XL) contains $\frac{100 - 86.7 \times 0.137}{86.7 + 100 - 86.7 \times 0.137} = 50.4\%$ ^{13}C incorporation. Loss of CHO from XL gives:

$\frac{29.2 - 85.7 \times 21.4/50}{85.7 + 29.2 - 85.7 \times 21.4/50} \cong 0$ ^{13}C incorporation.

The ^{18}O is totally retained in the M - CHO fragment of XXXIX and the ^{13}C is totally absent in the M - CHO fragment of XL from the above calculation; therefore, loss of CHO is not from the C_1 carbon and the carbonyl oxygen as proposed in the case of α-tropolone methyl ether.

The tentative suggestion in the literature of α-tropolone methyl ether for the origin of the M - 31 ion (M - OCH_3) and M - 30 ion (M - OCH_2) is certainly consistent with the results obtained for the labelled 2-methoxy-4,5-benztropone. It is suggested that the OCH_3 and OCH_2 groups are lost directly from the molecule ion. Subsequent loss of CO from M - 31 ion (m/e 155) gives m/e 128 peak with metastable ion at 105.5. The m/e 115 peak is the indenyl cation which gives m/e 89 ion by loss of C_2H_2 with metastable ion at 69.0.

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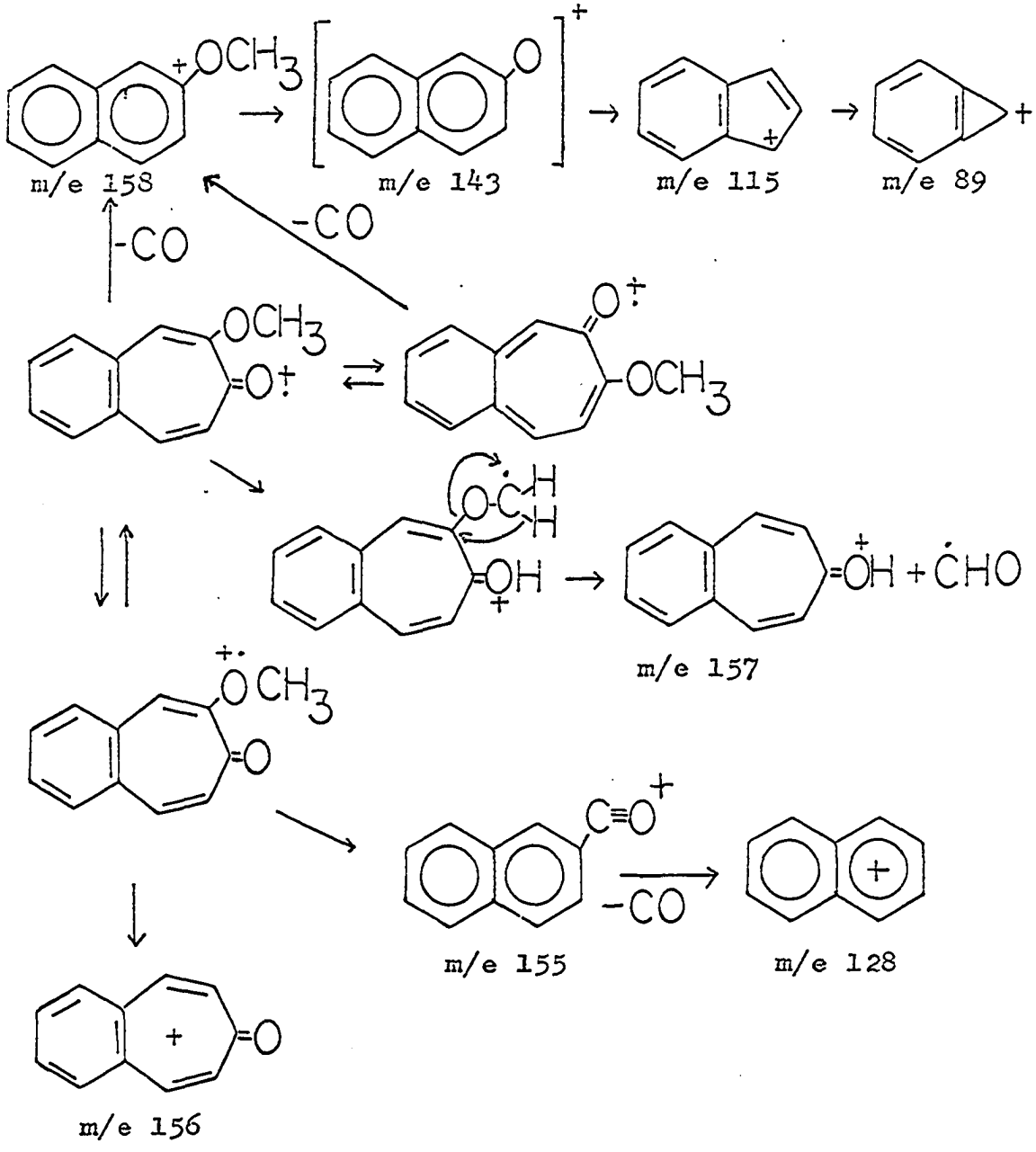
[a]The relative intersity at m/e 157 is partly contributed by loss of OCH_3 from labelled molecule ion.

The m/e 115 ion is possibly formed from m/e 143 by loss of CO with metastable ion at 92.5. The mechanism for the formation of these ions is shown below.



Mass spectrometry of Dimer B and Dimer B diol diacetate

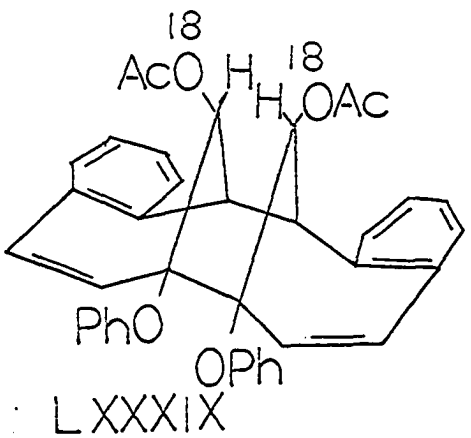
Mass spectrum of Dimer B is shown in Table 13. The parent ion of Dimer B which is very weak is decomposed to the monomer upon electron impact. The spectrum is analogous to the monomer.

Table 13. Mass spectrum of Dimer B

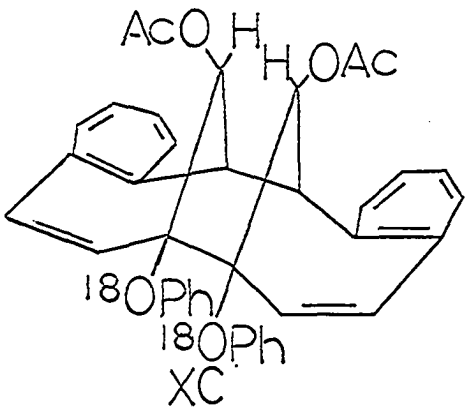
m/e	Rel. Int.	m/e	Rel. Int.
496	9.7	165	7.4
248	58	144	6.8
231	35.5	127	31.3
220	100	115	33.4
192	30	89	58
191	32.3	77	30

The mass spectrum of Dimer B diol diacetate (LXIII) was very interesting. In the study of the mass spectra of this diacetate and its derivatives both ^{18}O-diacetate (LXXXIX) and ^{18}O-phenoxy diacetate (XC) were prepared by reduction and acetylation of the corresponding ^{18}O-labelled Dimer B. The o,p-trideuteriophenoxy derivative of Dimer B diol diacetate (XCI) was prepared from o,p-trideuteriophenoxy derivative of Dimer B. Hexadeuteriodiacetate (XCII) was also prepared by acetylation of Dimer B diol with trideuterioacetyl chloride. The mass spectra of Dimer B diol diacetate and its derivatives

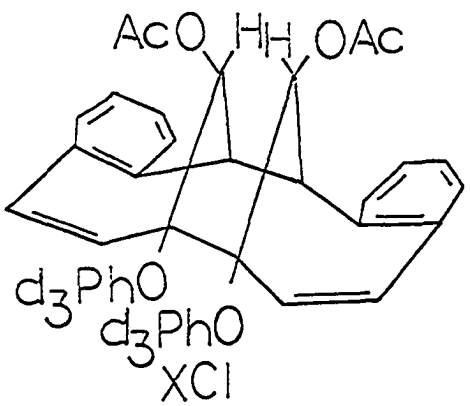
is shown in Table 14, page 141. The significant fragments are at m/e 291, 249 and 233. The m/e 291 is formed from the loss of hydrogen of the monomer. The monomer m/e 292 is not a very important peak compared to m/e 291. The m/e 249 peak which retains one deuterium atom from (XCII) is formed from m/e 291 by loss of $CH_2{=}C{=}O$ with a metastable peak at 213.5.



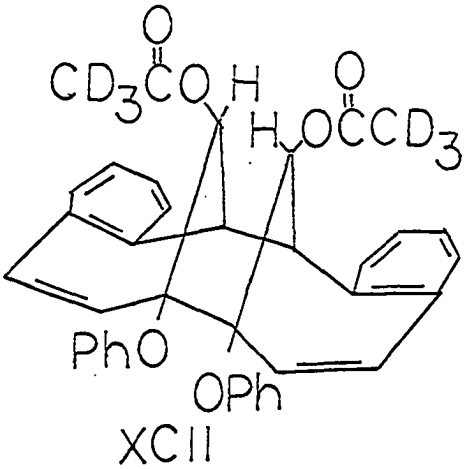
LXXXIX



XC



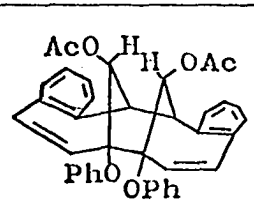
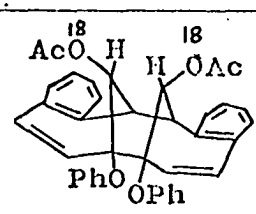
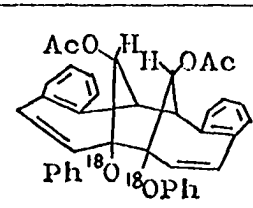
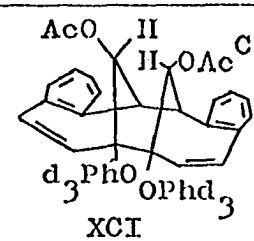
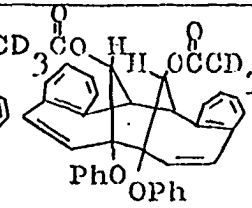
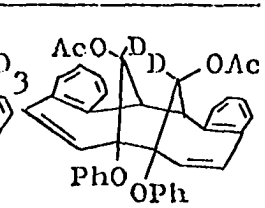
XCI



XCII

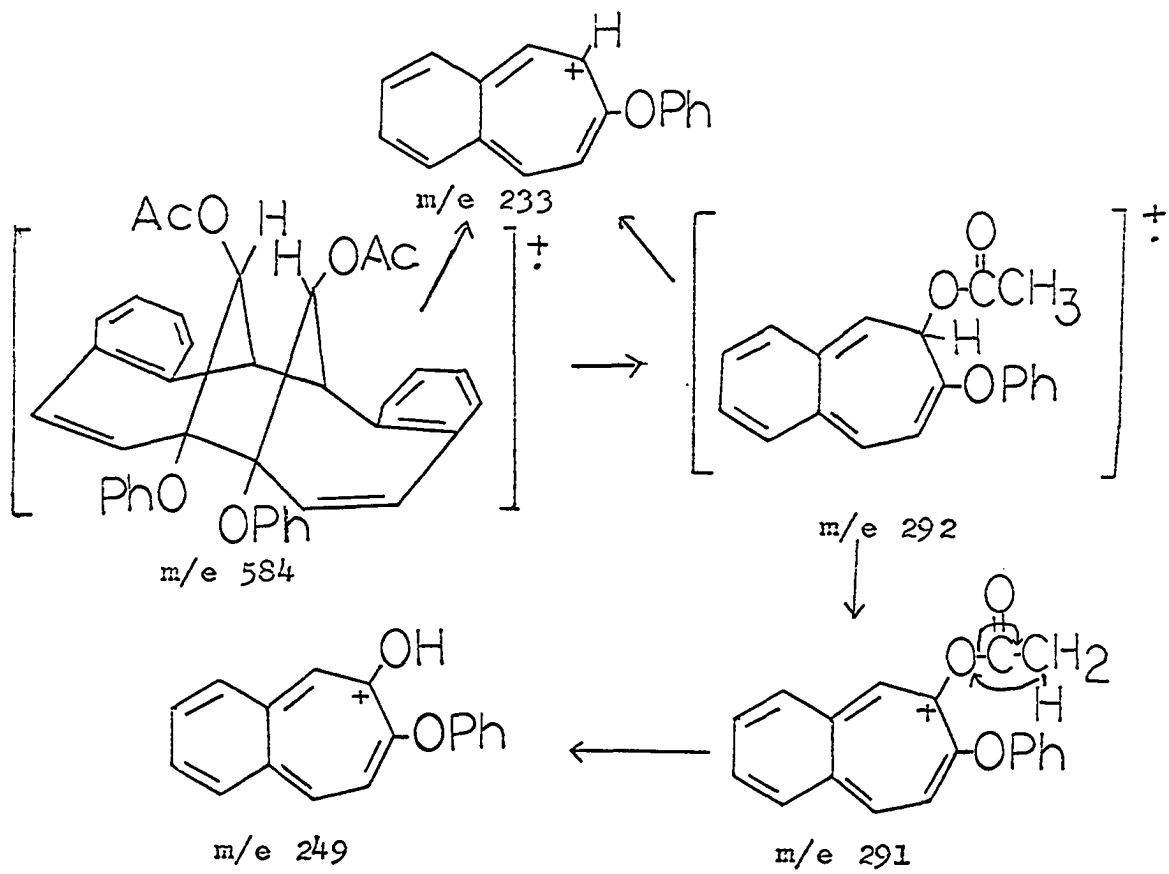
The formation of m/e 233 peak is uncertain because it is not related to any ion of higher mass by a metastable ion. The m/e 233 peak retains deuterium from the 13,14-dideuterio-derivative (LXIV) and contains ^{18}O from ^{18}O-phenoxy derivative

Table 14. Mass spectra of Dimer B diol diacetate and its derivatives[a]

m/e	 LXIII	 LXXXIX	 XC	 XCI	 XCII	 LXIV
590				10.5	10.8	
588		1.3	3.1			
586						10.6
584	10.5	8.5	10.6			
295				9.3	10.0	
294				39.5	37.4	
293		5.7	10.4			
292	10.0	8.0	7.5			7.1
291	40.0	33.0	32.5			29.0
252				30.5		
251		4.6	9.7			
250					32.8	13.5
249	33.6	27.2	28.7			26.5
236				100		
235		16.5	28.7			
234						100
233	100	100	100		100	

[a]Intensity expressed as per cent of base peak

(XC). This information clearly shows the m/e 233 ion to be phenoxybenztropylium cation which might comes from the parent ion or the monomer. The mechanism of formation of these ions is shown below.



EXPERIMENTAL

Instruments and Methods

All melting points are uncorrected and were measured on a Fischer-Johns melting point apparatus

The infrared spectra of all solids were obtained in potassium bromide pellets unless otherwise indicated; the spectra of liquids were obtained with capillary film cells. The spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

The ultraviolet spectra were obtained in 95% ethanol solution unless otherwise noted. The spectra and absorbance measurements were recorded on a Beckman Model DK-2A spectrophotometer.

The nuclear magnetic resonance spectra were run in deuteriochloroform unless otherwise noted. Spectra were measured on a Varian Associates Model HR-60 or A-60 spectrophotometer operating at 60 Mc. Spectra determined on the HR-60 instrument were calibrated by the sideband technique using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported as parts per million (p.p.m.) on the tau scale.

All mass spectra were obtained using an Atlas CH-4 spectrometer operated with a molecular beam inlet system

(TO-4 ion source) at temperatures less than 90°. The electron energy was varied between 11 and 70 ev and electron currents of 1-10 μA were employed.

Analyses were performed by Spang Microanalytic Laboratory, Ann Arbor, Michigan.

Isotopic Chemical Sources

Deuterium oxide was obtained from Columbia Organic Chemicals Co.,Inc. Columbia, South Carolina. Lithium aluminum deuteride and sodium borodeuteride were obtained from Metal Hydrides, Incorporated, Beverly, Massachusetts. ^{18}O-labelled water (80% enriched) was from Yeda Research and Development Co. LTD., Rehovoth , Isreal. Potassium cyanide-^{13}C (50-55%) was obtained from Bio-Rad Laboratories, Richmond, California. Methanol-^{13}C and trideuterioacetyl chloride were obtained from Merck Sharp and Dohme of Canada Limited, Montreal, Canada.

Experimental for the Synthesis of 2-Phenoxy-4,5-benztropone and Related Compounds

Preparation of 2-phenoxy-4,5-benztropone (XXV)

The method of Tarbell et al.(33) was used to prepare XXV. o-Phthalaldehyde (5 g.) and phenoxyacetone (5.6 g.) were dissolved in methanol (300 ml.) and water (500 ml.). A

solution of sodium hydroxide (1 g.) in 50% methanol (10 ml.) was added with stirring. The mixture was allowed to stand at room temperature for five days. The mixture was filtered to give brown solid. Recrystallization from 95% ethanol gave XXV (2.8 g., 30.4%) as white needle crystals, m.p.134-135°. Lit.(33) m.p. 136-137°.

Preparation of 2-phenoxy-4,5-benztropone-3,6-d_2 (XXX)

N,N,N',N'-Tetramethylphthalamide (11g. 0.05 moles) was dissolved in tetrahydrofuran (140 ml. distilled from lithium aluminum hydride) and cooled to 0°. Lithium aluminum deuteride (2 g., 0.05 mole) was added to the solution. The reaction mixture was stirred for 24 hours at 18-20° and then poured onto ice. Sulfuric acid (10%, 5 ml.) was added and the solution was extracted with ether. The ether was removed and the residue was dissolved in hot Skelly B. Upon cooling phthalaldehyde-d_2 (2.55 g.,37.5%) (61) was deposited,m.p.52-54°. The absence of a peak at 0.05 τ in the nuclear magnetic resonance spectrum previously assigned to the aldehydic protons was taken as evidence of the extent and position of deuterium. Phthalaldehyde-d_2 (3.3 g., 0.024 moles) and phenoxyacetone (3.7 g., 0.025moles) were dissolved in 350 ml. of methanol and the solution was diluted with 500 ml. of water. Sodium hydroxide (0.7 g.) in 15 ml. of 50% methanol was then added slowly with stirring. The solution changed from yellow

to cloudy cream and then to brown in color. The reaction mixture was allowed to stand at room temperature for five days. The yellow solid on crystallization from 95% ethanol gave 2-phenoxy-4,5-benztropone-3,6-d_2 (1.7 g., 28.3%), m.p. 135-136°. The ultraviolet spectrum is similar to 2-phenoxy-4,5-benztropone. The infrared and nuclear magnetic resonance spectra are shown in Figure 12, page 54 and Figure 26, page 80, respectively. The mass spectrum of XXX shows 100% deuterium incorporation.

Preparation of 2-phenoxy-4,5-benztropone-7-d (XXXI)

Phenoxyacetone (7 g.) was placed in a 50 ml. flask sealed with a rubber septum. Deuterium oxide (10 ml.) and sodium carbonate (10 mg.) were added to the flask, and the contents were stirred with a magnetic stirrer. After 12 hours the deuterium oxide was removed and fresh deuterium oxide and sodium carbonate were added. The process was repeated until a total of 180 ml. of deuterium oxide was used. An nuclear magnetic resonance analysis of the phenoxyacetone showed 90% deuterium exchange in the methyl group essentially complete exchange in the methylene group.

Phenoxyacetone-d_5 (5 g., 0.032 moles) and phthalaldehyde (4.5 g., 0.033 moles) were dissolved in 160 ml. of methanol-O-d and diluted with 150 ml. of deuterium oxide. Sodium methoxide (1 g. in 10 ml. of deuterium oxide) was added

slowly with stirring and the mixture was allowed to stand for five days. The solid was collected and chromatographed over alumina using benzene as eluent to give 2-phenoxy-4,5-benztropone-7-d (2.2 g., 29%), m.p.135-136° after recrystallization from ethanol. The nuclear magnetic resonance spectrum (Figure 26, page 80) shows only a multiplet in the aromatic region. The infrared spectrum is shown in Figure 12, page 54. The mass spectrum of XXXI shows 100% deuterium incorporation.

Preparation of 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone (XXXII)

A mixture of phenol (10 g., 0.106 moles), sodium hydroxide (2 g., 0.05 moles) and deuterium oxide (40 ml.) was heated in a sealed tube at 90° for 40 hours. After the tube was cooled and opened, the contents were made acidic with 10% hydrochloric acid and extracted into ether. The ether was removed, and the recovered phenol was retreated in the same manner to give 2,4,6-trideuteriophenol (62) after distillation.

2,4,6-Trideuteriophenoxyacetone was prepared by the method of Hurd and Perletz (63). A solution of chloroacetone (10 g., 0.09 moles), potassium iodide (0.3 g.) and acetone (15 ml.) was allowed to stand overnight. In a three necked flask 2,4,6-trideuteriophenol (7 g., 0.07 moles),potassium carbonate (2.5 g.) and acetone (50 ml.) were stirred and heated at reflux for 15 minutes, then the dropwise addition of

the chloroacetone mixture was begun. After one-fourth of the mixture was added, another 2.5 g. of potassium carbonate was added. This process was repeated three times. After which the mixture was stirred for an additional 18 hours, the solid material was removed by filtration and washed with acetone. The acetone was removed under reduced pressure, and the residue was distilled under vacuum to yield 2,4,6-trideuteriophenoxyacetone (8 g.,78%), b.p. 63-65°(0.3 mm). Condensation of this material with o-phthalaldehyde in the usual manner resulted in formation of 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone, m.p. 135-136°. The infrared and nuclear magnetic resonance spectra are shown in Figure 14, page 58 and Figure 25, page 80 respectively. The mass spectrum of XXXII shows 76.6% three deuterium atoms incorporation, 21.4% two deuterium atoms incorporation and 2.2% one deuterium atom incorporation.

Preparation of 2-phenoxy-4,5-benztropone-carbonyl-^{18}O (XXXIII)

A solution of 2-phenoxy-4,5-benztropone (200 mg.) in dry tetrahydrofuran (1 ml.), $H_2{}^{18}O$ (80% enriched, 0.15 ml.) and 0.1 N hydrochloric acid (0.001 ml.) was sealed in a glass tube and heated in a hot water bath for 40 hours. Extensive vacuum evaporation yielded 2-phenoxy-4,5-benztropone-carbonyl-^{18}O (XXXIII) which contained (by mass spectrometry) 29.4% excess ^{18}O. The infrared spectrum (Figure 13, page 56) shows two carbonyl absorption peaks at 1600 (CO) and 1570 cm^{-1}($C^{18}O$).

Preparation of 2-phenoxy-4,5-benztropone-ether-^{18}O (XXXIV)

Phenol-^{18}O was synthesized by alkali fusion of sodium benzenesulfonate (64). In a 20 ml. nickel crucible were placed sodium hydroxide-^{18}O (1 g. prepared by the reaction of 0.46 g. of sodium with 0.4 g. of water-60% ^{18}O) and sodium hydroxide (2 g.) and heat applied until the alkali melted. The temperature was allowed to fall to 230° and while stirring with a copper encased thermometer. Sodium benzenesulfonate (0.6 g.) was added to the crucible. During the next five min. an additional 2 g. of sodium benzenesulfonate was added and the temperature was raised to 270°, then to 330° for an additional 2 min. The cooled reaction mixture was dissolved in sulfuric acid solution (4 ml. of concentrated sulfuric acid in 25 ml. of water) and extracted with three 25 ml. portions of ether. The ether extracts were washed with 5% sodium bicarbonate solution and extracted with dilute sodium hydroxide (10%). Neutralization of these extracts with hydrochloric acid, extraction into ether and evaporation of solvent yielded a crude product which was distilled to give phenol-^{18}O (0.35 g.). Condensation with chloroacetone to produce ^{18}O-labelled phenoxyacetone and further condensation with o-phthalaldehyde using the procedures previoulsy described resulted in the formation of 2-phenoxy-4,5-benztropone labelled in the ether oxygen with ^{18}O, 16% excess ^{18}O by mass spectrometry, m.p. 135-136°.

Preparation of 2-phenoxy-4.5-benztropone-1-^{13}C (XXXV)

A mixture of crystalline sodium sulfite (101 g., 0.8 moles), dichloromethane (69 g., 0.8 moles), water (350 ml.), ethanol (30 ml.) and cupric chloride (0.001 g.) was heated 30 hours at 100° in an autoclave with stirring. The mixture was evaporated on a steam bath and dried at 100° to give powdered solid, which was extracted in a soxhlet apparatus with ethanol for one week. The extracts were cooled and sodium chloromethane sulphonate (100 g.) was collected (65).

Sodium chloromethane sulphonate (26 g.) and phenol (18 g.) were put in a round bottomed flask. Sodium hydroxide (7.5 g. in 7.5 ml. of water) was added to the flask and heated on an oil bath to 200° and maintained at that temperature until no more water distilled off. Heating was continued for a further 4 hours at a bath temperature of 200-240°. The solid mass which resulted was broken up by warming on the steam bath with water and washed out from the flask. After cooling the solid was filtered and washed with ice water, alcohol and ether. The solid was dissolved in water and treated with charcoal giving light brown solid sodium phenoxymethanesulfonate (8 g.).

Sodium phenoxymethane sulphonate (8 g., 0.05 moles) and phosphorous pentachloride (20 g., 0.1 moles) were ground together in a mortar, after a short delay interaction set in and the mass liquified. About 15 min. after the first

vigorous reaction had subsided the yellow oily mass was diluted with ether and poured into ice and water. The mixture was stirred to decompose phosphoryl chloride and thionyl chloride. Then the ether layer was separated, washed twice with ice cold 1 N sodium hydroxide solution and twice with iced water and dried over anhydrous magnesium sulfate. The ether was distilled off and the residue was distilled under vacuum to give phenoxymethyl chloride (3.1 g.), b.p. 53-56°(2.8 mm.), Lit. (35) b.p. 88-90° (15mm.)

To a stirred solution of potassium cyanide-^{13}C (0.585 g., 0.009 moles) in 2 ml. of water and 3 ml. of acetone was added phenoxymethyl chloride (1.3 g., 0.009 moles) in 4 ml. of acetone during one hour. The mixture was heated to 65° and then held at 80° for an additional hour. The dark solution was poured into 10 ml. of ice water containing 2 ml. of 2 N sodium hydroxide and extracted with ether. The residue after drying and evaporation of the solvent was distilled to afford phenoxyacetonitrile-1-^{13}C (0.8 g.,66%), b.p. 105-110° (2.7 mm). Mass spectrum shows parent peak at 134.

A solution of phenoxyacetonitrile-1-^{13}C (0.7 g.) in 5 ml. of ether was added to excess Grignard reagent (from 6 g. of methyliodide and 1 g. of magnesium in 25 ml. of ether) dropwise with stirring. After 18 hours the reaction mixture was hydrolyzed with 2 N hydrochloric acid and extracted with ether. The ether extracts were washed with sodium carbonate

solution (5%), dried and evaporated to yield phenoxyacetone-2-^{13}C (0.55 g.,70.5%), whose infrared spectrum shows two carbonyl stretching peaks at 5.84 and 5.97μ.

Crude phenoxyacetone-2-^{13}C (0.3 g.) and o-phthalaldehyde (0.3 g.) were dissolved in methanol (30 ml.) and diluted with water (35 ml.). A solution of sodium hydroxide (0.1 g.) in 2 ml. of water was added, and the mixture was allowed to stand at room temperature for three days. The precipitate and the oil on the bottom of the flask were collected and purified by alumina chromatography (benzene-ether eluent) to afford 2-phenoxy-4,5-benztropone-1-^{13}C (80 mg.), m.p. 135-136° after recrystallization from 95% ethanol. Mass spectrum shows XXXV contains 52% of ^{13}C.

Preparation of 2-thiophenoxy-4,5-benztropone (XXXVI)

Thiophenoxyacetone (66) was prepared by treatment of chloroacetone with thiophenol in an aqueous sodium hydroxide in modest yield. Condensation of thiophenoxyacetone (3.1 g.) and o-phthalaldehyde (2.5 g.) was effected by allowing a methanol-water solution containing these reactants and sodium hydroxide (0.5 g.) to remain at room temperature for two days. The reaction mixture was then filtered to give dirty yellow solid and tarry material which was purified by chromatography. Elution of the material from an alumina column with benzene afforded 2-thiophenoxy-4,5-benztropone (1.2 g.). Recrystal-

lization from 2-propanol gave yellow crystals, m.p. 108-109°, Lit.(42) m.p.108.5-109.5°.

Preparation of 2-(N-methylanilino)-4,5-benztropone (XXXVII)

Phenylmethylaminoacetone was prepared according to a published procedure (67). Condensation of this material with o-phthalaldehyde was effected under the same general condition as previously discussed using a reaction time of five days. The crude product was very tarry and was purified by elution of the material through alumina with benzene. Recrystallization several times from Skelly B gave yellow crystals (24%), m.p. 116-117° for analysis. The infrared spectrum is shown in Figure 14, page 58. The nuclear magnetic resonance spectrum shows singlet at 6.73 τ and multiplet at 2.87 τ (see Figure 27, page 84).

Anal. Calcd. for $C_{18}H_{15}NO$: C,82.75; H, 5.75; N, 5.36. Found: C,82.52; H, 5.90; N, 5.22.

Preparation of 2-methoxy-4,5-benztropone (XXXVIII)

2-Methoxy-4,5-benztropone was prepared (36) by the condensation of methoxyacetone with o-phthalaldehyde in basic methanol-water solution. The yield of product which had m.p. 85-87°, Lit. m.p. 89-90°, after recrystallization from dibutyl ether was 25%.

Preparation of 2-methoxy-4,5-benztropone-carbonyl-^{18}O (XXXIX)

2-Methoxy-4,5-benztropone (10 mg.), $H_2{}^{18}O$ (50 µl. 80% ^{18}O), 0.1 N hydroxide acid (2 µl.) and dry tetrahydrofuran (100 µl.) were sealed in a glass tube for four days. Evaporation to dryness in high vacuum deposited a non-crystalline material which was used directly for mass spectral analysis. Mass spectrum shows it contains 60% ^{18}O.

Preparation of 2-(methoxy-^{13}C)-4,5-benztropone (XL)

A glass tube containing propylene oxide (0.9 ml.), methanol-^{13}C (0.5 ml.) and sodium (0.03 g.) was sealed and heated at 100°for 12 hours. The resulting product was distilled giving colorless 1-(methoxy-^{13}C)-2-propanol (68), b.p. 80-100°.

To a solution of sodium dicromate (1.67 g.) in water (0.9 ml.) and 1-(methoxy-^{13}C)-2-propanol (0.9 g.) was added dropwise over a period of 2 hours a solution of sulfuric acid (2 g.) in 0.5 ml. of water. The reaction mixture was stirred during the addition and the temperature was kept between 20-25°. After standing at room temperature for 12 hours the green mixture was extracted four times with 2 ml. portions of ether. Removal of the ether gave crude 1-(methoxy-^{13}C)-2-propanone (0.31 g., 34%). Condensation of this labelled ketone with o-phthalaldehyde was accomplished in 11 % yield using the procedure described above for the unlabelled

material. The m.p. of the final product was 87-88° after elution through alumina column with 1 to 1 benzene and chloroform mixture and recrystallization from dibutyl ether. The mass spectrum shows XL contains 50.4% ^{13}C. The nuclear magnetic resonance spectrum (Figure 27, page 84) shows the methyl protons at 6.08 τ which was split to a doublet by ^{13}C, $J_{^{13}CH}$ = 146 c.p.s.

Preparation of 2-phenoxynaphthalene-2-^{13}C (XLI)

Potassium cyanide-^{13}C (0.56 g., 0.0086 moles) was treated (69) with benzyl chloride (1.1 g., 0.009 moles) to give phenyl acetonitrile-1-^{13}C (0.75 g., 75%), whose infrared spectrum showed twinned nitrile absorption bands at 4.45 and 4.56 μ.

Phenylacetonitrile-1-^{13}C (0.7 g.) was hydrolyzed (70) by refluxing with 6N sulfuric acid (1.5 ml.) and acetic acid (0.7 ml.) mixture. After 45 min. the reaction mixture was then poured into water (10 ml.). The phenylacetic acid-1-^{13}C was extracted with ether, washed with water and dried. Distillation under reduced pressure gave phenylacetic acid-1-^{13}C (0.6 g., 70%) which showed two acid absorption peaks at 5.94 and 6.03 μ in the infrared spectrum, b.p. 130-132°(2 mm.).

A mixture of phenylacetic acid-1-^{13}C (0.6 g.) and thionyl chloride (0.5 g.) was refluxed until gas evolution stopped. Distillation of the solution gave a small amount of

unchanged thionyl chloride and phenylacetyl chloride-1-^{13}C as reddish oil (0.6 g., 90%), b.p. 70-72°(2.3 mm). The infrared spectrum showed two acid chloride absorption peaks at 5.55 and 5.66 μ.

Phenylacetyl chloride-1-^{13}C (0.56 g., 0.004 moles) was dissolved in dry carbon disulfide (11.2 ml.) and added to a stirred suspension of anhydrous aluminum chloride (0.95 g., 0.004 moles) in 15 ml. of dry carbon disulfide. The mixture was cooled in an ice bath and dry ethylene (71) was passed in for 5 hours. The dark red mixture was poured onto ice and concentrated hydrochloride acid, The organic material was extracted with ether, washed with dilute sodium hydroxide and water, dried and evaporated to yield a dark residue which was distilled to give 2-tetralone-2-^{13}C(0.35 g.), b.p. 105-110° (2 mm.). The infrared spectrum showed two carbonyl absorption peaks at 5.85 and 5.98 μ.

2-Tetralone-2-^{13}C (0.25 g., 0.018 moles) in ether (2 ml.) was treated with bromine (0.29 g.) (72). When the addition of bromine was completed, the decolorized solution was poured into ice water, the ether layer was extracted with water and sodium carbonate solution (5%), dried and evaporated to a dark brown residue which was sublimed and crystallized from benzene-petroleum ether to give a colorless halogen free 2-naphthol-2-^{13}C (120 mg.), m.p. 115-117°.

2-Naphthol-2-^{13}C (50 mg.) was mixed (73) with potas-

sium hydroxide (17 mg.) and heated to 200° to remove all the water which formed. Bromobenzene (0.04 g.) and copper powder (0.001 g.) were added and the mixture was heated to 240° for 2.5 hours. The mixture was then sublimed to yield 2-phenoxynaphthalene-2-^{13}C (20 mg.), m.p. 42-43°. The mass spectrum is shown in Table 9.

Preparation of 1-deuterio-2-phenoxynaphthalene (XLII)

2-Naphthol-1-d was prepared by the method of Koller and Zollinger (74). 2-Naphthol (0.25 g.) and deuterium oxide (20 ml.) were sealed in a glass tube and heated at 60-70° for four days. After cooling, the solid was collected by filtration and purified by sublimation to give 2-naphthol-1-d. 1-Deuterio-2-phenoxynaphthalene was prepared by the reaction of 2-naphthol-1-d and bromobenzene as described above, m.p. 42-43°. The mass spectrum is shown in Table 9.

Irradiation of 2-Phenoxy-4,5-benztropone and Related Compounds

Irradiation of 2-phenoxy-4,5-benztropone (XXV)

A. 2-Phenoxy-4,5-benztropone (3 g.) in freshly distilled tetrahydrofuran (250 ml.) in a Pyrex vessel was flushed with nitrogen for 40 min. and irradiated with a Type A Hanovia immersion arc lamp (550 w.) in a Pyrex well. After

12 hours, the ultraviolet spectrum showed that the absorbance at 274 mμ was 45% of its original value. The solvent was removed to give a brown resin which was dissolved in small amount of benzene and poured into a column packed with 120 g. alumina (80-200 mesh). Elution of the column with 2:3 Skelly B-benzene gave Dimer A (300 mg.), after recrystallization from alcohol-chloroform, m.p. 194-195°. Elemental analysis was reported by Pasto (38). Elution with benzene gave Dimer B (500 mg.) as white crystals after recrystallization from benzene, m.p. 217-218°. Elemental analysis was reported in Pasto's thesis (38).

B. 2-Phenoxy-4,5-benztropone (3 g.), tetrahydrofuran (250 ml.) in a Pyrex vessel was irradiated for 17 hours. The ultraviolet spectrum showed that the absorbance at 274 mμ was 20% of its original value. The tetrahydrofuran was removed. The residue was dissolved in benzene (5 ml.) and poured into a column packed with chromatography grade alumina (120 g.). Elution of the column with 2:3 Skelly B-benzene gave Dimer B (450 mg.),m.p. 214-215.5°. Elution with benzene gave Dimer C (60 mg.), m.p. 243-245°. Elemental analysis was reported by Smith (39).

Irradiation of Dimer B

Dimer B (0.5 g.) in isopropyl alcohol (1900 ml.) was purged with nitrogen for 20 min. and irradiated with a

Type A Hanovia immersion arc lamp (550-watt) in a Pyrex well for 15 hours. The solution turned pale yellow. The solvent was evaporated leaving a brown resin which was dissolved in warm methanol. After cooling, crystals formed. The crystals were recrystallized from chloroform-Skelly B to give Dimer C (30 mg.), m.p. 245-247°.

Irradiation of 2-phenoxy-4,5-benztropone-3,6-d_2 (XXX)

A solution of XXX (2.5 g.) in tetrahydrofuran (200 ml.) (freshly distilled over lithium aluminum hydride) was placed in a Pyrex immersion irradiation apparatus, flushed with nitrogen for 40 min., and irradiated with a Type A Hanovia immersion arc lamp in a Pyrex well. The solution was stirred with a magnetic stirrer and cooled with tap water running through the well. After 14 hours, the ultraviolet spectrum showed that the absorbance of the peak at 274 mμ was 20% of its original value. The solvent was removed under reduced pressure on a rotary evaporator to give a brown resin which was dissolved in benzene (5 ml.) and poured into a column prepared with chromatography grade alumina (Chicago Apparatus Co., 80-200 mesh) (100 g.). Elution with 3:2 benzene-Skelly B gave Dimer B-1,?,5,10-d_4. Recrystallization from benzene gave 350 mg. of colorless crystals, m.p. 217-218°. The yield was 17%. Elution with benzene yielded Dimer C-1,?,5,10-d_4 (50 mg.) as colorless crystals after recrystallization from ethanol-

chloroform, m.p. 245-246°.

Thermal rearrangement of Dimer B-1,2,5,10-d_4 to Dimer A-1,2,5,8-d_4

Dimer B-1,2,5,10-d_4 (160 mg.) was placed in a small Erlenmeyer flask. The flask was immersed in a oil bath which had previously been heated to 210-220°. A slow stream of nitrogen was blown into the flask. After about 3 min. the Dimer B-1,2,5,10-d_4 had melted, the heating was continued for an additional 2 min. The flask was allowed to cool, and the material was dissolved in 1:3 benzene-Skelly B and eluted through a column prepared with alumina (10 g.). Elution with benzene gave colorless Dimer A-1,2,5,8-d_4 (95 mg., 53%), after recrystallization from ethanol-chloroform, m.p. 193-194.5°.

Irradiation of 2-phenoxy-4,5-benztropone-7-d (XXXI)

A solution of 2-phenoxy-4,5-benztropone-7-d (2 g.) in freshly distilled tetrahydrofuran (200 ml.) was irradiated with a Hanovia Type A arc lamp (550-watt) in a Pyrex immersion well. After 14 hours, the absorbance of the solution at 274 mμ was 21% of its original value. The solvent was evaporated and the residue was chromatographed on a column prepared with alumina (100 g.). Elution with ether-benzene gave Dimer B-6,9-d_2 (300 mg.) m.p. 215-216°. The infrared and nuclear magnetic resonance spectra are shown in Figure 19, page 68 and

Figure 29, page 88. Elution with ether-chloroform gave Dimer C-6,9-d_2 (5 mg.) m.p. 243-245° after recrystallization from ethanol-chloroform. The infrared and nuclear magnetic resonance spectra are shown in Figure 23, page 76 and Figure 40, page 110 respectively.

Thermal rearrangement of Dimer B-6,9-d_2 to Dimer A-6,9-d_2

Dimer B-6,9-d_2 (300 mg.) was converted to Dimer A-6,9-d_2 (50 mg.), m.p. 194-195°, by the same method used to convert Dimer B-1,2,5,10-d_4 to Dimer A-1,2,5,8-d_4. The infrared of Dimer A-6,9-d_2 is shown in Figure 16, page 62. The nuclear magnetic resonance spectrum is shown in Figure 33, page 94.

Irradiation of 2-(2,4,6-trideuteriophenoxy)-4,5-benztropone (XXXII)

2-(2,4,6-Trideuteriophenoxy)-4,5-benztropone (2.5 g.) in dry tetrahydrofuran (250 ml.) was irradiated for 14 hours. The solvent was removed giving a brown resin which was dissolved in benzene and passed through an alumina column by elution with benzene giving o,p-trideuteriophenoxy-Dimer B (XLVII) (300 mg.), m.p. 216-217°. The nuclear magnetic resonance spectrum (Figure 29, page 88) is similiar to Dimer B. Elution with 9:1 ether-chloroform gave o,p-trideuteriophenoxy-Dimer C (50 mg.), m.p. 243.5-245°. The nuclear magnetic resonance spectrum (Figure 40, page 110) shows two singlet peaks in the

aromatic region. The infrared spectrum is shown in Figure 24, page 78.

Irradiation of 2-phenoxy-4,5-benztropone-carbonyl-^{18}O (XXXIII)

2-Phenoxy-4,5-benztropone-carbonyl-^{18}O (90 mg.) was dissolved in dry tetrahydrofuran (5 ml.) and placed in a small Pyrex irradiation tube, flushed with nitrogen for 20 min. and irradiated with an external Hanovia Type A arc lamp for 16 hours. The tetrahydrofuran was removed with a rotary evaporator. Benzene (3 ml.) was added and then evaporated. The residue was dissolved in hot benzene, after standing at room temperature for an hour Dimer B-ether-^{18}O crystallized. Filtration and recrystallization from benzene gave white crystals of Dimer B-ether-^{18}O (20 mg.), m.p. 217-218°.

Irradiation of 2-phenoxy-4,5-benztropone-ether-^{18}O (XXXIV)

2-Phenoxy-4,5-benztropone-ether-^{18}O (200 mg.) in dry tetrahydrofuran (10 ml.) was irradiated in the same manner as above to give Dimer B-carbonyl-^{18}O (40 mg.), m.p. 217-218°. The infrared spectrum of Dimer B-carbonyl-^{18}O (LXXIV) (Figure 20, page 70) shows two carbonyl absorption at 1690 and 1737 cm^{-1} ($C^{18}{=}O$).

Irradiation of 2-phenoxy-4,5-benztropone-1-^{13}C (XXXV)

2-Phenoxy-4,5-benztropone-1-^{13}C (75 mg.) in dry

tetrahydrofuran (7 ml.) irradiated in the usual manner gave Dimer B-7,8-^{13}C (8 mg.), m.p. 217-218°. The infrared and nuclear magnetic resonance spectra are shown in Figure 20, page 70 and Figure 30, page 90 respectively.

Attempted irradiation of 2-(N-methylanilino)-4,5-benztropone (XXXVII)

2-(N-Methylanilino)-4,5-benztropone (0.51 g.) was dissolved in freshly distilled tetrahydrofuran (250 ml.) and flushed with nitrogen for 30 min. The solution was irradiated with a Hanovia Type A immersion lamp in a Pyrex well. After 10 hours the ultraviolet spectrum showed that the absorbance of the peak at 272 mμ was 40% of its original value. Only starting material and tars were obtained by eluting the mixture through an alumina column.

Attempted irradiation of 2-methoxy-4,5-benztropone (XXXVIII)

2-Methoxy-4,5-benztropone (2 g.) in dry tetrahydrofuran (200 ml.) was flushed with nitrogen for 40 min. and irradiated for 18 hours. A brown precipitate, m.p. >280° was formed. The precipitate might be a polymer. Only starting material and tars were obtained from the solution by chromatography through alumina column.

Similar results were obtained by irradiation for 14 hours in 1:1 methanol and water.

Photosensitization by 2-phenoxy-4,5-benztropone

Piperylene (68 mg. trans/cis = 1.83) and 2-phenoxy-4,5-benztropone (125 mg.) in benzene (5 ml.) was flushed with nitrogen for 30 minutes and irradiated with an external Hanovia lamp for 5 hours. The mixtures were analyzed by vapor phase chromatography (a 6 ft. column packed with 25% saturated silver nitrate in ethylene glycol on fire brick (30-60 mesh) connecting with 6 ft. column packed with 25% β,β'-oxydipropionitrile on fire brick were used) (45). The ratio of trans/cis was 1.83 and no appreciate change was observed.

cis-Piperylene (41 mg.) which was isolated from the technical piperylene by the method of Frank (75), and 2-phenoxy-4,5-benztropone (75 mg.) in benzene (3 ml.) were placed in a Pyrex tube and degassed. The mixture was irradiated by an external lamp for 10 hours, and was analyzed by vapor phese chromatography (using the same column as above). The ratio of cis/trans was changed to 10.

trans-Stilbene (27 mg.), 2-phenoxy-4,5-benztropone (36.9 mg.) and benzene (3 ml.) were placed in a small Pyrex tube. The mixture was degassed and irradiated through a filter solution, prepared by $CuSO_4 \cdot 5\ H_2O$ (10 g.) and conc. ammonia (18 ml.) diluting to 250 ml. with water, in which 10% of light at 366 mμ are transmitted. The irradiation was carried out for 3 hours. The mixture was analyzed by vapor phase chromatography (3.5 ft. by $\frac{1}{4}$ inch column packed with

20% apiezon N in 30-60 mesh fire brick at 200°). The ratio of cis/trans was 5. Irradiation of trans-stilbene without 2-phenoxy-4,5-benztropone under the same conditions for same time gave only trans-stilbene.

Attempted preparation of Dimer B-carbonyl-^{18}O by exchange with $H_2{}^{18}O$

Dimer B (100 mg.), $H_2{}^{18}O$ (80% enriched 0.2 ml.), dry tetrahydrofuran (1 ml.)and 0.01 N hydrochloric acid (0.01 ml.) were sealed in a glass tube and heated on a steam bath for five days. The solvent was removed to give Dimer B which contained no ^{18}O (shown by mass spectrum).

Attempted preparation of Dimer A-carbonyl-^{18}O by exchange with $H_2{}^{18}O$

Dimer A was exchanged with $H_2{}^{18}O$ in tetrahydrofuran in the presence of acid. Mass spectrum showed the isolated Dimer A had no ^{18}O incorporation.

Preparation of Dimer A diol (XLIX)

Dimer A (500 mg.) was dissolved in tetrahydrofuran (15 ml.) and a solution of sodium borohydride (500 mg.) in 5 ml. of water was added. The solution was stirred at room temperature for 20 hours. Water (10 ml.) was added, and the solution was stirred for another hour. The tetrahydrofuran

was removed, and Dimer A diol was collected and recrystallized from aqueous methanol, m.p. 160-163°. The elemental analysis was reported by Smith (39). The infrared and nuclear magnetic resonance spectra are shown in Figure 17, page 64 and Figure 33, page 96 respectively.

Preparation of Dimer A diol-11,14-d_2 (LVII)

Dimer A (120 mg.) was dissolved in tetrahydrofuran (8 ml.). Sodium borodeuteride (120 mg.) and water (1 ml.) were added, and the solution was stirred. After 20 hours water (8 ml.) was added to the mixture, and the solution stirred for another hour. The tetrahydrofuran was removed giving Dimer A diol-11,14-d_2(90 mg.), m.p. 161-163°. The nuclear magnetic resonance spectrum (Figure 35, page 100) shows the peaks at 4.90 and 5.33 τ are absent. The infrared spectrum is shown in Figure 17, page 64.

Preparation of Dimer A diol-6,9-d_2 (LVIII)

Dimer A-6,9-d_2 was reduced by sodium borohydride as the usual manner to give Dimer A diol-6,9-d_2, m.p. 159-162°. The infrared and nuclear magnetic resonance spectra are shown in Figure 17, page 64 and Figure 36, page 102.

Preparation of Dimer A alcohol ether (L)

Dimer A diol (100 mg.) was dissolved in hot 95%

ethanol. Hot concentrated hydrochloric acid (0.4 ml.) was added slowly. After cooling the solid was collected and crystallized from alcohol giving Dimer A alcohol ether (80 mg.), m.p. 215-220°. Elemental analysis was reported by Smith (39). The infrared and nuclear magnetic resonance spectra are shown in Figure 18, page 66 and Figure 37, page 104.

Preparation of Dimer A alcohol ether-11,14-d_2 (LIX)

Treatment of the Dimer A diol-11,14-d_2 with hydrochloric acid by the above procedure gave Dimer A alcohol ether-11,14-d_2, m.p. 216-220°. The nuclear magnetic resonance spectrum (Figure 38, page 106) shows two peaks at 4.90 and 6.06 τ are absent. The infrared spectrum is shown in Figure 18, page 66.

Preparation of Dimer A alcohol ether-6.9a-d_2 (LX)

Dimer A diol-6,9-d_2 was treated with hydrochloric acid to give the corresponding Dimer A alcohol ether-6,9a-d_2, m.p. 215-219°. The nuclear magnetic resonance spectrum shows the doublet peaks at 4.07 and 8.19 τ are changed to singlet (Figure 38, page 106). The infrared spectrum of Dimer A alcohol ether 6,9a,0-d_3 is shown in Figure 18, page 66.

Preparation of Dimer B diol (LXI)

Dimer B (80 mg.) and sodium borohydride (80 mg.) were refluxed in pure tetrahydrofuran (10 ml.) with stirring for 24 hours. Water (1 ml.) was added to remove the turbidity. After stirring 3 hours, water (10 ml.) was then added and stirred for another hour. After cooling the solvent was removed and extracted with four 8 ml. portions benzene. The organic layer was dried over anhydrous magnesium sulfate and evaporated to give colorless solid. Recrystallization from benzene-Skelly B gave Dimer B diol (55 mg.), m.p. 257-258°. The infrared spectrum (Figure 21, page 72) shows no carbonyl absorption. The nuclear magnetic resonance spectrum is shown in Figure 30, page 90. Elemental analysis was reported by Pasto (38).

Preparation of Dimer B diol-13,14-d_2 (LXII)

Dimer B (100 mg.) and sodium borodeuteride (100 mg.) were refluxed in tetrahydrofuran (10 ml.) with stirring for 20 hours. Water (1 ml.) was added. After stirring for 3 hours, 10 ml. of water was added, and the solution was stirred for another hour. The tetrahydrofuran was removed and the residue was extracted with benzene. The extract was dried and evaporated to give Dimer B diol-13,14-d_2 (55 mg.), m.p. 257-258° after recrystallization from benzene-Skelly B. The nuclear magnetic resonance spectrum (Figure 35, page 100)

shows multiplets for the aromatic protons at 2.80 τ, styryl AB protons at 3.55 and 3.90 τ, singlet bridgehead proton at 6.12 τ and singlet alcohol protons at 7.00 τ.

Preparation of Dimer B diol diacetate (LXIII)

Dimer B diol (55 mg.) in 1:1 benzene-acetyl chloride (8 ml.) was refluxed for 2 hours, cooled, poured into ice(5 g.) and extracted with four 5 ml. portions benzene. The organic layer was washed with 5% sodium carbonate and water, dried with anhydrous magnesium sulfate, and evaporated. The residue was crystallized from Skelly B-cyclohexane to give Dimer B diol diacetate (30 mg.), m.p. 235-236°. The infrared spectrum (Figure 22, page 74) shows a strong ester absorption at 5.75 μ. The nuclear magnetic resonance spectrum is shown in Figure 31, page 92. Elemental analysis was reported by Pasto (38).

Preparation of Dimer B diol diacetate-13,14-d_2 (LXIV)

Dimer B diol-13,14-d_2 (50 mg.) when acetylated by acetyl chloride gave Dimer B diol diacetate-13,14-d_2 (30 mg.), m.p. 235-236°, after recrystallization from cyclohexane. The infrared and nuclear magnetic resonance spectra are shown in Figure 22, page 74 and Figure 35, page 100.

Preparation of Dimer B diol-^{18}O-diacetate (LXXXIX)

Dimer B carbonyl-^{18}O (15 mg.) was reduced by sodium

borohydride to give Dimer B diol-^{18}O (10 mg.), m.p. 255-257° which was acetylated by acetyl chloride to Dimer B diol-^{18}O diacetate (3 mg.), m.p. 234-235° after recrystallization from cyclohexane-Skelly B. The mass spectrum is shown in Table 14.

Preparation of Dimer B diol diacetate ether-^{18}O (XC)

Dimer B ether ^{18}O (15 mg.) was reduced to Dimer B diol ether-^{18}O and acetylated as usual manner to give Dimer B diol diacetate ether-^{18}O (2 mg.), recrystallization from Skelly B, m.p. 234-235.5°. The mass spectrum is shown in Table 14.

Preparation of Dimer B diol diacetate-d_6 (XCI)

Dimer B diol (20 mg.) was acetylated by trideuterio-acetyl chloride by the method described for unlabelled compound to give Dimer B diol diacetate-d_6 (10 mg.), m.p. 235-236°. The infrared spectrum is shown in Figure 22, page 74. The mass spectrum is shown in Table 14, page 141.

Preparation of o,p-trideuteriophenoxy Dimer B diol diacetate (XCII)

o,p-trideuteriophenoxy Dimer B was reduced to the diol which was then acetylated to o,p-trideuteriophenoxy Dimer B diol diacetate, m.p. 234-235°. The infrared spectrum is shown in Figure 24, page 78.

Preparation of Dimer C diol (LXV)

Dimer C (25 mg,) was dissolved in tetrahydrofuran (2 ml.). To the solution was added sodium borohydride (50 mg.) dissolved in water (1 ml.). The mixture was stirred at room temperature for 12 hours. Water (5 ml.) was added and stirred for another 2 hours. The tetrahydrofuran was removed on a rotary evaporator. The aqueous mixture was extracted with chloroform. The extract was evaporated to give a resinous solid. Recrystallization from benzene-Skelly B gave white crystals of Dimer C diol (15 mg.), m.p. 224-225° for analysis. The infrared spectrum shows hydroxyl absorption at 2.8 μ (Figure 24, page 78). The nuclear magnetic resonance spectrum is shown in Figure 41, page 112.

Anal. Calcd. for $C_{34}H_{28}O_4$: C, 81.6; H, 5.6. Found: C, 81.68; H, 5.64.

SUMMARY

Irradiation of 2-phenoxy-4,5-benztropone in tetrahydrofuran solution gives dimeric products, Dimers A, B and C. Two deuterium labelled compounds, 2-phenoxy-4,5-benztropone-3,6-d_2 and 2-phenoxy-4,5-benztropone-7-d, were prepared and irradiated. The nuclear magnetic resonance spectra of the resulting dimers show that carbon skeleton rearrangement does not occur. The dimers appear to be derived formally from a rearranged intermediate in which the phenoxy and carbonyl groups are exchanged in position. Since attempts to trap the intermediate with dienophiles were unsuccessful, both ^{18}O-labelled (carbonyl or ether) and 1-^{13}C-labelled 2-phenoxy-4,5-benztropones were prepared and irradiated to provide evidence of the phenyl migration in the dimerization process. It was found the phenyl group does migrate during the photochemical dimerization. A mechanism for the photodimerization was proposed.

The mass spectra of 2-phenoxy-4,5-benztropone and its labelled derivatives were studied. Two particularly novel fragmentations have been observed (1) loss of OH and (2) loss of CO which involve in both cases the carbonyl oxygen and the ether oxygen. These processes are correlated by demonstration of a 1,4-phenyl migration from one oxygen to the other. A corresponding phenyl migration has been shown to occur from

a sulfur to an oxygen atom, but not from nitrogen to oxygen, in the analogous compounds. Similar 1,4 shift of a methyl group either does not occur or is a very minor process. Loss of carbon monoxide from 2-phenoxy-4,5-benztropone gives the 2-phenoxynaphthalene radical cation. Further fragmentation of this radical cation to the 2-naphthol radical cation and benzyne, to phenyl cation, and to hydrocarbon cation and carbon monoxide is documented by the labelled materials. The mass spectrum of Dimer B is similar to that of the monomer except it shows a parent peak at m/e 496. The mass spectra of Dimer B diol diacetate and its labelled derivatives were also studied.

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