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Photochemical studies on 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone

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PHOTOCHEMICAL STUDIES ON 4a-METHYL-4,4a,9,10-TETRAHYDRO-2(3H)-PHENANTHRONE

by

James Bernard Sieja

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

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1965

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VITA

The author was born in Bay City, Michigan on June 30, 1939 to Mr. and Mrs. B. J. Sieja. He attended T. L. Handy High School and was graduated in June, 1957. In September of 1957 he enrolled at Bay City Junior College and was graduated with his Associate in Science degree in June, 1959. In September of 1959 he enrolled at the University of Michigan and was graduated with his Bachelor of Science degree in June, 1961. During the summers of 1960 and 1961 the author was an employee of the Dow Chemical Company at Midland, Michigan.

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INTRODUCTION

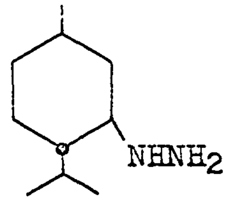
When a certain body of knowledge concerning a segment of chemistry has been collected, attempts to explain and correlate this knowledge through mechanistic reasoning, soon come to the fore. Such is the time for the segment of the field of solution photochemistry concerning the rearrangements of unsaturated ketones. Although many rearrangements have been recorded in the literature, only one attempt has been made to set forth a detailed scheme by which these rearrangements take place (1, 2). This scheme must be corrected and refined whenever possible so that the end result will be closer to the truth. This work attempts to supply data which will hopefully facilitate this refinement.

HISTORICAL

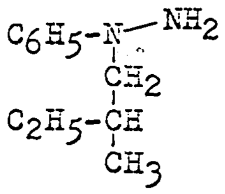
Resolution of Racemic Carbonyl Compounds

The methods for resolution of racemic ketones and aldehydes using optically active reagents which react directly with the carbonyl function to produce diastereomeric compounds, from which the ketone or aldehyde can later be regenerated in a one-step process, are indeed limited in scope. An attempt has been made to review the more widely used methods which utilize these reagents.

In 1903 Neuberg (3) resolved racemic arabinose using *l*-menthylhydrazine (I) as the resolving reagent, and shortly thereafter, Neuberg and Federer (4) resolved racemic galactose using *as*-phenyl-*d*-amylhydrazine (II). Although many more optically active hydrazines have been prepared, none has been used successfully for the resolution of carbonyl compounds (5).



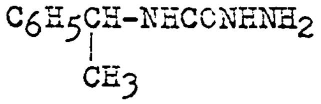
I



$C_6H_5-N(NH_2)-CH_2-CH(C_2H_5)-CH_3$

II

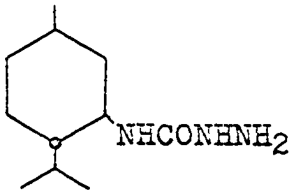
Because of their apparent ability to produce more crystalline derivatives, optically active semicarbazides have been of somewhat greater utility. Hopper and Wilson (6) obtained both *d*- and *l*-benzoin by utilizing both *d*- and *l*-δ-(α-phenethyl)semicarbazide (III).



$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}NHCONHNH_2$$

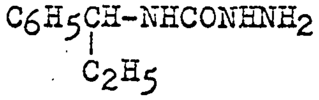
III

Benzoin has also been resolved by Crawford and Wilson (7) with *l*-δ-menthylsemicarbazide (IV). However, the deposition of the *l*-benzoin semicarbazone from the gummy reaction mixture required years for completion. Although successful, this resolution can hardly be called practical.



IV

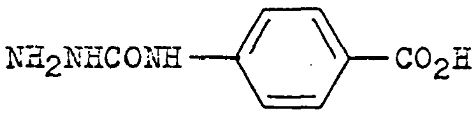
Again in 1940, benzoin was resolved by Little *et al.* (8) who used both *d*- and *l*-δ-(α-phenylpropyl)semicarbazides (V) prepared by the reaction of acetone semicarbazone with both *d*- and *l*-α-phenylpropyl amines. Their attempted resolution of camphor and 3-methylcyclohexanone, however, failed because of the non-crystallinity of the corresponding semicarbazones.



$$C_6H_5\underset{\displaystyle C_2H_5}{\underset{|}{C}}H\text{-}NHCONHNH_2$$

V

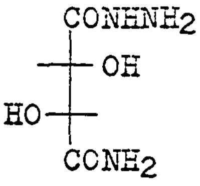
In 1958 a new and more versatile carbonyl reagent was introduced by Shillington *et al.* (9). 4-(4-Carboxyphenyl)-semicarbazide (VI) gave a crystalline semicarbazone with



VI

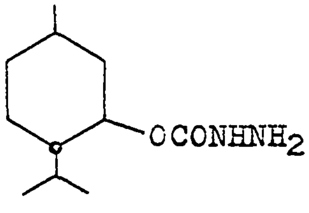
3-methylcyclohexanone and resolution of the derivative was effected by means of the *l*-brucine salt. With this reagent, any of several naturally occurring optically active bases may be used as the resolving agent.

The resolution of 2,6-dimethyl-8-octanal was carried out in 1952 by Nerdel and Henkel (10) using *d*-tartramide acid hydrazide (VII). Although no ketones were resolved by these authors, *d*-tartramazones of several ketones were prepared. Also using VII, Mislow and Hamermesh (11) resolved 2-phenylcyclopentanone.



VII

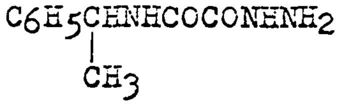
In 1941 Woodward *et al.* (5) succeeded in resolving camphor by using *l*-menthyl-N-aminocarbamate (VIII), which is a highly crystalline material. These authors prepared crystal-



VIII

line derivatives of several carbonyl compounds, but only one besides camphor is potentially optically active. Also using VIII, Sobotka *et al*. (12) resolved α-ionone, but only with difficulty. This was due to the relatively slight differences in solubility of the diastereomeric derivatives. This reagent was also used by Adams *et al*. (13) to resolve 3-methylcyclohexanone.

In 1950 Leonard and Boyer (14) introduced a new carbonyl reagent, *l*-5-(α-phenylethyl)semioxamazide (IX), utilizing

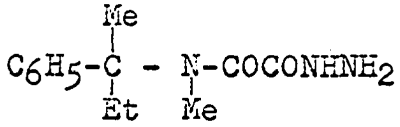


$$C_6H_5\underset{\displaystyle CH_3}{CH}NHCOCONHNH_2$$

IX

optically active α-phenylethylamine as the starting material for its preparation. 3-Methylcyclohexanone was successfully resolved with the reagent. The authors indicated that facile hydrolysis of the derivatives of this reagent is one of its advantages, but cleaved the 3-methylcyclohexanone derivative by boiling for a few minutes with excess 20% sulfuric acid.

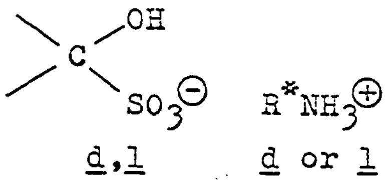
Kotake and Nakaminami (15) used *l*-5-methyl-5-(α-methylphenylethyl)semioxamazide (X) to resolve flavan-4-one.



$$C_6H_5-\overset{\displaystyle Me}{\underset{\displaystyle Et}{C}}-\underset{\displaystyle Me}{N}-COCONHNH_2$$

X

Adams and Garber (16) successfully resolved 3-methylcyclohexanone and β-methylhydrocinnamaldehyde by means of an optically active amine bisulfite addition product (XI). This



XI

method suffers from the introduction of a new optical center on formation of the addition compound.

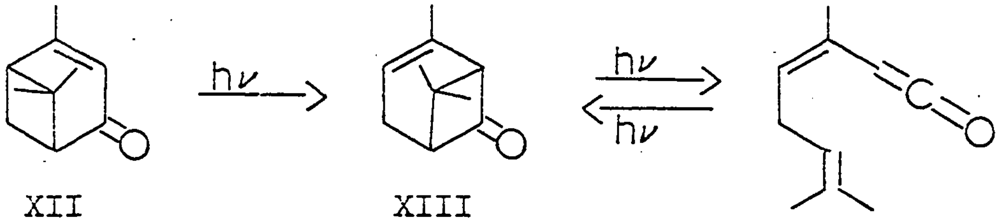
Casanova and Corey (17) have resolved camphor by means of its D(*l*)-2,3-butanediolketal. Gas-liquid phase chromatography was used to separate the diastereomeric ketals, but this method limits the workable scale considerably and necessitates an empirical search for a suitable liquid phase which will effect the separation. Also, only relatively volatile materials can be used.

Corey and Mitra (18) have prepared L(*d*)-2,3-butanedithiol and have successfully resolved flavan-4-one and logifolene by means of their optically active thioketals. The diastereomeric thioketals of flavan-4-one were separated by recrystallization and those of longifolene by gas-liquid phase chromatography.

Photochemistry of 2-Cyclohexenones

Although the number of photochemical rearrangements involving 2-cyclohexenones is limited, their importance in the study of photochemical mechanisms is quickly being realized.

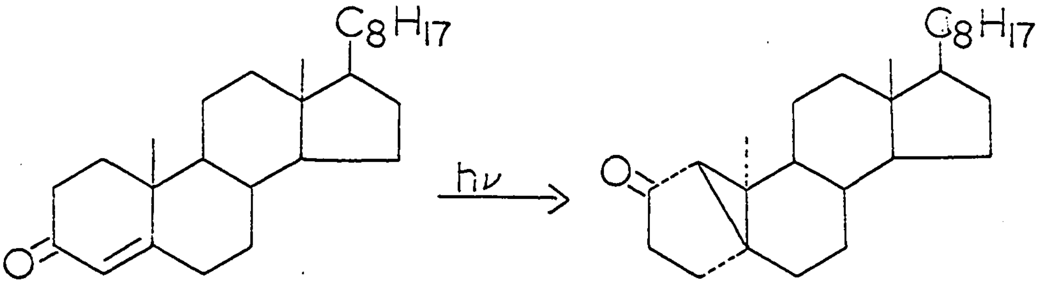
Irradiation of verbenone (XII) in refluxing cyclohexane gave chrysanthenone (XIII) in good yield (19, 20). Optically active XII gave XIII with an optical purity lower than that



XII XIII XIV

of the starting material. The optical purity of XIII decreased with longer irradiation times because of the photoequilibrium between XIII and XIV.

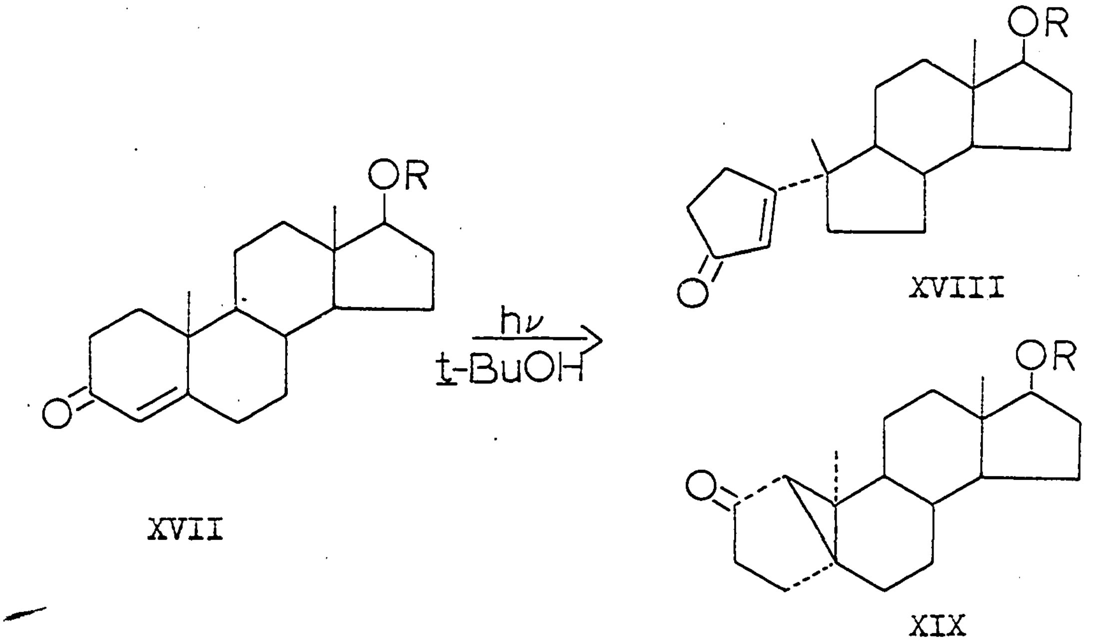
Kwie et al. (21) found that irradiation of Δ^4-cholesten-3-one (XV) in t-butanol gave the cyclopropyl ketone XVI. The



XV XVI

authors state that because the reaction is stereospecific it is almost certainly concerted and suggest a polar excited state for the reaction.

Analogously, Chapman et al. (22) found that irradiation of testosterone acetate (XVII, R=Ac) also gave stereospecific products (XVIII and XIX). This reaction did not proceed



XVII

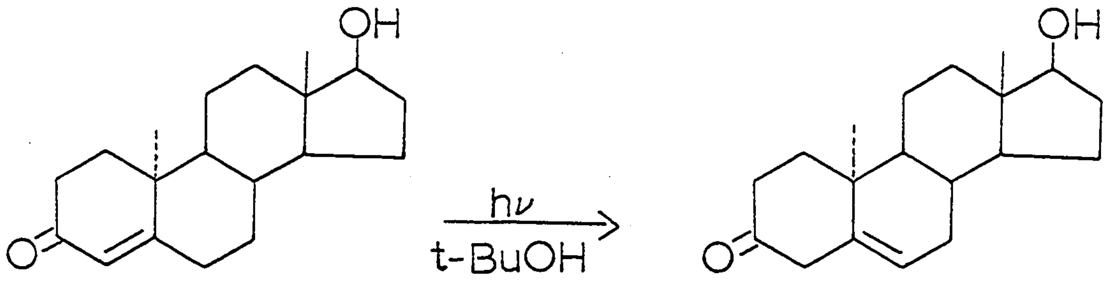
XVIII

XIX

smoothly in aprotic media and therefore proton donation at some stage of the rearrangement was suggested.

Independently, Jeger <u>et</u> <u>al</u>. (23, 24) found that testosterone itself (XVII, R=H) gave the analogous products (XVIII and XIX). He further states that there exists an equilibrium between XVII and XIX, and that XVIII is not derived directly from XIX.

In sharp contrast is the photochemical rearrangement of 10α-methyltestosterone (XX) to give XXI (25). In this system,

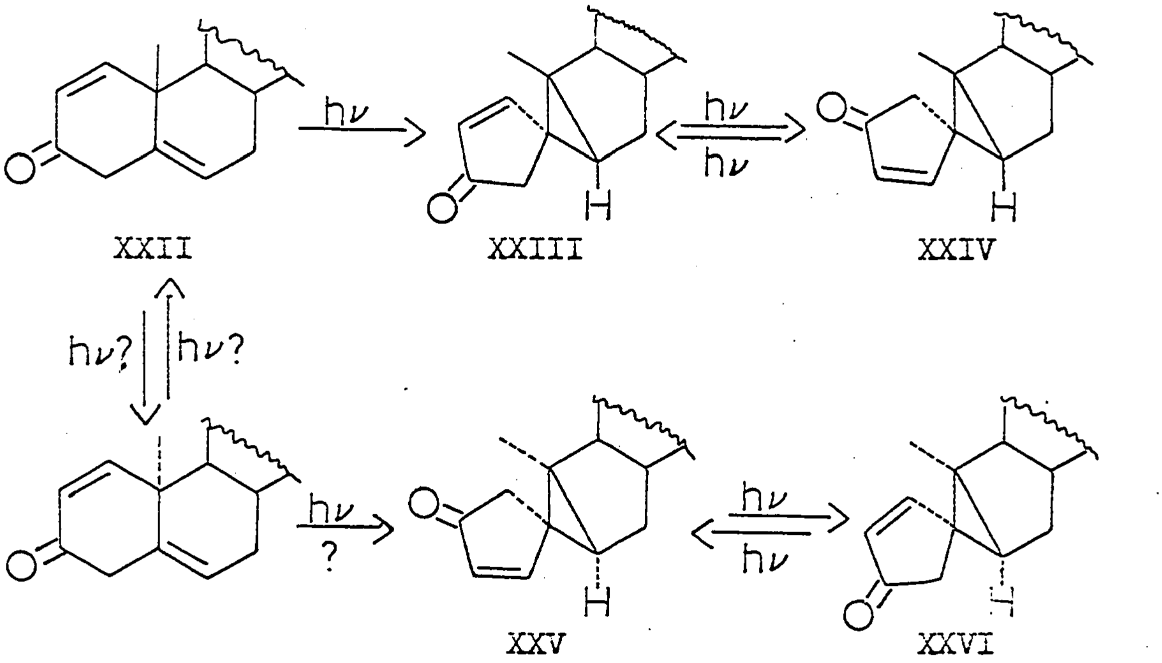


XX

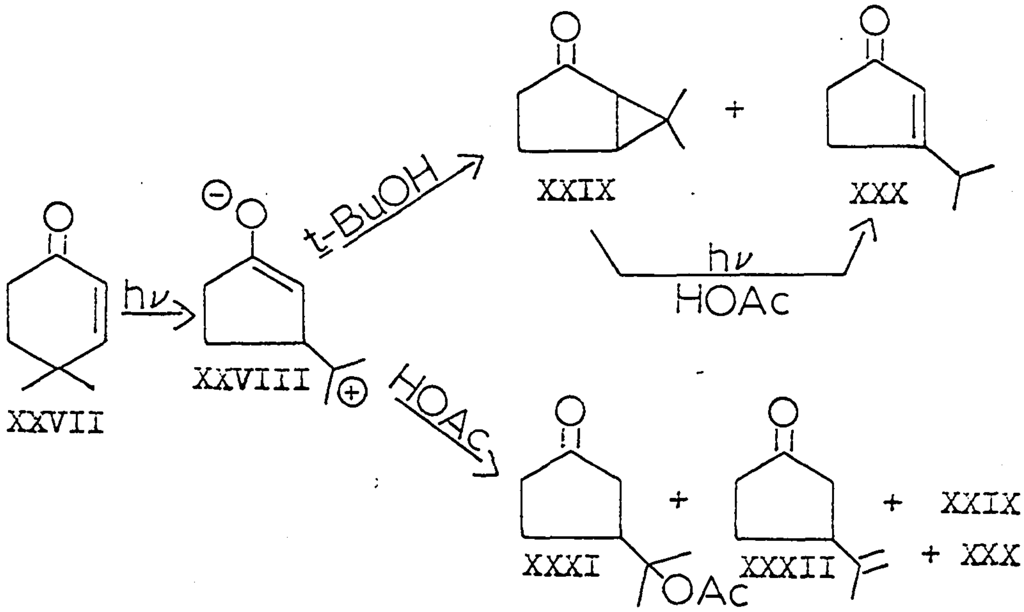
XXI

a seemingly subtle change in stereochemistry opened a completely different photochemical pathway.

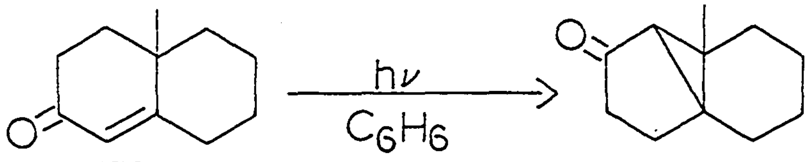
3-Oxo-17β-acetoxy-$\Delta^{1,5}$-androstadiene (XXII, 23, 24) has been shown to give four products (XXIII, XXIV, XXV, XXVI). The interconversion of epimeric pairs XXIII and XXIV, and XXV and XXVI has been shown to occur. However, the interconversion between these pairs is still a matter of speculation.



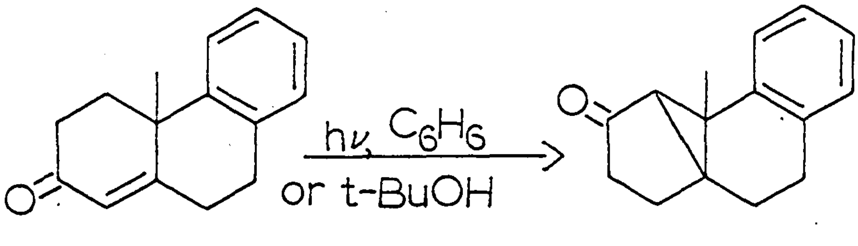
An equally interesting and somewhat simpler system was investigated by Chapman <u>et</u> <u>al</u>. (22). Irradiation of 4,4-dimethyl-2-cyclohexenone (XXVII) in <u>t</u>-butanol gave two products (XXIX and XXX), while irradiation in acetic acid gave two additional products (XXXI and XXXII). A dipolar excited state (XXVIII) was used to explain the products.



Zimmerman has found (26) that irradiation of 10-methyl-$\Delta^{1,9}$-octalone-2 (XXXIII) and 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) gave rise to bicyclic ketones XXXVI and XXXV, respectively, which are analogous to XXIX, obtained from 4,4-dimethyl-2-cyclohexenone (XXVII). These



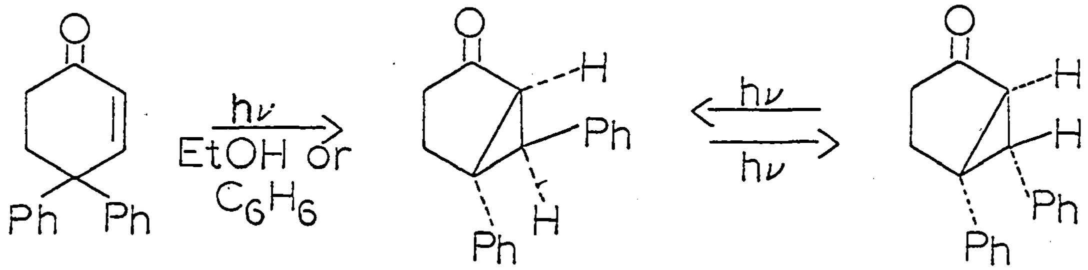
XXXIII XXXVI



XXXIV XXXV

results were referred to in a lecture presented at an International Symposium on Organic Photochemistry which was held after the work to be presented here had been well in progress.

Zimmerman and Wilson (27) carried out the irradiation of 4,4-diphenyl-2-cyclohexenone (XXXVII) and obtained two bicyclic products (XXXVIII and XXXIX) which are photochemically



XXXVII

XXXVIII

XXXIX

interconvertible. Although structurally similar to XXVII, XXXVII gave no bicyclic ketone analogous to XXIX, which requires 4,5-bond breakage rather than phenyl migration.

RESULTS AND DISCUSSION

Resolution of Racemic 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone and Racemic 4a-Methyl 1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone

Although several methods have been used for the resolution of racemic aldehydes and ketones, none has proven to be entirely satisfactory. Among the major difficulties encountered with these methods are:

a. Preparation of the optically active carbonyl reagent.

b. Lack of crystalline derivatives.

c. Production of geometrical isomers or a new optical center.

d. Stringent hydrolysis conditions used to regenerate the carbonyl compounds.

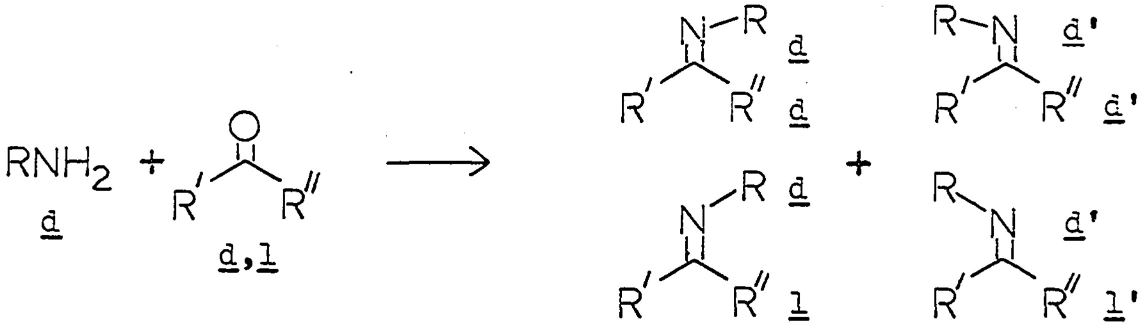
Difficulty a is present in most of the more common methods for resolution because of the lack of commercially available or naturally occurring optically active carbonyl reagents. In most cases, the preparation of the reagent is at best tedious and often is quite difficult. Once the preparation has been carried out, the reagent may be difficult to purify, and may itself be non-crystalline.

The best results in resolution procedures are obtained when crystalline derivatives of the carbonyl compound are obtainable. If oily derivatives are obtained, gas-liquid phase chromatography may, in some cases, be used to separate the diastereomers. However, separation is not assured and only relatively small quantities of compounds can be isolated in a reasonable length of time.

In discussing *c*, it is convenient to classify carbonyl reagents into two categories, (e) reagents which maintain sp^2 hybridization at the carbonyl carbon subsequent to reaction, and (f) reagents which change the hybridization at the carbonyl carbon from sp^2 to sp^3. Ideally, if we assume use of a *d* resolving reagent, its reaction with the carbonyl compound will yield two diastereomeric derivatives *d*,*d* and *d*,*l*. The separation of these two compounds is then, the basic problem

d resolving reagent + *d*,*l* carbonyl compound ⟶ *d*,*d* + *d*,*l*

involved in this method of resolution. However, where the resolving agent is of type *e* (usually a nitrogen compound), the number of product compounds is generally increased by the existence of geometrical isomers *d*',*d*' and *d*',*l*'. This usually results in less crystalline crude reaction mixtures and more difficulty in separation of the products.



Type f reagents give rise to only two product compounds (except in the case of the amine bisulfite reagents where a new optical center is produced), and the chance for successful separation of the diastereomers appears to be greater than with type e reagents.

The hydrolysis of derivatives produced by use of type e reagents is generally more difficult than that of derivatives obtained from reagents of type f. In the former case, temperatures near 100° and moderate concentrations of mineral acid are needed while in the latter case, dilute acids at room temperature may be sufficient.

In order to obtain optically active ketones for a photochemical study, a method of resolution was needed which would, in particular, allow mild conditions for the regeneration of the carbonyl component. Two ketones were to be resolved, 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (phenanthrone, XXXIV) and 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (cyclophenanthrone, XXXV). It was feared that rigorous acid hydrolysis of any derivative of XXXV would cause the three membered ring to be ruptured. After attempting the resolution of XXXIV by means of an optically active ketal and acting on the suggestion of Dr. William Breitbeil,* Dr. William Welstead obtained partial

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*This author wishes to acknowledge the original suggestion of Dr. Breitbeil.

resolution of XXXIV by means of an optically active iminium salt. This method of resolution proved to be very fruitful, first because the d-camphor-10-sulfonic acid used for the resolution is commercially available and eliminated the need to synthesize an optically active reagent, secondly, no geometric isomers or new optical centers are produced during the resolution and lastly, perhaps most importantly, very mild conditions could be used for the regeneration of the carbonyl compound. This method of resolution, very promising at this point, was used by the present author in obtaining optically pure XXXIV and XXXV.

Treatment of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV d,l, Figure 1, page 17) with pyrrolidine in methanol gave the enamine XL (m.p. 107-109°) in excellent yield. The infrared spectrum (KBr) showed double bond absorption bands at 6.09 and 6.21 μ. The ultraviolet spectrum showed $\lambda_{max}^{abs.\ EtOH}$ 284mμ (22,200).* Johnson et al. (28) report 6.12 and 6.23μ and λ_{max}^{MeOH} 277mμ (20,925) for the pyrrolidine enamine of progesterone. Support for the heteroannular diene structure comes from the work of Bowden et al. (29) who report that 1-diethylamino-1,3-butadiene shows $\lambda_{max}^{Alcohol}$ 281mμ (23,500). This compound, like butadiene itself (30), probably exists almost entirely in the transoid

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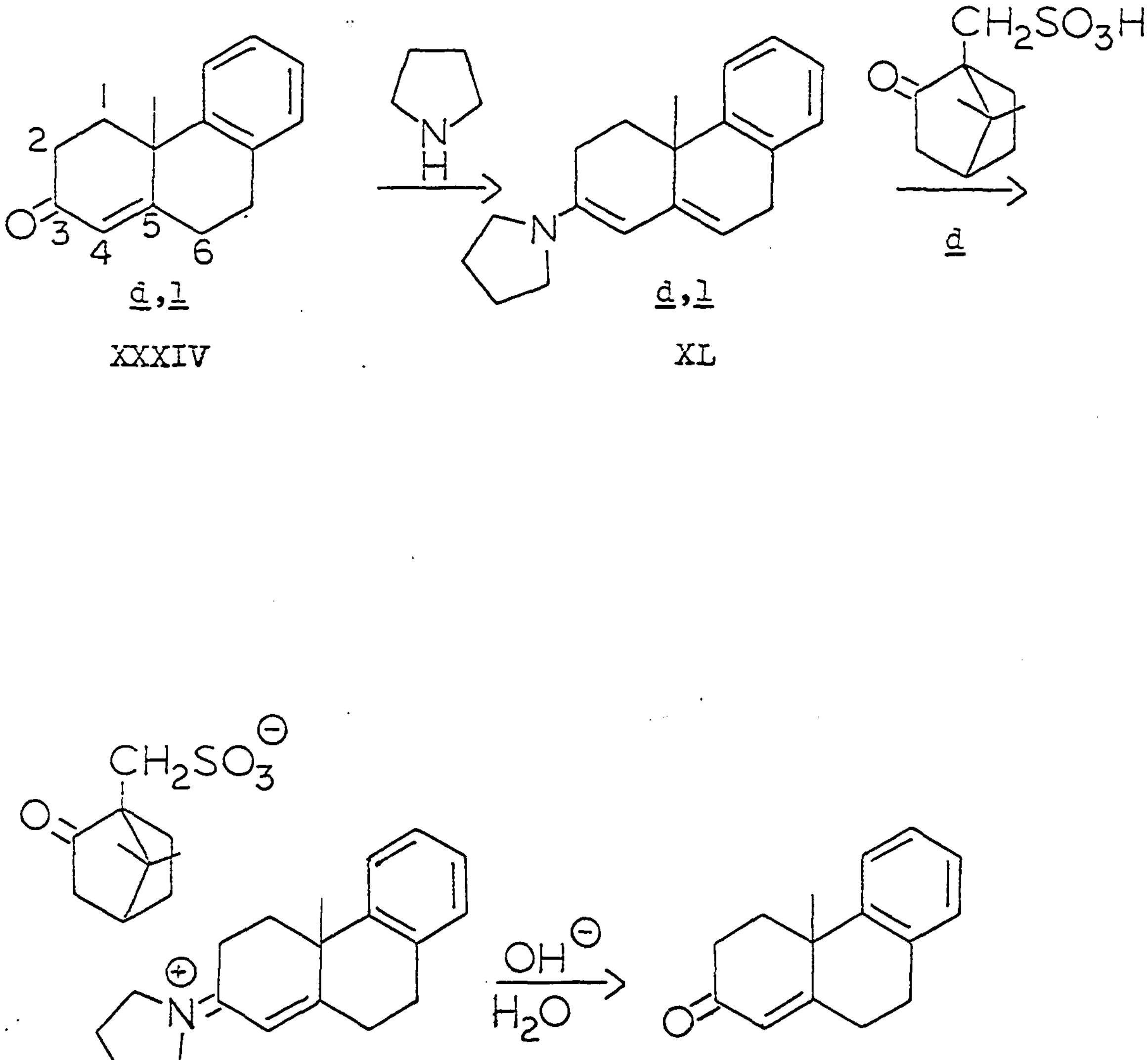
*The author is indebted to Dr. William Welstead for the spectral data.

Figure 1. Resolution of racemic phenanthrone (XXXIV d,l)



d,l
XXXIV

d,l
XL

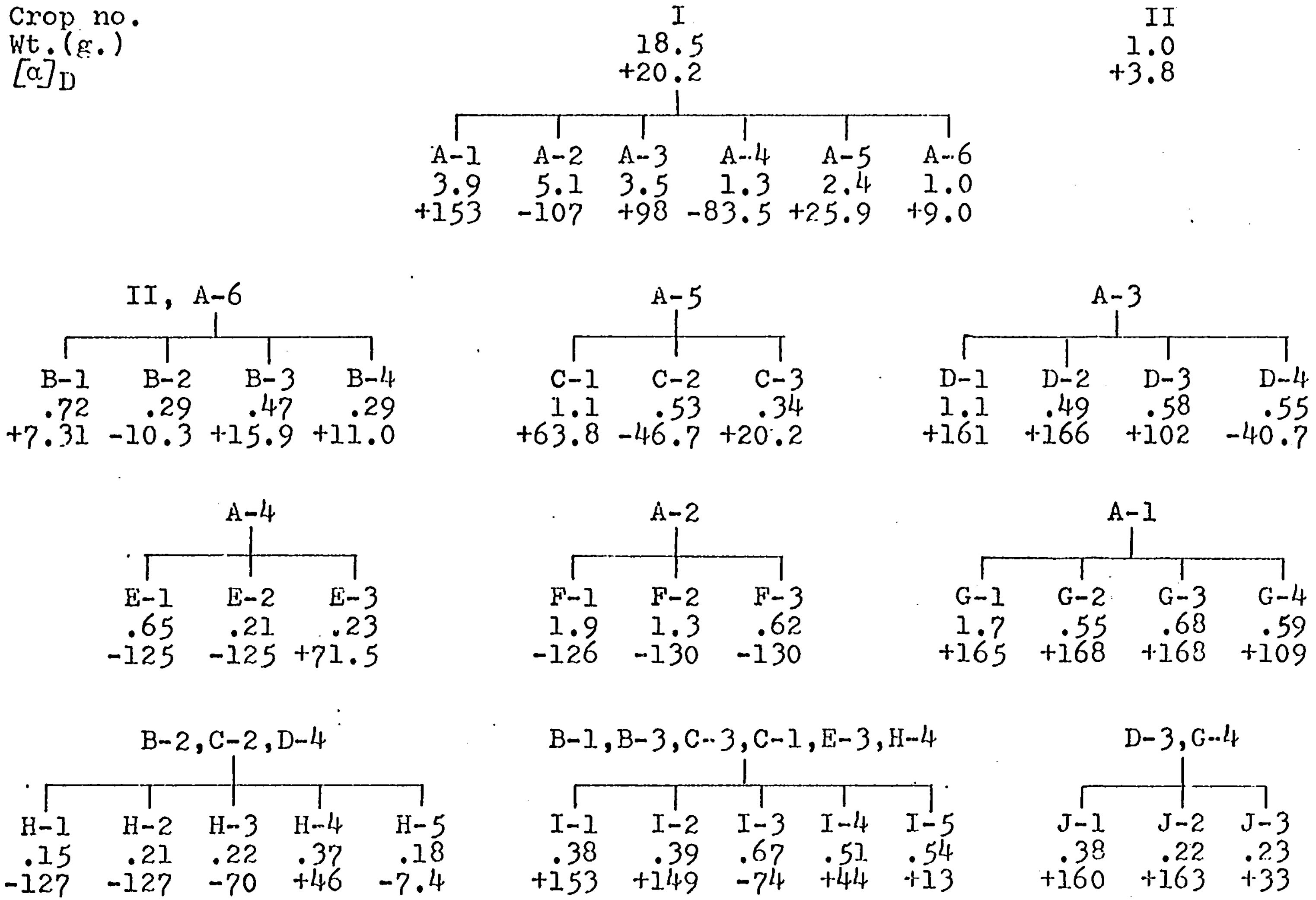
d and l
XLI

d and l
XXXV

conformation. Also Dorfman (31) has found that transoid dienes have ultraviolet molar extinction values of 14,000-28,000 whereas those of cisoid dienes are in the range 5,000-15,000.

Treatment of the realtively stable enamine XL with *d*-camphor-10-sulfonic acid gave a yellow iminium salt (XLI) in good yield. Systematic recrystallization of the salt from ethyl acetate-methanol (Table 1, page 19) gave two diastereomeric salts (XLI *d* and XLI *l*). The dextrorotatory salt (XLI *d*) showed $[\alpha]_D^{27} = +168^\circ$ (c 1.0, 95% ethanol), $\lambda_{max}^{95\%\ EtOH}$ 269mμ (23,400). Its infrared spectrum (Figure 2, page 22) shows the 5.75μ carbonyl absorptions of the camphor sulfonic acid anion and the 6.13μ absorption of the $\rangle C = N\langle^{\oplus}$ moiety (32). The n.m.r. spectrum (Figure 3, page 24) shows the vinyl singlet at 3.42τ, the protons α to nitrogen as a broad absorption band at 5.87τ (32), the quartet at 6.64, 6.88, 7.22 and 7.46τ due to the non-equivalent hydrogens of the methylene group adjacent to sulfur (33), the angular methyl singlet at 8.39τ and the camphor sulfonic acid methyl singlets at 8.90 and 9.22τ. That the protonation actually occurs at C-6 rather than on nitrogen or at C-4 is supported by several data. Protonation of nitrogen is excluded by the absence of two olefinic proton absorptions in the n.m.r. spectrum. Protonation of C-4 is excluded by the appearance of the $\rangle C = N\langle^{\oplus}$ at 6.13μ. Leonard and Paukstelis (32) report infrared absorption of XLII at 6.17μ and that of XLIII at 6.00μ.

Table 1. Recrystallization scheme for XLI



Crop no.	I	II
Wt. (g.)	18.5	1.0
$[\alpha]_D$	+20.2	+3.8

I

Crop no.	A-1	A-2	A-3	A-4	A-5	A-6
Wt. (g.)	3.9	5.1	3.5	1.3	2.4	1.0
$[\alpha]_D$	+153	-107	+98	-83.5	+25.9	+9.0

II, A-6

Crop no.	B-1	B-2	B-3	B-4
Wt. (g.)	.72	.29	.47	.29
$[\alpha]_D$	+7.31	-10.3	+15.9	+11.0

A-5

Crop no.	C-1	C-2	C-3
Wt. (g.)	1.1	.53	.34
$[\alpha]_D$	+63.8	-46.7	+20.2

A-3

Crop no.	D-1	D-2	D-3	D-4
Wt. (g.)	1.1	.49	.58	.55
$[\alpha]_D$	+161	+166	+102	-40.7

A-4

Crop no.	E-1	E-2	E-3
Wt. (g.)	.65	.21	.23
$[\alpha]_D$	-125	-125	+71.5

A-2

Crop no.	F-1	F-2	F-3
Wt. (g.)	1.9	1.3	.62
$[\alpha]_D$	-126	-130	-130

A-1

Crop no.	G-1	G-2	G-3	G-4
Wt. (g.)	1.7	.55	.68	.59
$[\alpha]_D$	+165	+168	+168	+109

B-2, C-2, D-4

Crop no.	H-1	H-2	H-3	H-4	H-5
Wt. (g.)	.15	.21	.22	.37	.18
$[\alpha]_D$	-127	-127	-70	+46	-7.4

B-1, B-3, C-3, C-1, E-3, H-4

Crop no.	I-1	I-2	I-3	I-4	I-5
Wt. (g.)	.38	.39	.67	.51	.54
$[\alpha]_D$	+153	+149	-74	+44	+13

D-3, G-4

Crop no.	J-1	J-2	J-3
Wt. (g.)	.38	.22	.23
$[\alpha]_D$	+160	+163	+33

Table 1. (continued)

H-3,I-3

K-1	K-2	K-3
.27	.12	.22
-125	-126	-31

J-3,I-4,I-5

L-1	L-2	L-3
.39	.39	.14
+87	-23	+33

I-1,I-2

M-1	M-2
.51	.09
+165	+166

E-1,E-2,F-1,F-2,F-3,H-1,H-2,K-1,K-2

N-1	N-2	N-3	N-4
2.4	.97	.83	.46
-131	-130	-130	-131

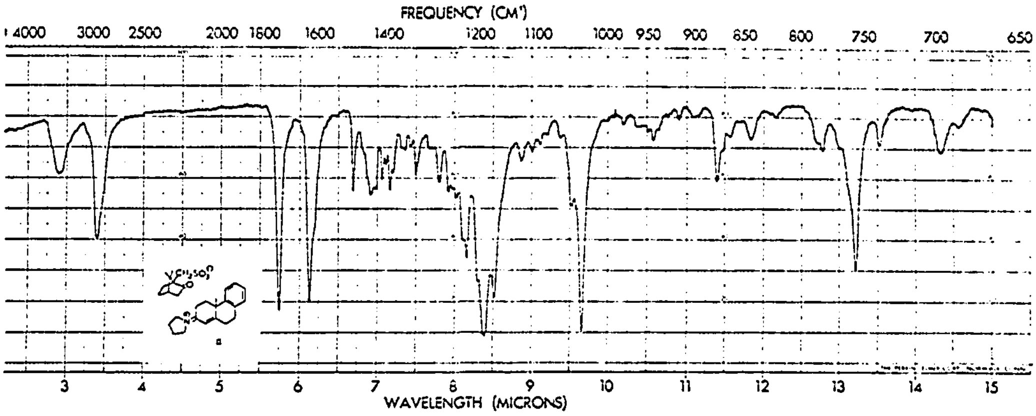
D-1,D-2,G-1,G-2,G-3,J-1,J-2,M-1,M-2

0-1	0-2	0-3	0-4	0-5	0-6
1.8	1.1	.59	.68	.54	.15
+168	+168	+169	+169	+168	

Figure 2. Infrared spectra

Top - d-Iminium salt (XLI d) (potassium bromide pellet)

Bottom - l-Iminium salt (XLI l) (potassium bromide pellet)


FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
CH2SO3
O
N
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

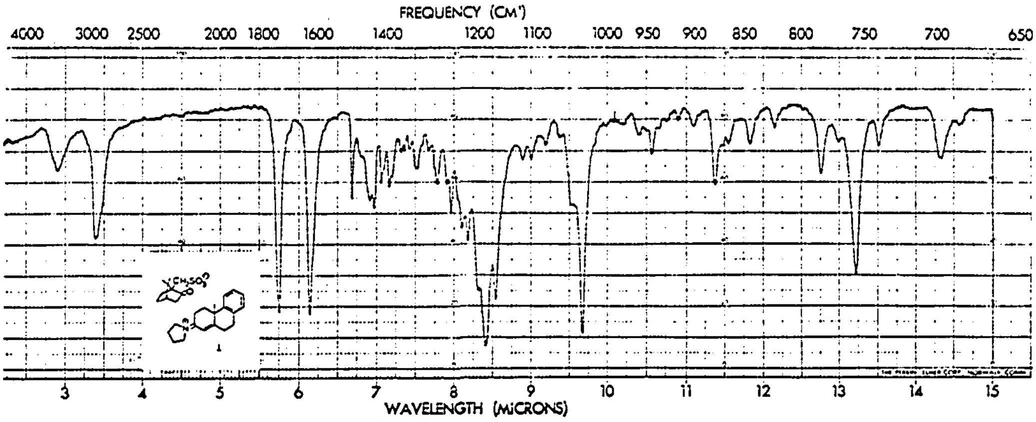
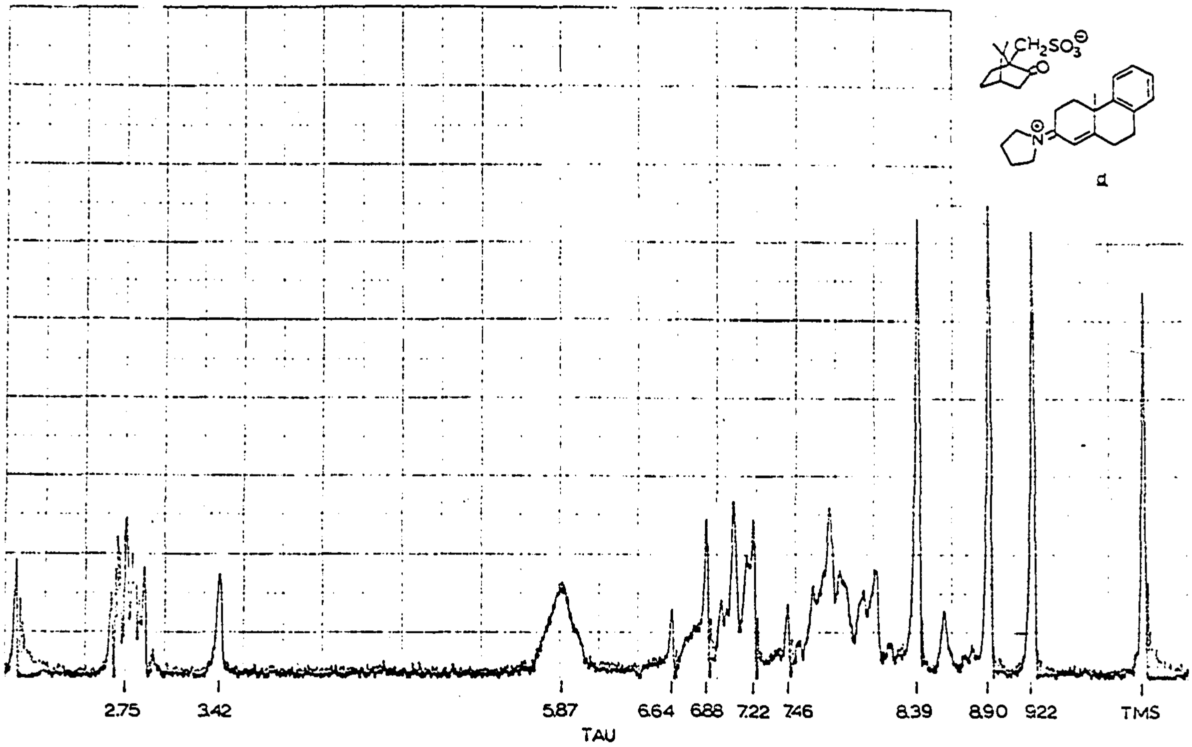
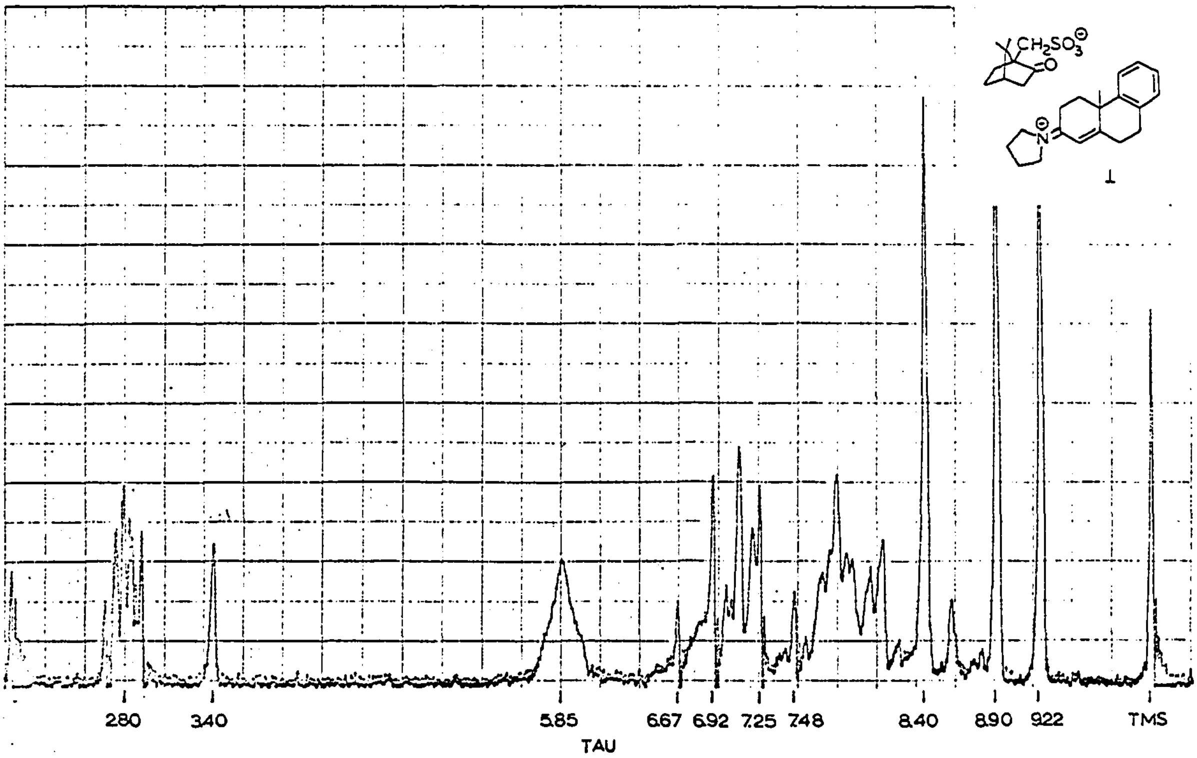

FREQUENCY (CM⁻¹)
4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
CH2SO3
O
N
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

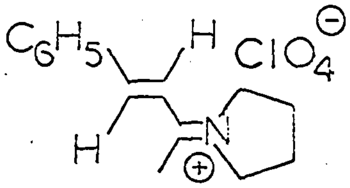
Figure 3. Nuclear magnetic resonance spectra

Top - d-Iminium salt (XLI d) (deuteriochloroform solution)

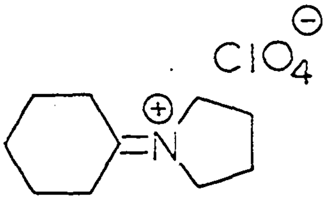
Bottom - l-Iminium salt (XLI l) (deutereochloroform solution)


CH₂SO₃⊖
O
N⊕
α
2.75
3.42
5.87
6.64
6.88
7.22
7.46
8.39
8.90
9.22
TMS
TAU


CH₂SO₃⊖
O
N⊕
⊥
2.80
3.40
5.85
6.67
6.92
7.25
7.48
8.40
8.90
9.22
TMS
TAU



XLII



XLIII

Also, the high molar extinction coefficient of the ultraviolet absorption indicates a conjugated system. The levorotatory, salt XLI l showed $[\alpha]_D^{27} = -131°$ (c 1.0, 95% ethanol), $\lambda_{max}^{95\%\ EtOH}$ 269mμ (23,000). Its infrared spectrum is shown in Figure 2, page 22. Its n.m.r. spectrum is shown in Figure 3, page 24.

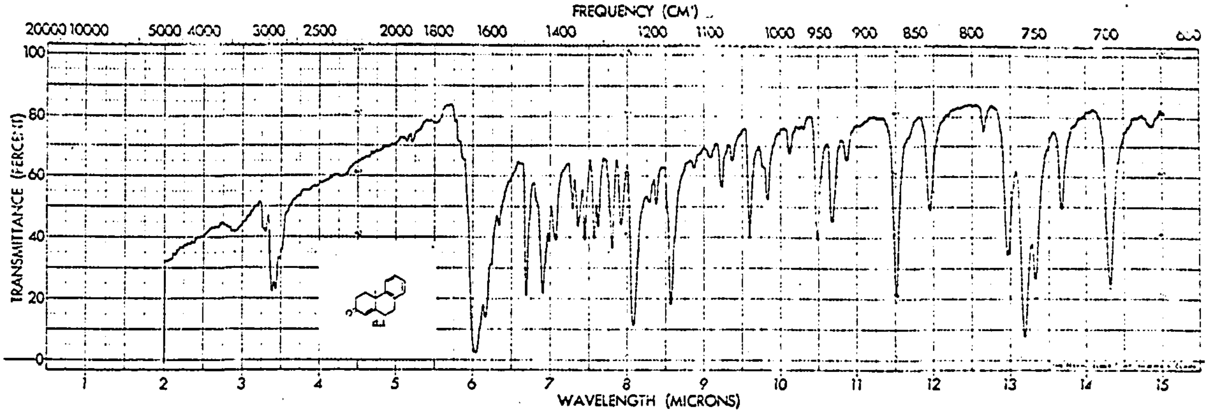
Hydrolysis of the iminium salts proved to be extremely facile. Treatment of the dextrorotatory salt (XLI d) with 0.1 N aqueous potassium hydroxide solution for five minutes at room temperature gave dextrorotatory phenanthrone (XXXIV d) with melting point 68-68.5°, $[\alpha]_D^{27} = +332°$ (c 1.0, 95% ethanol). Hydrolysis of the levorotatory salt (XLI l) gave levorotatory phenanthrone (XXXIV l) with melting point 68-69°, $[\alpha]_D^{27} = -332°$ (c 1.0, 95% ethanol). The solid state infrared spectra of XXXIV d and XXXIV l (Figure 4, page 27) are superimposable and neither shows any absorption attributable to the racemic compound XXXIV d,l. The optical purity of the enantiomers is strongly supported by their identical melting points, their superimposable solid state infrared spectra and their equivalent specific rotations. That no structural alteration had taken place during the resolution was shown by combining equal weights of d- and l-phenanthrone, dissolving

Figure 4. Infrared spectra

Top - Racemic phenanthrone (XXXIV d,l) (potassium bromide pellet)

Middle - Dextrorotatory phenanthrone (XXXIV d) (potassium bromide pellet)

Bottom - Levorotatory phenanthrone (XXXIV l) (potassium bromide pellet)


FREQUENCY (CM⁻¹)
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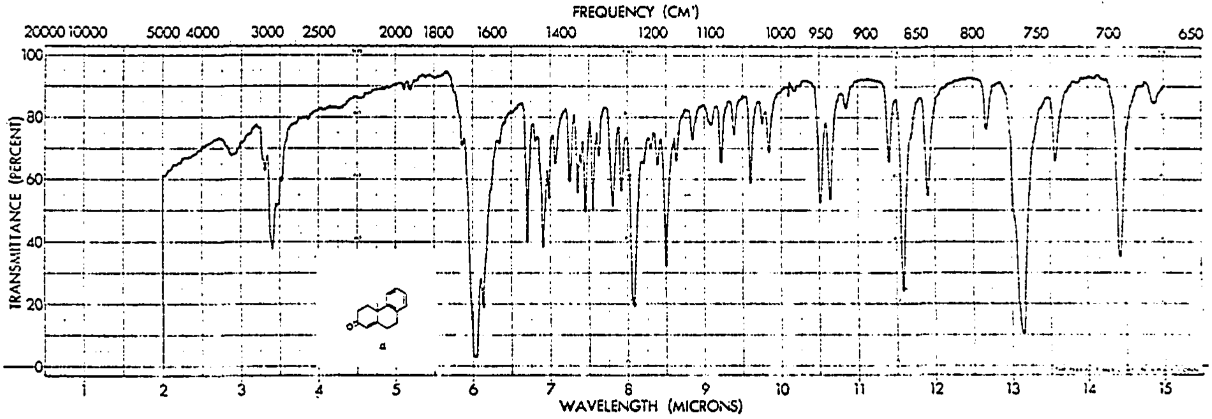
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
d,l


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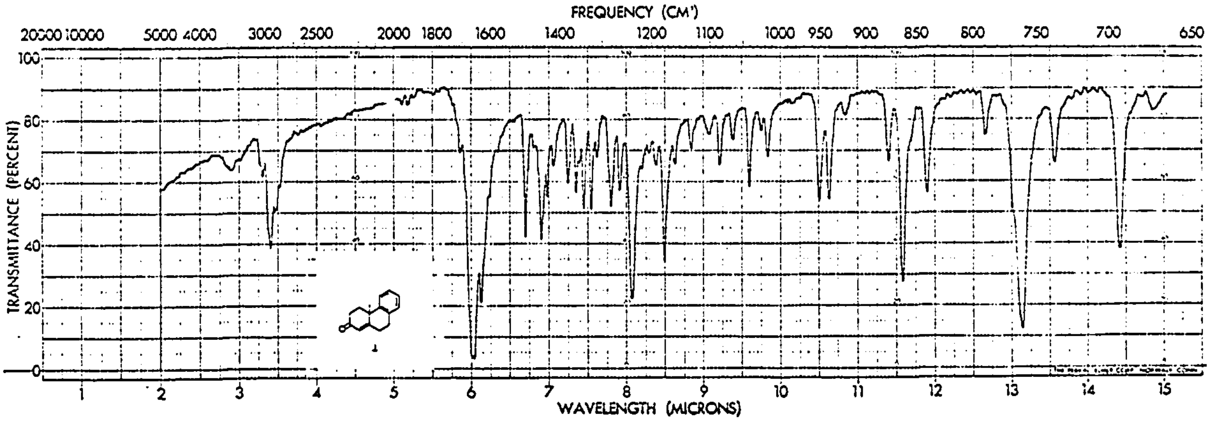
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
d


FREQUENCY (CM⁻¹)
20000 10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
l

the mixture in ether and allowing the ether to evaporate. The residue had the same melting point and solid state infrared spectrum as the racemic compound.

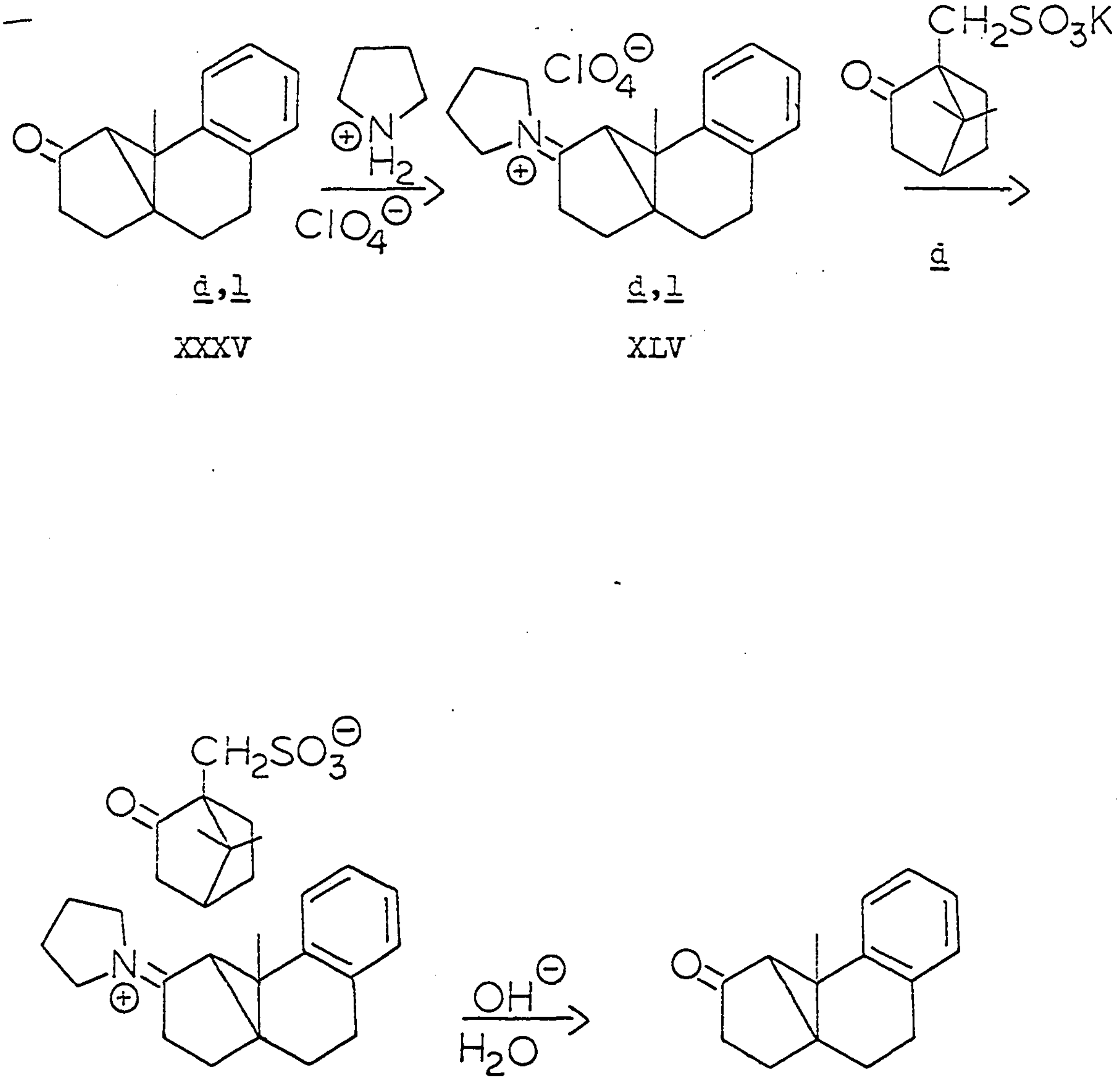
Although the separation of the diastereomeric iminium salts XLI d and XLI l proceeded very well, the recrystallizations had to be carried out with rapid cooling and stirring. If the deposition of crystals from solution was allowed to proceed slowly at room temperature a bright orange salt (m.p. 250-255°) isomeric with XLI (elemental analysis) began to deposit after about six hours. This salt was difficult to purify, but recrystallization from acetonitrile gave a sample which analyzed for XLI. Hydrolysis of this salt in base did not give phenanthrone XXXIV but a poor yield of what appeared to be a complex mixture of products (thin layer and infrared analysis). This salt was not investigated further.

In contrast to the relative ease with which phenanthrone was resolved, the resolution of cyclophenanthrone (XXXV) proved to be rather difficult. Attempted preparation of the enamine of XXXV resulted in a brown gum which, however, showed the 6.18μ infrared absorption band required for the enamine. Because of the difficulty in characterizing this gum further, it was added to d-camphor-10-sulfonic acid in hopes of isolating the desired iminium salt XLIV. Although this mixture showed the infrared bands required for XLIV, no crystalline material could be obtained. A new approach was definitely indicated.

A mixture of cyclophenanthrone and pyrrolidine *d*-camphor-10-sulfonate was refluxed in toluene with hopes of isolating the desired salt (XLIV) directly. After 16 hours the solvent was removed and an infrared spectrum (KBr) of the resulting solid was recorded. The presence of a 5.89μ band and the absence of 5.98μ absorption band ($>C=N^{\oplus}<$; (32)) indicated that this was merely a mixture of the two components and not the desired XLIV. Again, another route was indicated.

In 1963 Leonard and Paukstelis (32) prepared the iminium perchlorate salts of several ketones and aldehydes. Treatment of XXXV with pyrrolidine perchlorate in ethanol at room temperature resulted in a high yield of the stable iminium perchlorate salt XLV *d*,*l* (Figure 5, page 31). The infrared spectrum (KBr) exhibited the expected $>C=N^{\oplus}<$ absorption at 5.98μ and the expected broad perchlorate band at 9.15μ. The desired salt (XLIV) could now be obtained by exchanging the perchlorate anion for the *d*-camphor-10-sulfonate anion. Treatment of XLV with potassium *d*-camphor-10-sulfonate in methanol at room temperature gave potassium perchlorate by metathesis. This was filtered off, and the solvent was removed from the filtrate giving a clear, colorless glass which deposited crystals of XLIV on trituration in cold ethyl acetate. Systematic recrystallization (Table 2, page 32) of

Figure 5. Resolution of racemic cyclophenanthrone (XXXV d,l)



d,l

XXXV

d,l

XLV

d and l

XLIV

d and l

XXXV

Table 2. Recrystallization scheme for XLIV

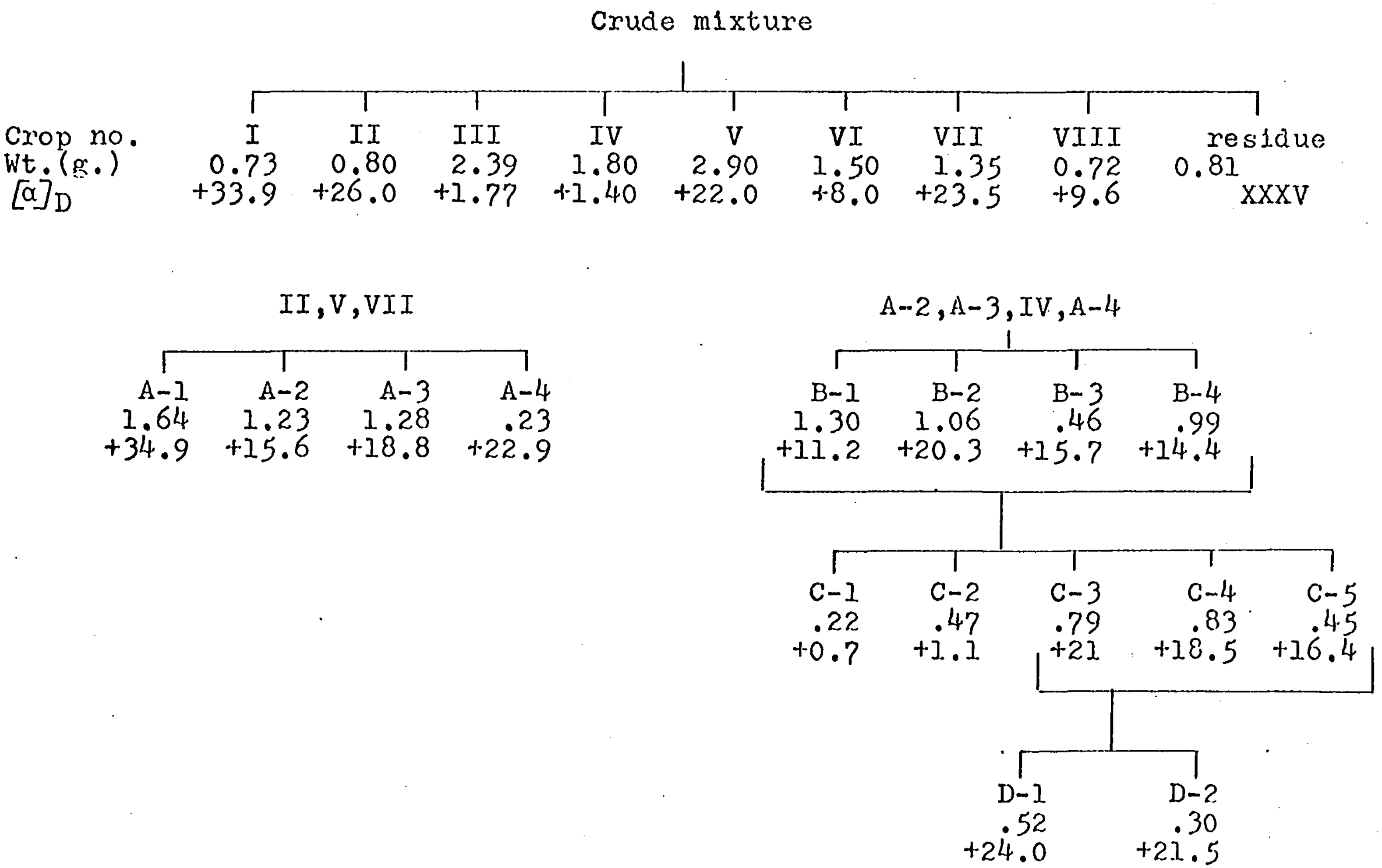
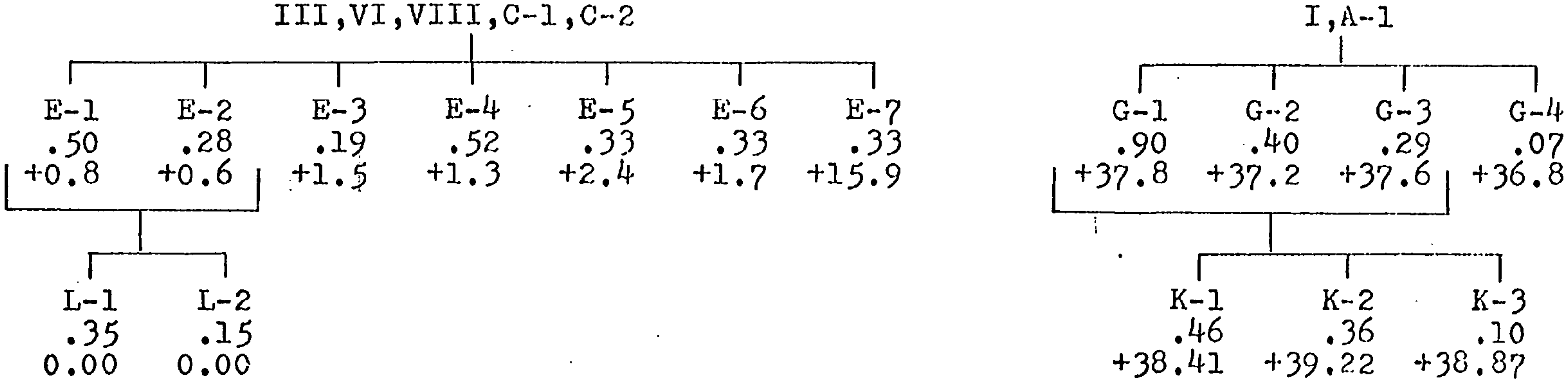


Table 2. (continued)



this material gave a dextrorotatory salt (XLIV d) with $[\alpha]_D^{27} = +39.2^\circ$ (c 1.0, 95% ethanol), $\lambda_{max}^{95\%\ EtOH}$ 268mμ (9,000), 232mμ (8,100) (calculated for the monohydrate). Its infrared spectrum (Figure 6, page 36) shows the 5.75μ carbonyl absorption of the camphorsulfonic acid anion and the 5.97μ absorption of the $\rangle C = N \langle \oplus$ moiety (32). The n.m.r. spectrum (Figure 7, page 38) shows the 6.64, 6.89, 7.22 and 7.46 τ quartet (half of which is just discernible) due to the non-equivalent hydrogens of the methylene group adjacent to sulfur (33), the angular methyl singlet at 8.38 τ and the camphor sulfonic acid methyl singlets at 8.87 and 9.17 τ. The levorotatory salt (XLIV l) showed $[\alpha]_D^{27} = 0.00^\circ$ (c 1.0, 95% ethanol), $\lambda_{max}^{95\%\ EtOH}$ 268mμ (9,500), 232mμ (7,800) (calculated for the monohydrate). Its infrared and n.m.r. spectra are shown in Figure 6, page 36, and Figure 7, page 38, respectively.

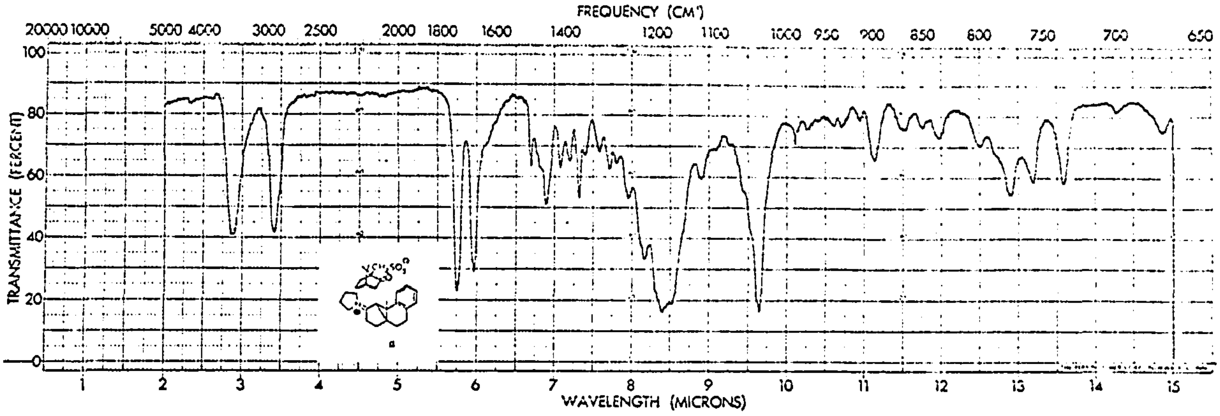
Hydrolysis of the dextrorotatory iminium salt (XLIV d) gave dextrorotatory cyclophenanthrone (XXXV d) with m.p. 110-111°, $[\alpha]_D^{27} = +42.5^\circ$ (c 1.0, 95% ethanol). Hydrolysis of the levorotatory salt (XLIV l) gave levorotatory cyclophenanthrone (XXXV l) with m.p. 109.5-111.5°, $[\alpha]_D^{27} = -42.3^\circ$ (c 1.0, 95% ethanol). The solid state infrared spectra of XXXV d and XXXV l (Figure 8, page 40) are superimposable and neither shows any absorption attributable to the racemic compound XXXV d,l.

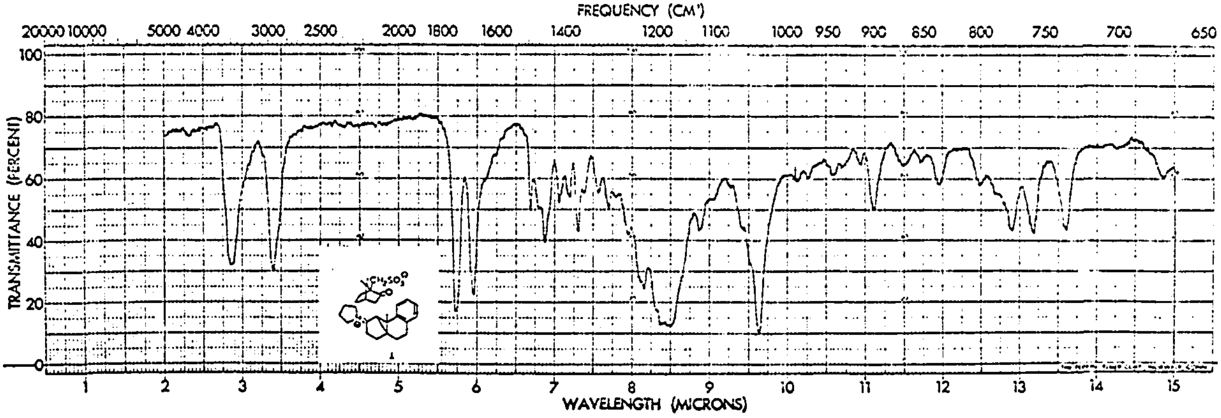
The optical purity of the enantiomers is strongly sup-

Figure 6. Infrared spectra

Top - d-Iminium salt (XLIV d) (potassium bromide pellet)

Bottom - l-Iminium salt (XLIV l) (potassium bromide pellet)


FREQUENCY (CM^{-1})
20000 10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
a


FREQUENCY (CM^{-1})
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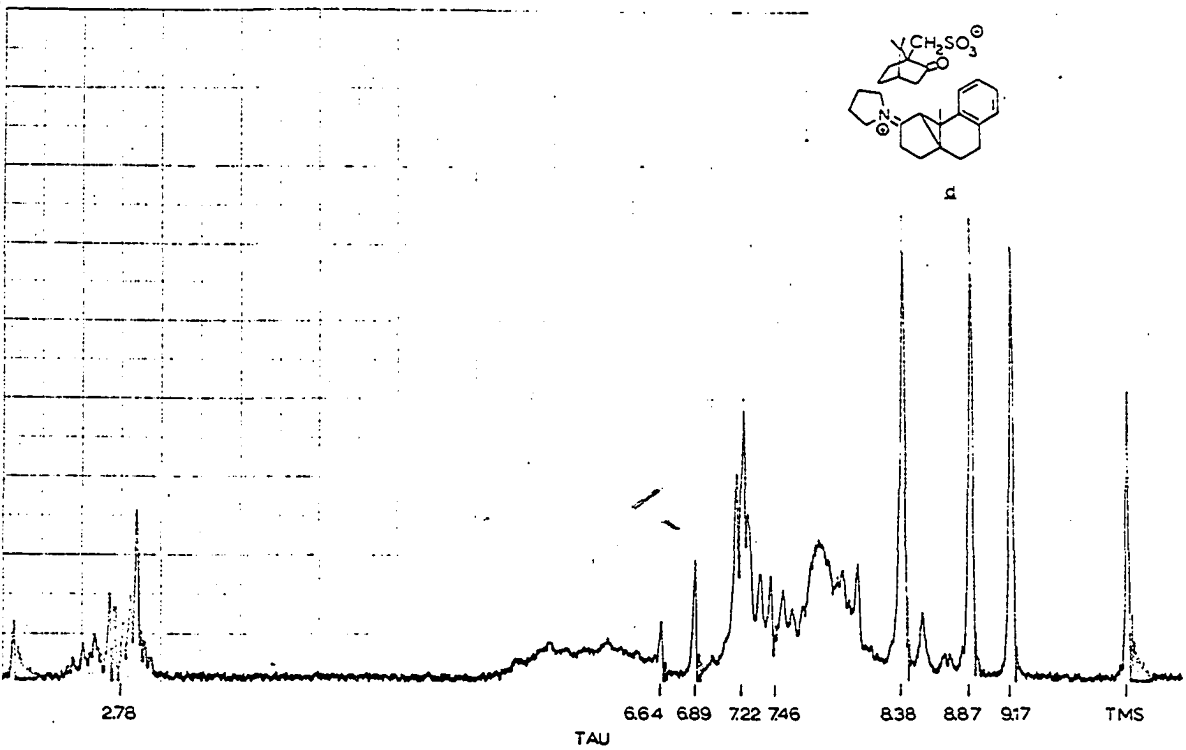
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
b

Figure 7. Nuclear magnetic resonance spectra

Top - d-Iminium salt (XLIV d) (deuteriochloroform solution)

Bottom - l-Iminium salt (XLIV l) (deuteriochloroform solution)


CH2SO3⊖
O
N
⊕
a
2.78
6.64
6.89
7.22
7.46
8.38
8.87
9.17
TMS
TAU

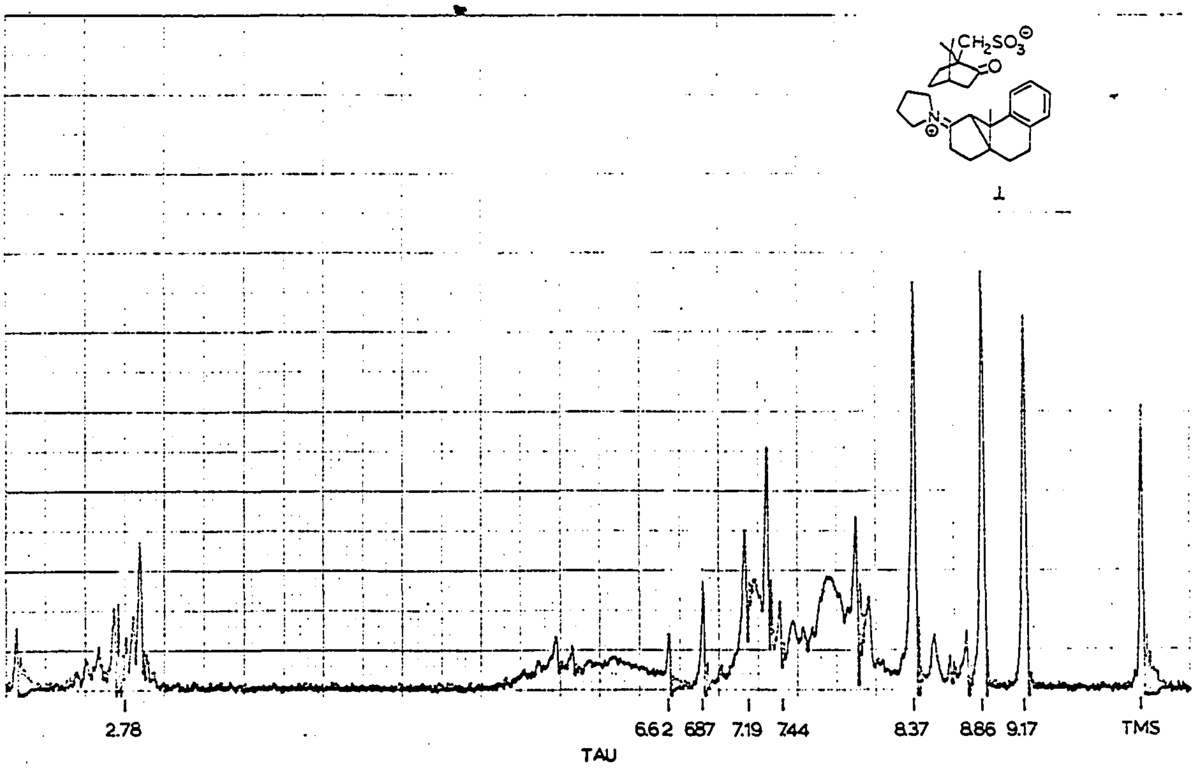
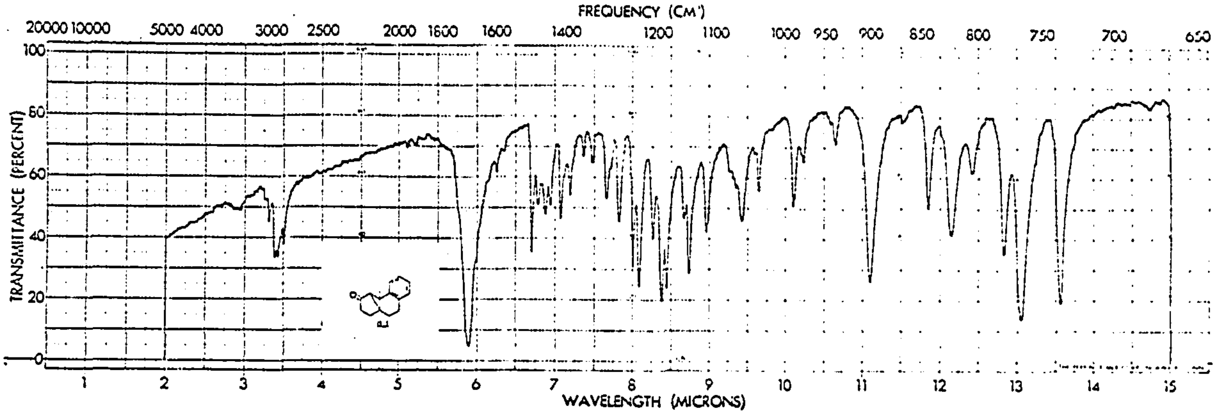

CH2SO3⊖
O
N
⊕
⊥
2.78
6.62
6.87
7.19
7.44
8.37
8.86
9.17
TMS
TAU

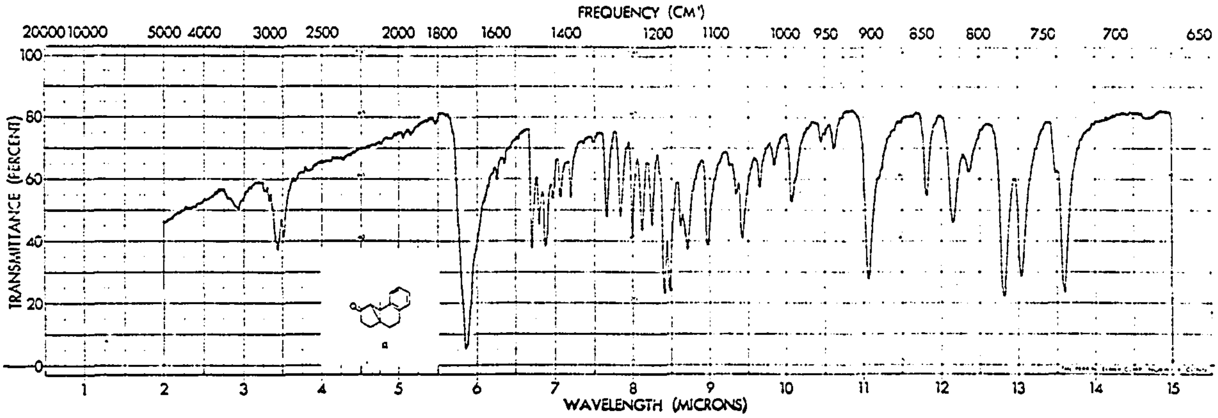
Figure 8. Infrared spectra

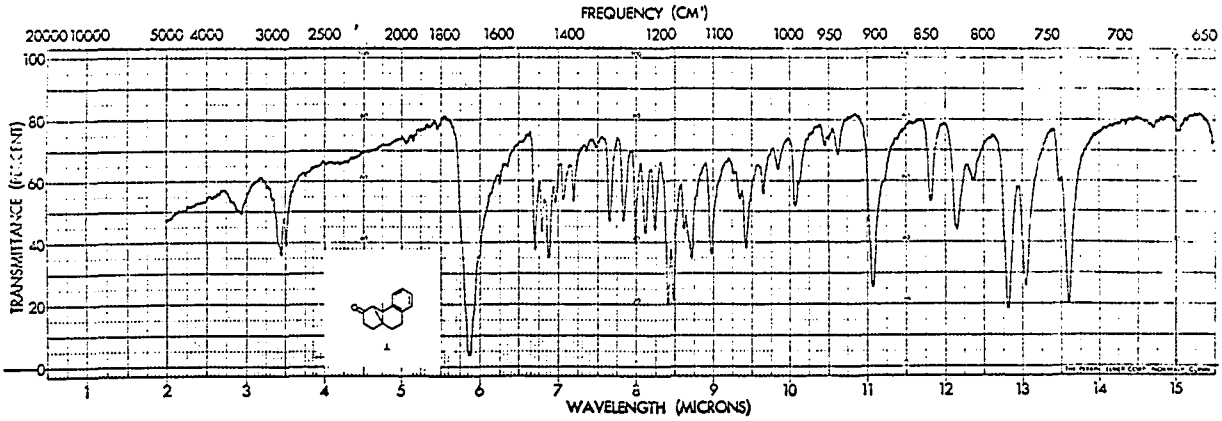
Top - Racemic cyclophenanthrone (XXXV d,l)
(potassium bromide pellet)

Middle - Dextrorotatory cyclophenanthrone (XXXV d)
(potassium bromide pellet)

Bottom - Levorotatory cyclophenanthrone (XXXV l)
(potassium bromide pellet)


FREQUENCY (CM⁻¹)
20000 10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
20000 10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
20000 10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1100 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

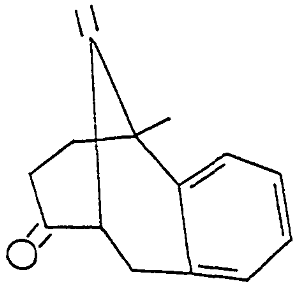
ported by their identical melting points, their superimposable solid state infrared spectra and their equivalent specific rotations. That no structural alteration had taken place during the resolution was shown by combining equal weights of d and l cyclophenanthrone, dissolving the mixture in ether and allowing the ether to evaporate. The residue had the same melting point and solid state infrared spectrum as the racemic compound.

A study on the generality of the resolution of ketones through iminium salts has been carried out by Adams (34). He found that α,β-unsaturated ketones can be resolved fairly readily, but the iminium salts of saturated ketones are extremely sensitive to hydrolysis.

Photochemistry of 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone

In the past several years there has been a substantial increase in the number of papers published concerning photochemical rearrangements of unsaturated ketones. Very recently, several of these papers have dealt with the mechanisms by which these rearrangements occur. The mechanistic pathways proposed for rearrangements of 2-cyclohexenones are no exception to the controversies which exist in the field of photochemistry. A study of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) was undertaken with hopes of elucidating these pathways. Because of the profound effects which solvents impress upon photochemical reactions, three solvent systems were investigated in this study, glacial acetic acid, aqueous acetic acid and t-butanol.

Irradiation of phenanthrone (XXXIV) in glacial acetic acid produced a very complex mixture of products. Column chromatography of the mixture failed to separate cleanly any products except one (ca. 1%), which is tentatively assigned structure XLVI on the following evidence. The presence of an exo-methylene group is indicated by the 3.25, 6.07 and 11.13μ bands in the infrared spectrum (Figure 9, page 44).



XLVI

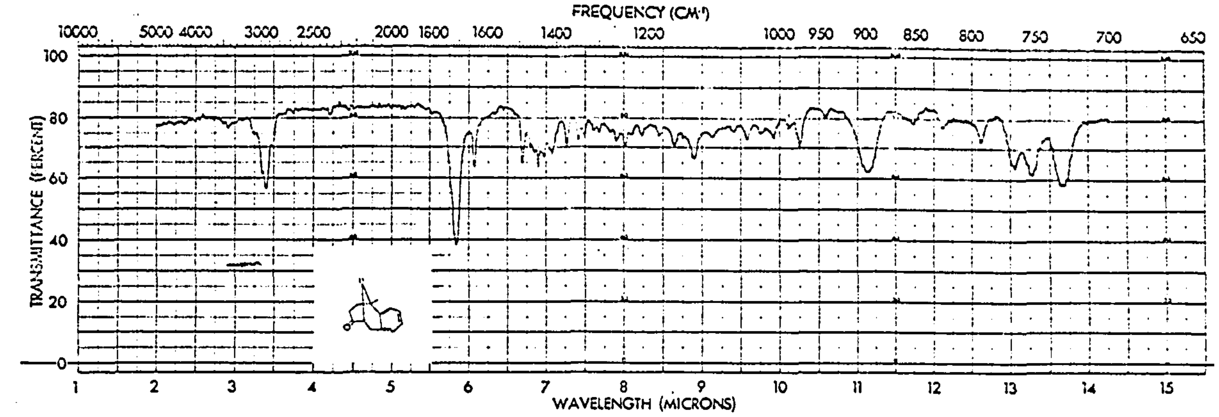
The 5.84μ band is consistent with a six-membered ring ketone. The n.m.r. spectrum (Figure 10, page 46) shows a four-proton multiplet at 2.84τ assignable to the four aromatic protons and a two-proton singlet at 5.12τ assignable to the exo-methylene protons, which are apparently magnetically equivalent. The two-proton multiplet near 6.88τ is assigned to the benzylic protons and the methyl group appears at 8.37τ. Although 8.75τ is high for the methine proton, the lack of large splitting for the broad one-proton band dictates this

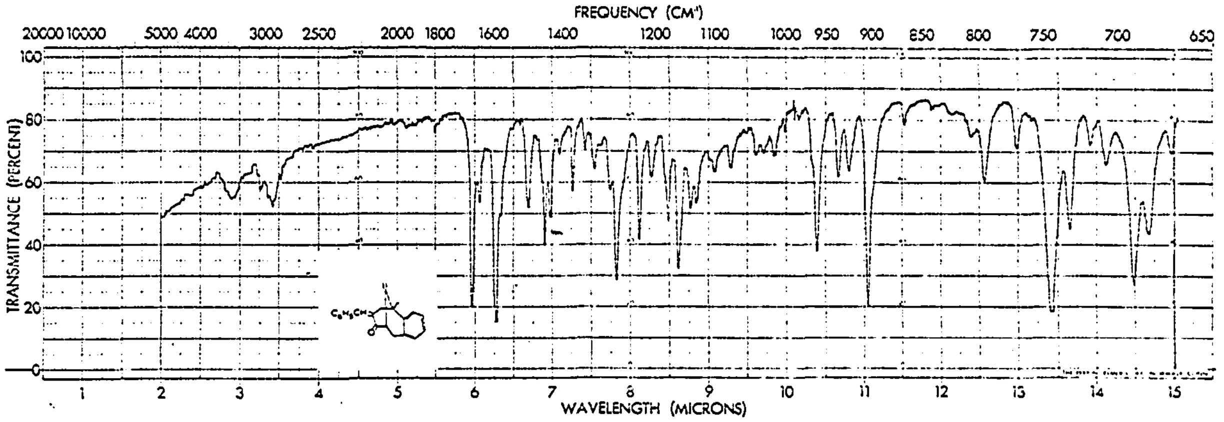
Figure 9. Infrared spectra

Top - Keto-olefin (XLVI) (capillary film)

Middle - Monobenzylidene derivative of keto-olefin (XLVII) (potassium bromide pellet)

Bottom - Ketols (XLVIII a,b) (capillary film)


FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
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TRANSMITTANCE (PERCENT)
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$C_6H_5CH_2$
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

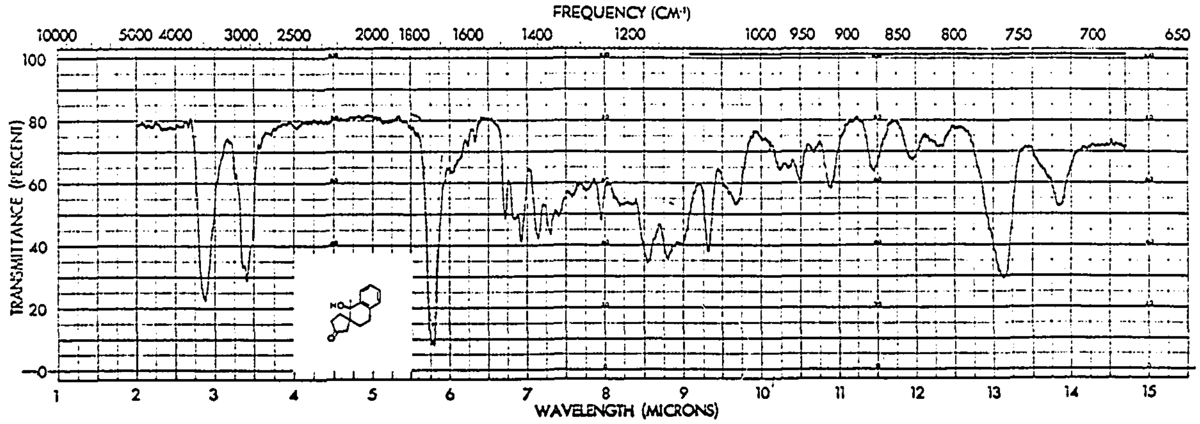
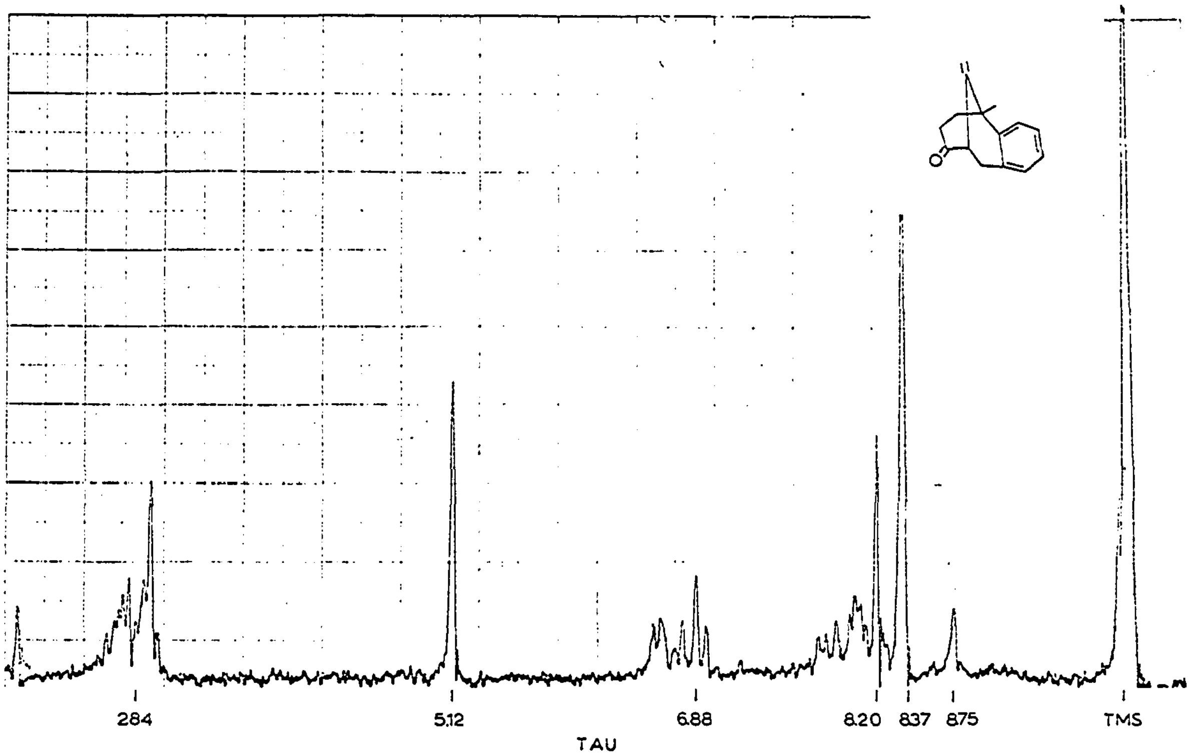
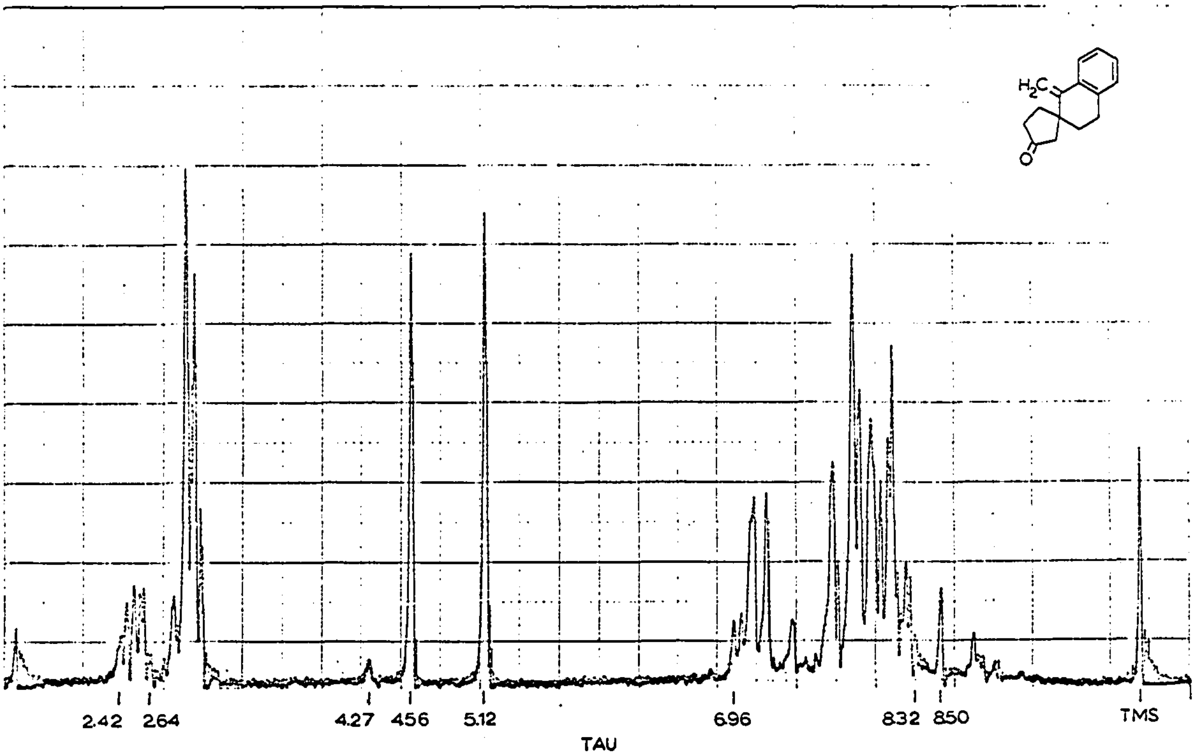

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
HO
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 10. Nuclear magnetic resonance spectra

Top - Keto-olefin (XLVI) (carbon tetrachloride solution)

Bottom - Keto-olefin (XLIX) (carbon tetrachloride solution)


O
2.84
5.12
6.88
8.20
8.37
8.75
TMS
TAU


H_2C
O
2.42
2.64
4.27
4.56
5.12
6.96
8.32
8.50
TMS
TAU

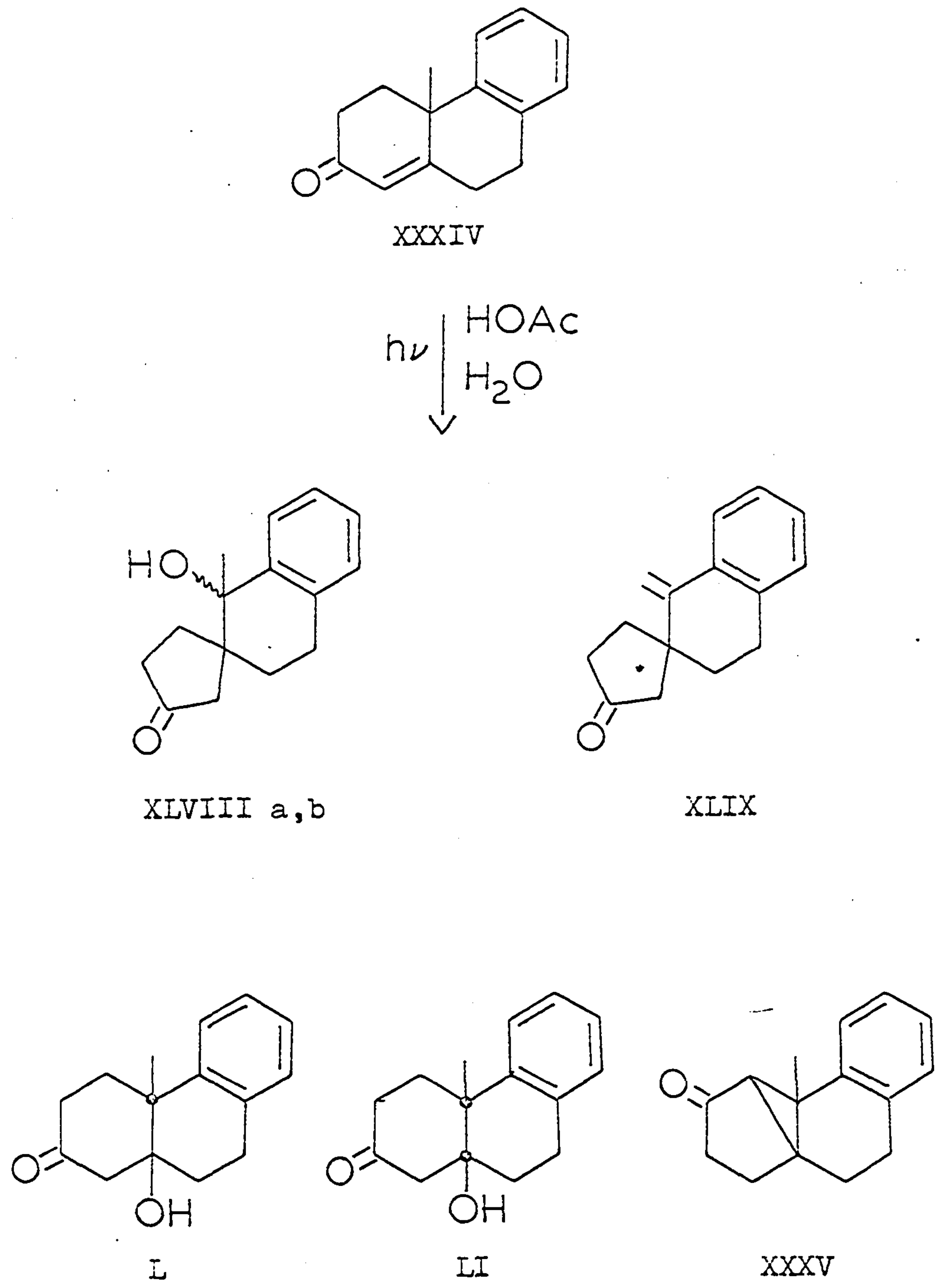
assignment. The four-proton multiplet downfield from the methyl group is then caused by the protons α and β to the carbonyl group.

Treatment of XLVI with benzaldehyde and base gave a white monobenzylidene derivative (XLVII), m.p. 119-123°, $\lambda_{max}^{95\%\ EtOH}$ 300mμ (16,600) and 231mμ(s) (5,500). Monobenzylidenecyclohexanone shows $\lambda_{max}^{95\%\ EtOH}$ 290mμ (11,200) (35). The infrared spectrum spectrum (Figure 9, page 44) shows double bond absorption bands at 3.27, 6.07 and 11.07μ and the expected (36) carbonyl band at 5.96μ.

Because of the small amount of material available and the inability to isolate more material from a second irradiation, no more data for this compound were collected, and the structure must be considered tentative. Also, that XLVI was produced via a photochemical pathway has not been shown.

Because of the difficulty in separating and characterizing products from the irradiation of phenanthrone (XXXIV) in glacial acetic acid, a different solvent system was chosen. Irradiation of phenanthrone in aqueous acetic acid (75% acetic acid by volume) for 126 hours gave rise to a complex product mixture which was separated by column chromatography on alumina. From the mixture, four products were identified (XLVIII a,b 30%; XLIX, 5%; L, 3%; LI, 1%; Figure 11, page 49; based on recovered crude XXXIV) and the possibility of a fifth (XXXV, 2%) was indicated by thin layer analysis only. That

Figure 11. Irradiation of phenanthrone (XXXIV) in aqueous acetic acid


XXXIV
hν
HOAc
H_2O
HO
XLVIII a,b
XLIX
OH
L
OH
LI
XXXV

XLVIII a,b, L and LI were not artifacts produced during work-up is supported by the presence of each of their methyl group absorptions in n.m.r. spectra of the crude reaction mixture both in benzene and in carbontetrachloride. These spectra showed broad absorption bands at 6.38 and 6.65τ respectively, which disappeared on shaking the samples with D_2O indicating that alcohols were present. The stability of an aqueous acetic acid solution of XXXIV in the absence of light was shown by the stability of its ultraviolet absorbance and by the recovery of unchanged XXXIV from the solution (see Experimental).

Support for the validity of structure XLVIII a,b, is obtained from the 2.88μ hydroxyl and 5.75-5.80μ carbonyl absorption bands in its infrared spectrum (Figure 9, page 44). The n.m.r. spectrum (Figure 20, page 74) shows two methyl peaks at 8.62 and 8.67τ , which could not be collapsed to a single peak during irradiation at all frequencies encompassed by the spectrum. This proves that the two peaks do not comprise a doublet caused by coupling to an adjacent proton, but, in fact, are the absorption bands of two discrete compounds. The peak at 6.90τ disappears on shaking the sample with D_2O and on addition of dimethyl sulfoxide to a separate sample is shifted to a 5.13τ singlet. These data indicate the presence of tertiary alcohol (37).

Dehydration of XLVIII a,b with phosphorous oxychloride gave XLIX in 45% yield, $\lambda_{max}^{95\%\ EtOH}$ 245mμ (10,900) and 282mμ (s) (1,200). α-Methylstyrene shows $\lambda_{max}^{95\%\ EtOH}$ 242mμ (10,000) and 282mμ (300) (38). The infrared spectrum (Figure 12, page 53) shows the 3.27, 6.16 and 11.15μ absorption bands of the terminal methylene group and the 5.73μ absorption band of the carbonyl group. The n.m.r. spectrum (Figure 10, page 46) shows two sharp, one-proton singlets at 4.56 and 5.12τ, the former being the absorption band of the proton nearest the benzene ring. The peaks at 4.27 and 8.50τ are presumably due to the presence of a small amount of phenanthrone (XXXIV) as also indicated by the absorption band at 5.98μ in the infrared spectrum of XLIX (presumably this was derived from L or/and LI). Since the dehydration of XLVIII a,b proceeded in only 45% yield, its epimeric nature is not proven. However, the inability to separate XLVIII a,b by column or thin layer chromatography, and the relative simplicity of its infrared and n.m.r. spectra, suggest that it is a simple epimeric mixture.

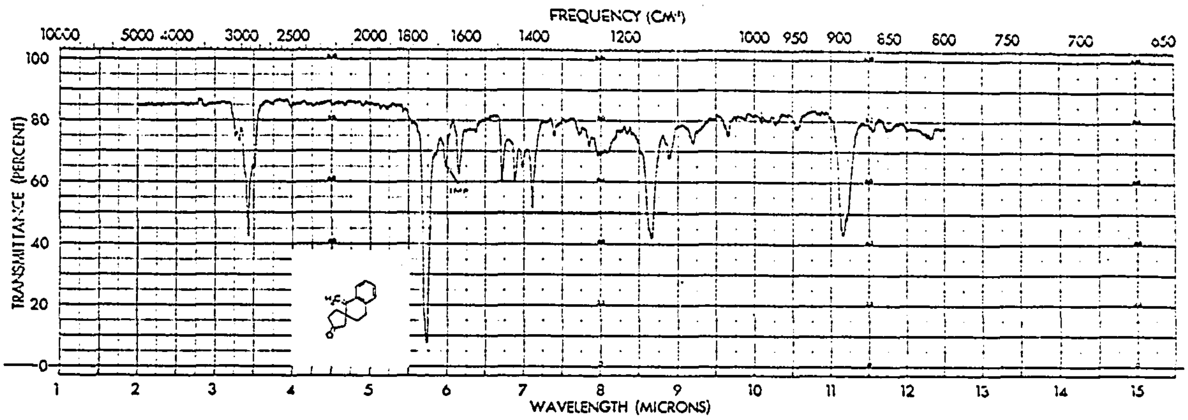
Treatment of keto-olefin XLIX with benzaldehyde and base gave two dibenzylidene derivatives LII and LIII (Figure 13, page 55). The former (LII) had a melting point of 136.5-138.5° and showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (30,100) and 239mμ (24,000). The infrared spectrum (Figure 12, page 53) shows double bond absorption bands at 3.27, 6.19, 6.37, 6.25 (s) and 11.18μ and a carbonyl band at 5.94μ. The latter (LIII)

Figure 12. Infrared spectra

Top - Keto-olefin (XLIX) (carbon tetrachloride solution)

Middle - Low melting dibenzylidene derivative (LII) (potassium bromide pellet)

Bottom - High melting dibenzylidene derivative (LIII) (potassium bromide pellet)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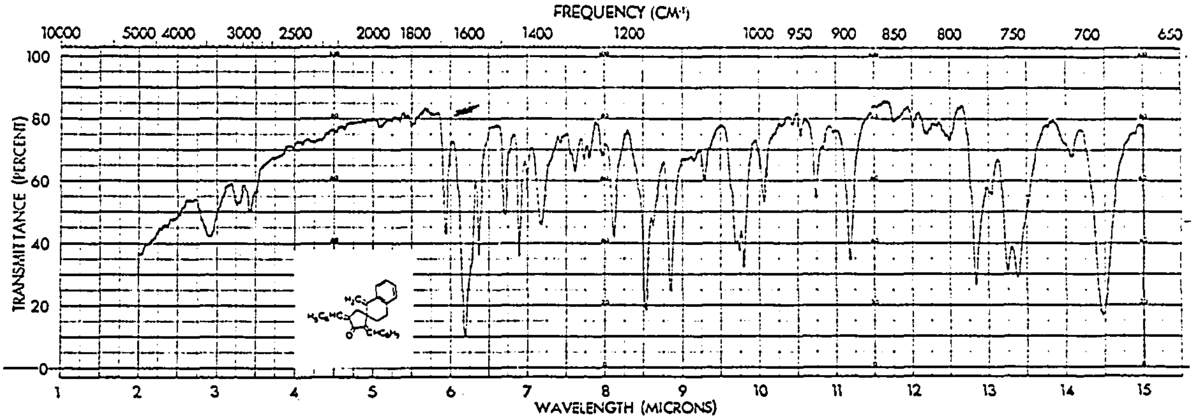
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
IMP
H₃C
WAVELENGTH (MICRONS)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15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TRANSMITTANCE (PERCENT)
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H₅C₆HC
CHC₆H₅
WAVELENGTH (MICRONS)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

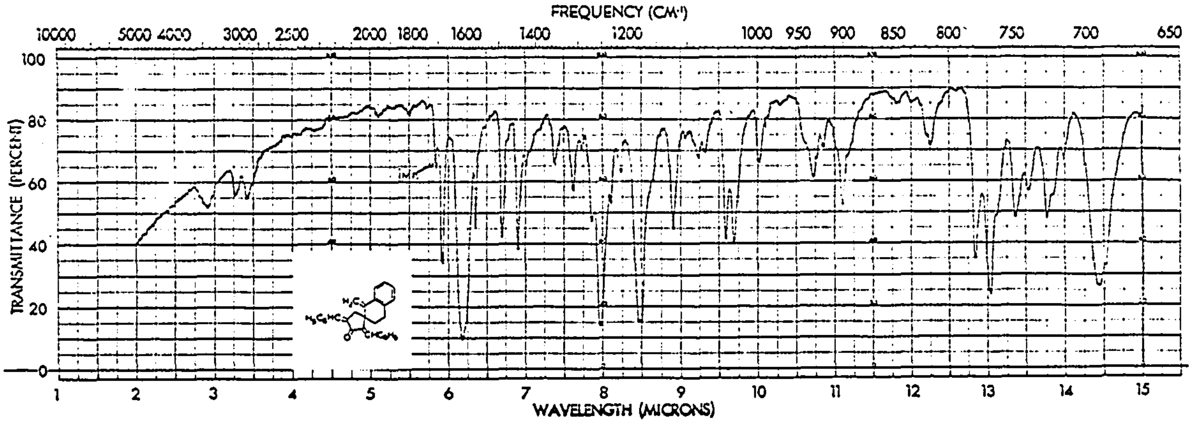
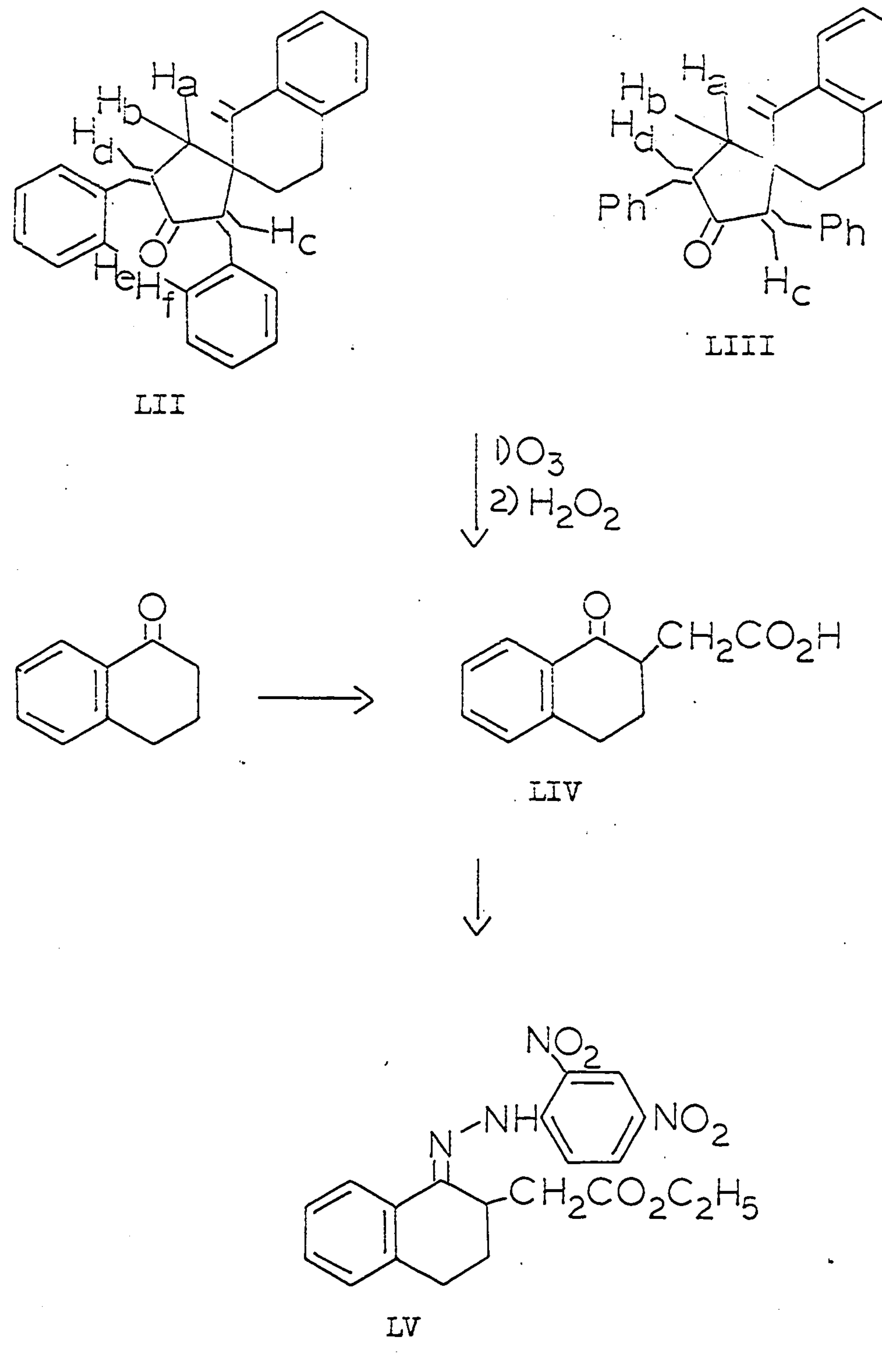

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
IMP
H₃C
H₅C₆HC
CHC₆H₅
WAVELENGTH (MICRONS)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

Figure 13. Ozonolysis of dibenzylidene derivatives LII and LIII


Ha
Hb
Hd
Hc
HeHf
LII
Ha
Hb
Hd
Ph
Ph
Hc
LIII
1) O_3
2) H_2O_2
O
O
CH_2CO_2H
LIV
NO_2
NO_2
N
NH
$CH_2CO_2C_2H_5$
LV

had a melting point of 173-175° and showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (30,400) and 239mμ (20,400). Since this isomer contained residual acetone not removed by drying (infrared spectrum 5.84μ and n.m.r. spectrum 7.89τ) the extinction values must be considered minimal. The infrared spectrum (Figure 12, page 53) shows absorption bands at 3.27, 5.93, 6.18, 6.25 (s), 6.36 and 11.10μ. Dibenzylidenecyclopentanone itself shows peaks in the infrared (KBr) at 5.95, 6.17, 6.22 (s) and 6.37μ while absorption in the ultraviolet occurs at $\lambda_{max}^{95\%\ EtOH}$ 344mμ (27,500) (35). That LII and LIII are merely stereoisomers is supported by their ultraviolet spectra recorded after allowing their ethanol solutions to stand in the laboratory for two weeks. LII then showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (24,700) and 241mμ (21,000) and LIII showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (23,900) and 241mμ (20,300). The ratios of their molar extinction coefficients before and after the two week period are:

$$\frac{\epsilon_{347}^{LII}}{\epsilon_{239}^{LII}} = 1.25 \qquad \frac{\epsilon_{347}^{LIII}}{\epsilon_{239}^{LIII}} = 1.49 \quad ; \quad \frac{\epsilon_{347}^{LII}}{\epsilon_{241}^{LII}} = 1.18 \qquad \frac{\epsilon_{347}^{LIII}}{\epsilon_{241}^{LIII}} = 1.18$$

Before After

That these ratios reach the same value strongly suggests that LII and LIII are equilibrating to a common mixture, probably photochemically. Also supporting their stereoisomeric relationship is that both have a molecular weight of 388 (mass spectrometric) and yield a common degradation product (Figure

13, page 55).

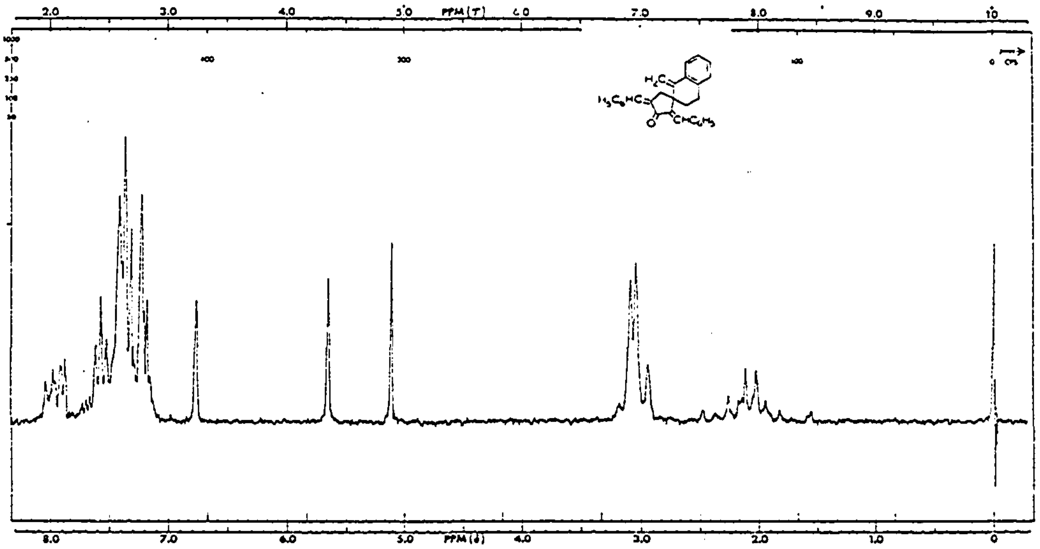
The stereochemistry of LII and LIII is assigned by examining their n.m.r. spectra (Figure 14, page 59). The two-proton multiplet of LII centered at about 2.06 τ is assigned to H_e and H_f which experience the deshielding effect of the carbonyl group and very probably both benzene rings. The one-proton singlet at 3.24 τ is assigned to H_c because of its lack of splitting. The two one-proton singlets at 4.36 and 4.90 τ are assigned to the exo-methylene group while the four-proton multiplet at 6.93 τ is assigned to H_a, H_b (39) and the benzylic protons. The highly split multiplet centered at about 7.94 τ is then assigned to the two remaining aliphatic protons α to the spiro-carbon. The two one-proton singlets of LIII at 4.30 and 4.94 τ are assigned to the exo-methylene protons. The one-proton singlet at 2.08 τ is assigned to H_c which experiences the deshielding effects of the carbonyl group and very probably the benzene ring cis to the carbonyl group. The benzene ring trans to the carbonyl group has been assigned this configuration because of the obvious change in position and splitting pattern of the protons α to the spiro-carbon.

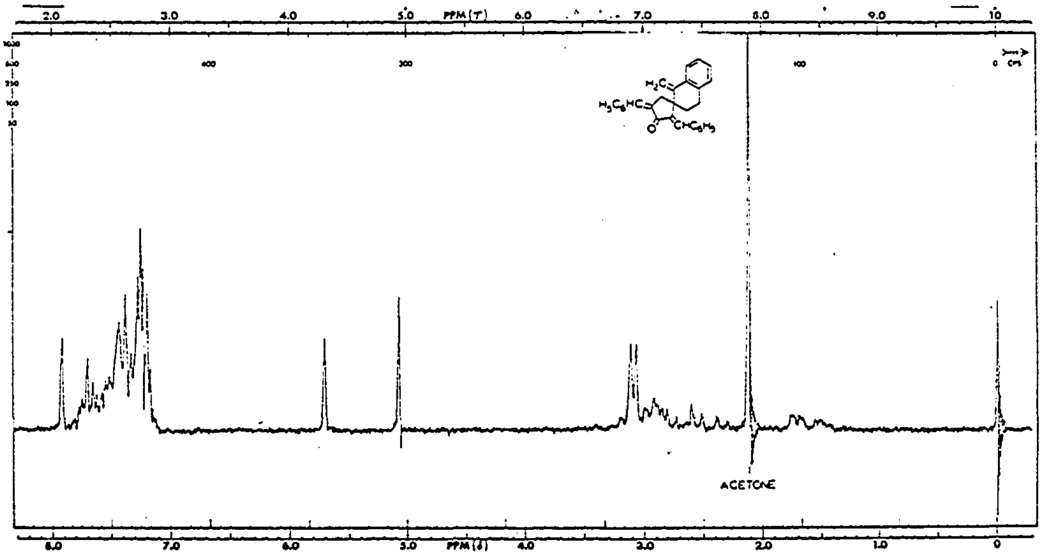
Ozonolysis of either LII or LIII followed by oxidative workup gave 1-tetralone-2-acetic acid (LIV) which was isolated and characterized as its 2,4-dinitrophenylhydrazone (LV) (Figure 13, page 55). This derivative had the same

Figure 14. Nuclear magnetic resonance spectra

Top - Low melting dibenzylidene derivative (LII) (deuteriochloroform solution)

Bottom - High melting dibenzylidene derivative (LIII) (deuteriochloroform solution)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
100
0 CPS
H2C=
H5C6HC=
O
CHC6H5
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
100
0 CPS
H2C=
H5C6HC=
O
CHC6H5
ACETONE
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

melting point and infrared spectrum (KBr) (Figure 15, page 62) as a sample which had been prepared by a synthetic route. This then, completes the structural proof for XLVIII a,b. Since XLIX obtained directly from the irradiation mixture had the same spectral characteristics as that obtained from the dehydration of XLVIII a,b, the structural proof for XLIX is also complete.

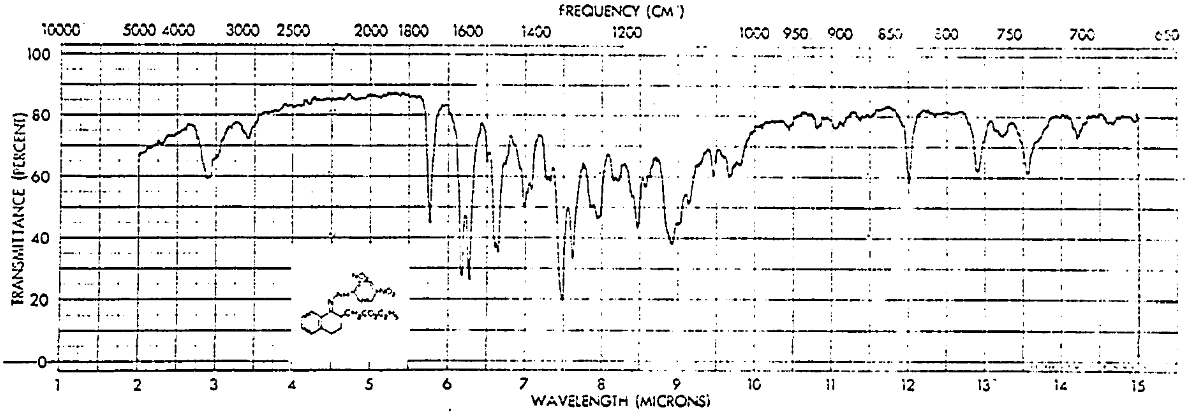
The gross structure proposed for L and LI is supported by degradative and synthetic routes and spectral data. L had a melting point of 155-157° and showed strong absorption at 2.95 and 5.90μ in its infrared spectrum (Figure 16, page 64). LI had a melting point of 195-197° and showed strong absorption at 2.95 and 5.88μ in its infrared spectrum (Figure 17, page 66). Both isomers were synthesized from phenanthrone (XXXIV) by the scheme shown in Figure 18, page 68. The infrared (KBr) and n.m.r. ($CDCl_3$) spectra and melting point of synthetic L are identical to those of L obtained from the irradiation of phenanthrone (XXXIV) in aqueous acetic acid (Figure 16, page 64). The infrared spectrum (KBr) and melting point of synthetic LI are identical to those of LI obtained from the irradiation of phenanthrone in aqueous acetic acid (Figure 17, page 66). Synthetic LI was obtained in quantities insufficient for an n.m.r. spectrum.

Further support for the gross structures of L and LI comes from dehydration studies. Treatment of a mixture of L

Figure 15. Infrared spectra

Top - 2,4-Dinitrophenylhydrazone derivative (LV) from ozonolysis of LII (potassium bromide pellet)

Bottom - 2,4-Dinitrophenylhydrazone derivative (LV) from LIV (potassium bromide pellet)


FREQUENCY (CM⁻¹)
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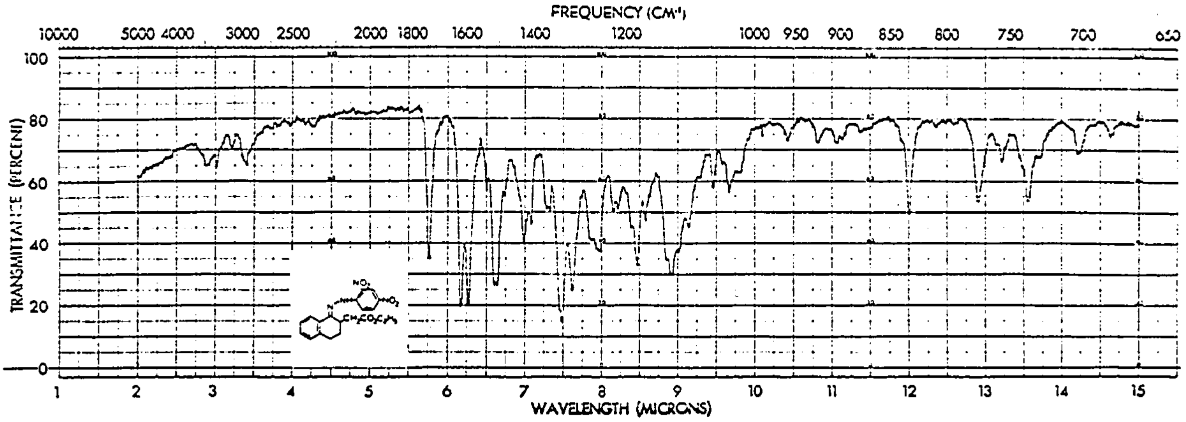
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
NO₂
NO₂
N
CH₂CO₂C₂H₅


FREQUENCY (CM⁻¹)
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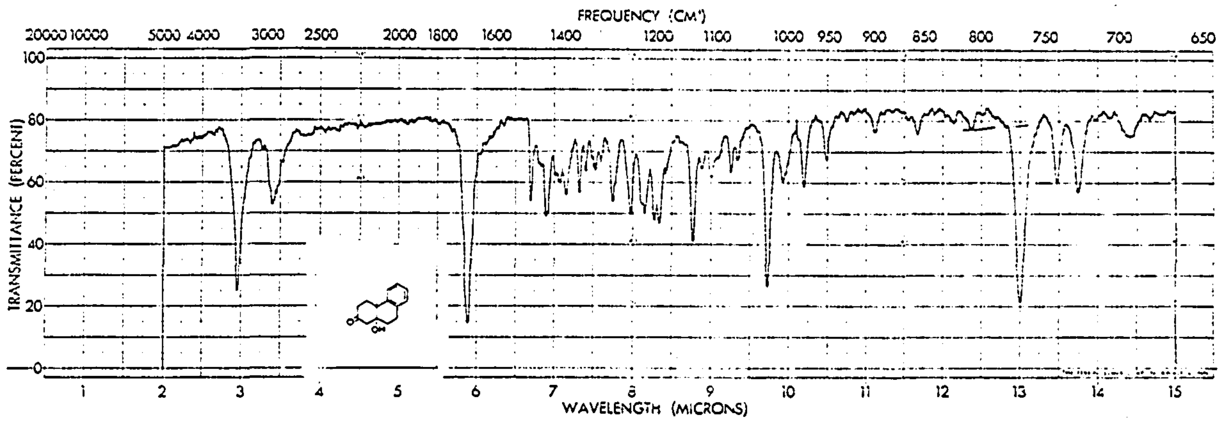
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
NO₂
NO₂
N
CH₂CO₂C₂H₅

Figure 16. Infrared spectra

Top - Ketol (L) from irradiation of XXXIV (potassium bromide pellet)

Bottom - Ketol (L) from synthetic preparation (potassium bromide pellet)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TRANSMITTANCE (PERCENT)
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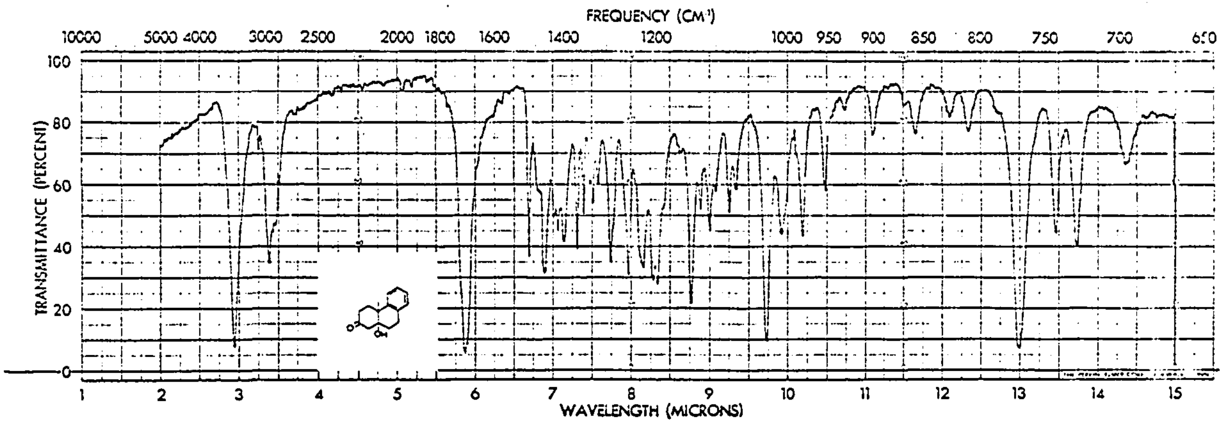
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
OH


FREQUENCY (CM⁻¹)
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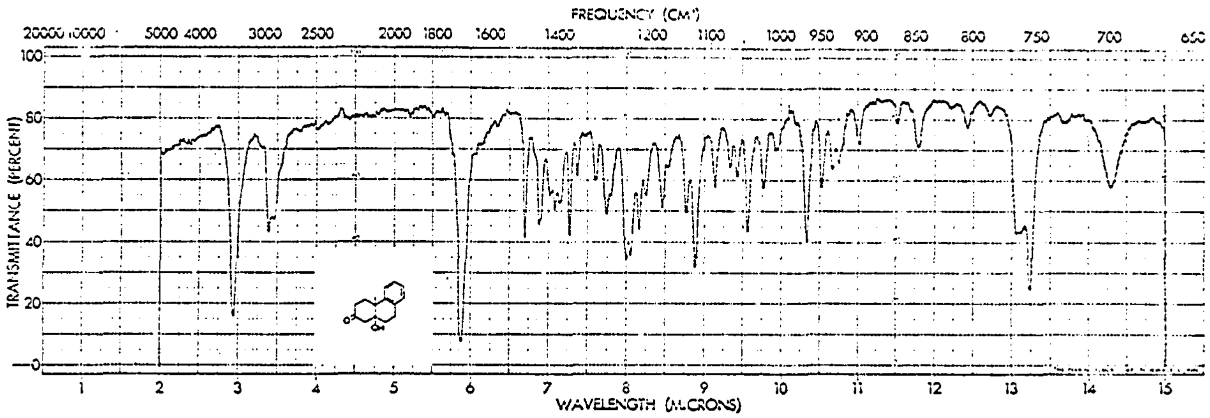
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
OH

Figure 17. Infrared spectra

Top - Ketol (LI) from irradiation of XXXIV (potassium bromide pellet)

Bottom - Ketol (LI) from synthetic preparation (potassium bromide pellet)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5000 4000
3000
2500
2000
1800
1600
1400
1200
1100
1000
950
900
850
800
750
700
650
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
OH
O

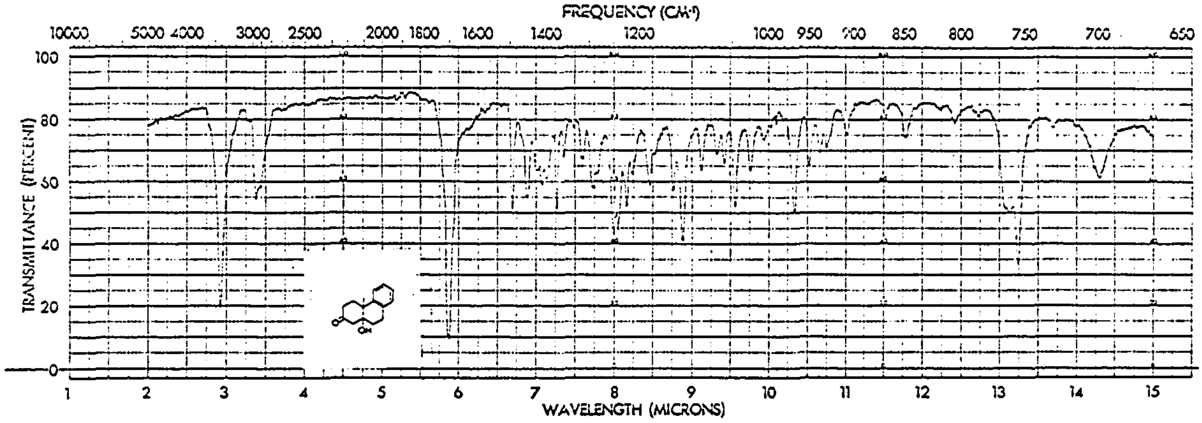
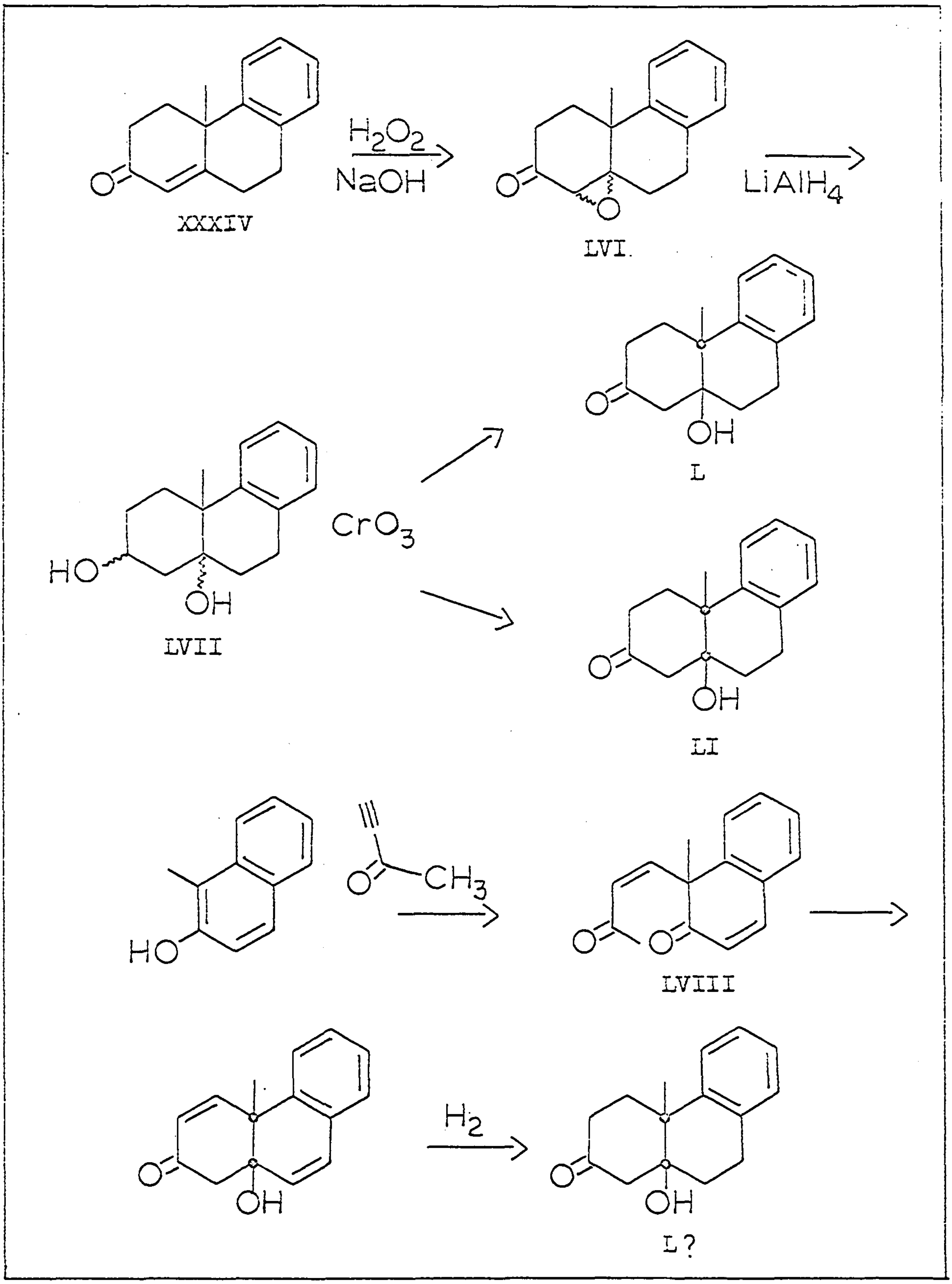

FREQUENCY (CM⁻¹)
10000
5000 4000
3000
2500
2000
1800
1600
1400
1200
1000
950
900
850
800
750
700
650
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)
OH
O

Figure 18. Scheme for synthesis of L and LI


XXXIV
H_2O_2
NaOH
LVI.
$LiAlH_4$
L
LVII
CrO_3
LI
CH_3
LVIII
H_2
L?

and LI with phosphorous oxychloride in pyridine produced a decrease in the intensity of the methyl groups of L and LI (n.m.r. analysis) and produced new peaks at 4.10 and 8.43τ, which are the identical absorption bands exhibited by the vinyl and methyl hydrogens of authentic phenanthrone (XXXIV).

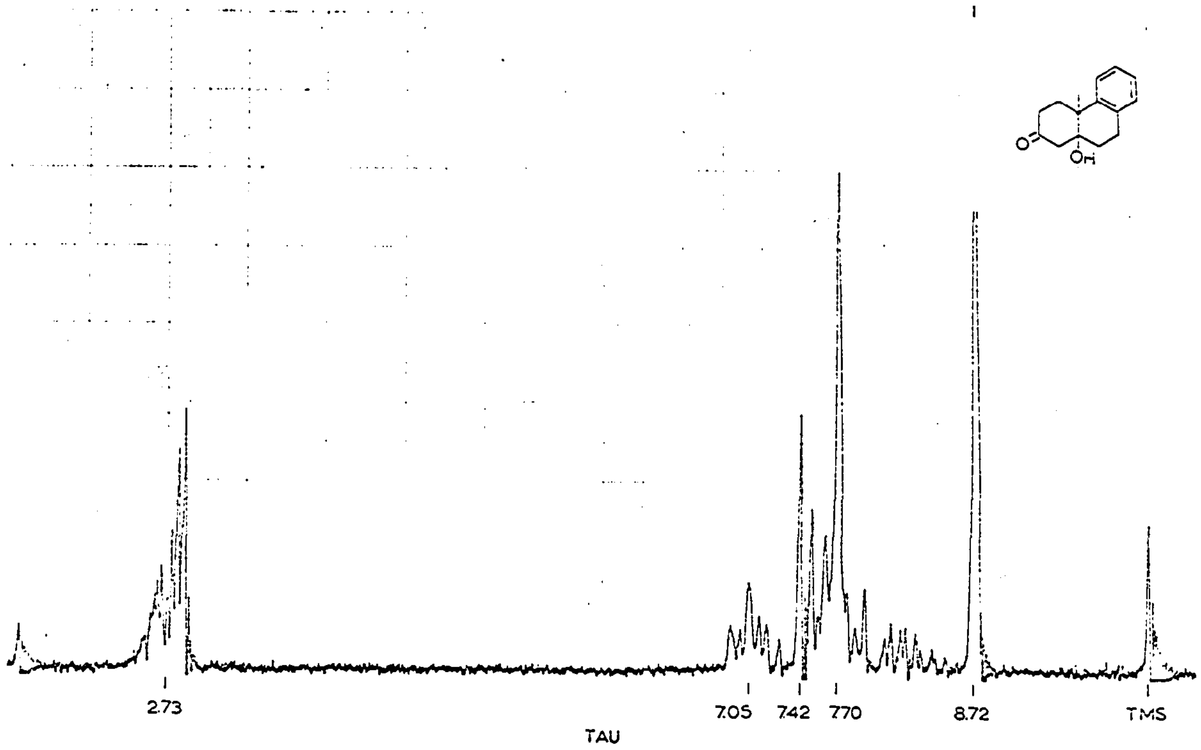
The stereochemistry shown for L and LI is tentatively assigned on the basis of the n.m.r. spectra (Figure 19, page 71). L exhibits a methyl absorption band at 8.72τ and because of its fixed conformation due to the <u>trans</u> ring juncture, the angular methyl group experiences little or no deshielding from the benzene ring. LI exhibits a methyl absorption band at 8.55τ. In one of the conformations of <u>cis</u>-LI, the methyl group becomes almost coplanar with the benzene ring and therefore experiences a deshielding effect due to the ring current of the aromatic ring. The peaks at 7.42τ and 8.15τ in the spectra of L and LI respectively, disappear on shaking the samples with D_2O with the simultaneous appearance of a peak at 5.37τ caused by HOD. It should be noted that Wenkert (40) has tentatively assigned the <u>cis</u> stereochemistry to the low melting isomer because of the lower likelihood of a butenone side chain forming a <u>trans</u> bridge (Figure 18, page 68).

The structures proposed for XLVIII a,b, XLIX, L and LI have, at this point, been proven. Questions as to their origins, however, still remain. Treatment of XXXV with 75%

Figure 19. Nuclear magnetic resonance spectra

Top - Ketol (L) obtained from irradiation of XXXIV (deuteriochloroform solution)

Bottom - Ketol (LI) obtained from irradiation of XXXIV (deuteriochloroform solution)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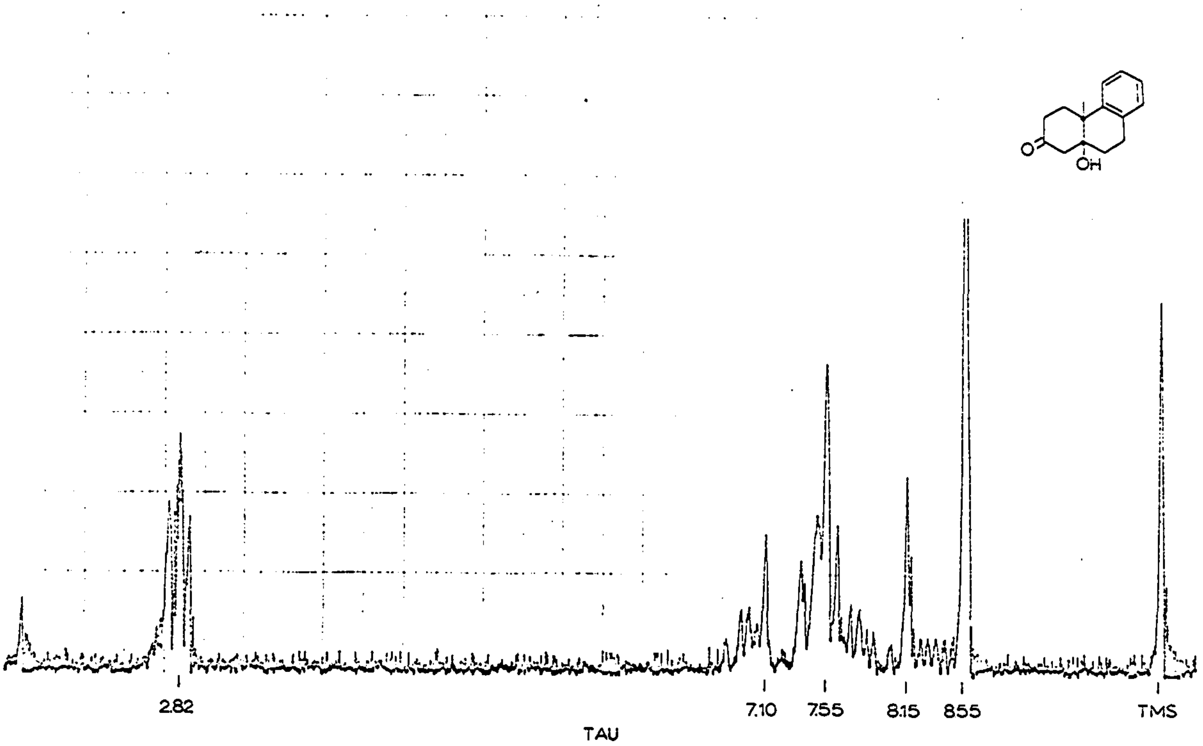
7.05
7.42
7.70
8.72
TMS
TAU
O
OH


2.82
7.10
7.55
8.15
8.55
TMS
TAU
O
OH

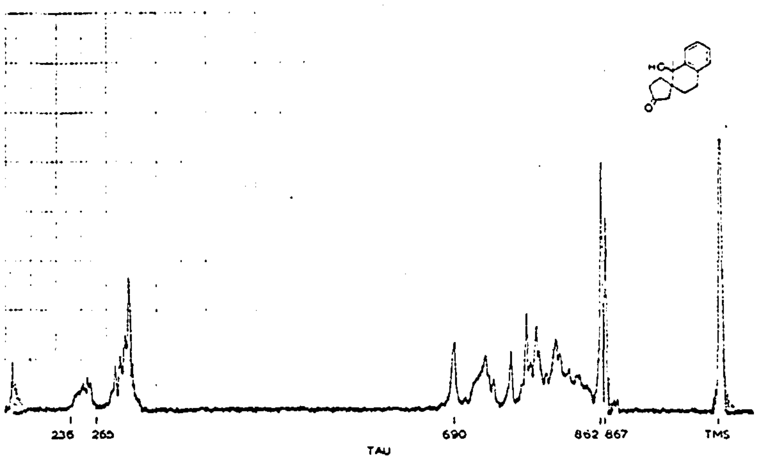
aqueous acetic acid at room temperature in the absence of light for the same period of time used for the irradiation of XXXIV (126 hours) resulted in a crude mixture whose n.m.r. spectrum is shown in Figure 20, page 74. The spectrum is almost identical to that of the ketols XLVIII a,b. The peak at 9.92τ is stopcock grease and the peak at 8.49τ is assigned to the methyl group of XXXV. On shaking the sample with D_2O, the broad singlet at 6.93τ disappeared with the simultaneous appearance of a singlet at 5.37τ due to HOD. The two characteristic spikes at 4.56 and 5.12τ are assigned to the exo-methylene protons of XLIX. The absence of absorptions at 8.5 and 8.7τ shows that L and LI are not produced via this pathway. Thus the acid catalyzed conversion of XXXV to XLVIII a,b and XLIX is almost quantitative during this period of time. A preliminary experiment in the acid catalyzed destruction of XXXV in dilute refluxing sulfuric acid gave a crude product whose infrared spectrum was almost superimposable upon that of XXXIV. This may be a case of kinetic vs. thermodynamic product control similar to that published by Freeman (41). It is interesting to note that acid treatment of XVI (21) and XIX, R=Ac (42) results in 1,5-bond cleavage while 1,10-bond cleavage is noted for LIX (43). Kropp (44) has recently studied the acid catalyzed rearrangements of the dehydro analogues. Irradiation of XXXV in 75% acetic acid for 126 hours, however, gives a completely different and

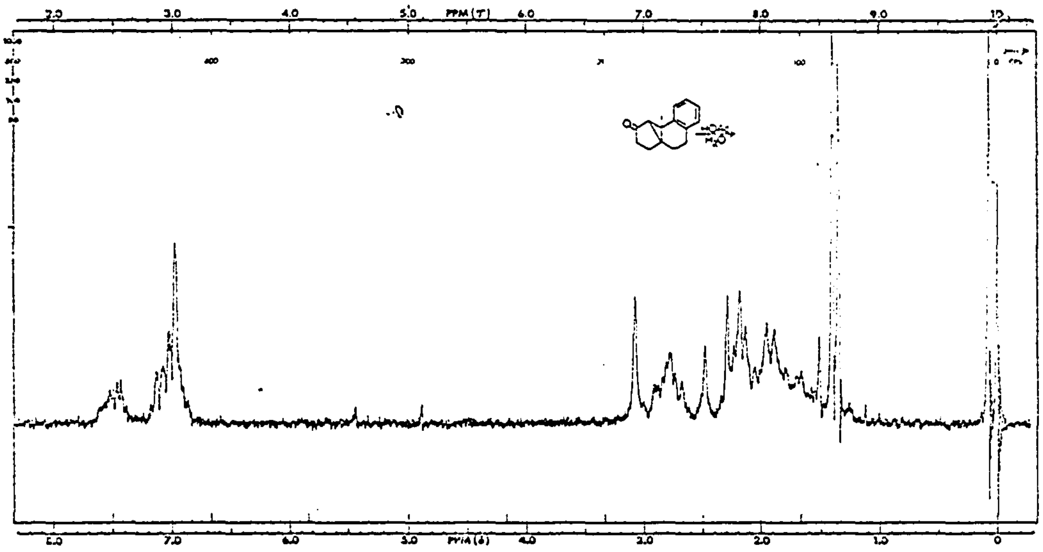
Figure 20. Nuclear magnetic resonance spectra

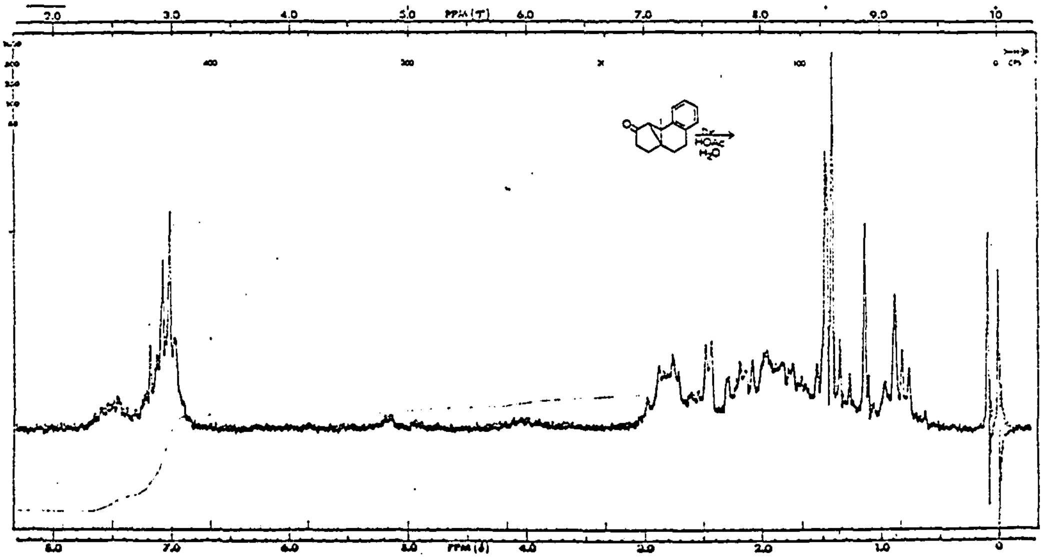
Top - Ketols XVIII a,b (carbon tetrachloride solution)

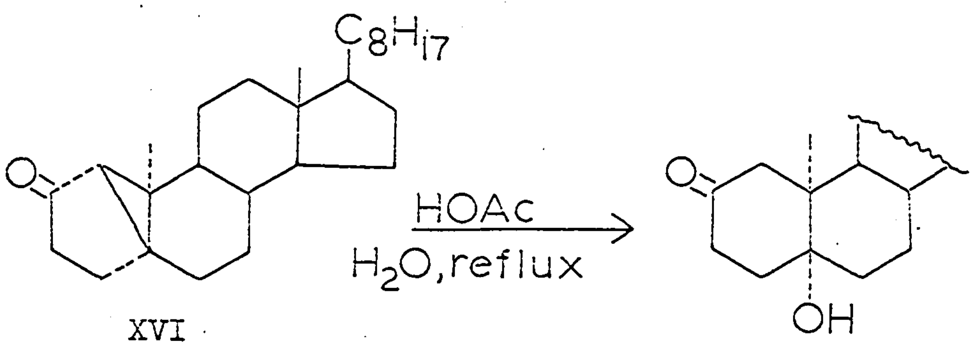
Middle - Acid catalyzed rearrangement of cyclophenanthrone (XXXV) (carbon tetrachloride solution)

Bottom - Irradiation of cyclophenanthrone (XXXV) in aqueous acetic acid (carbon tetrachloride solution)

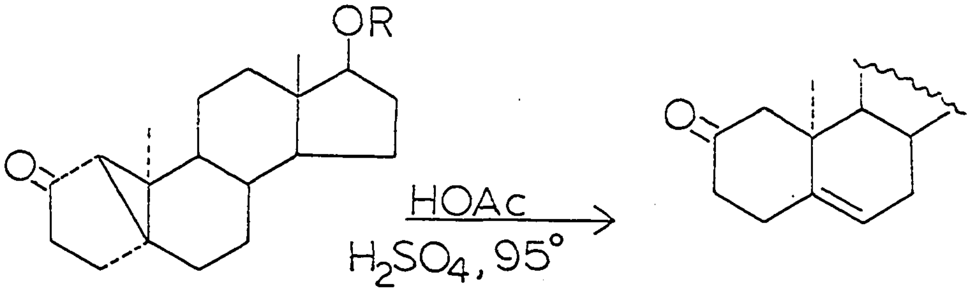

HC
236
265
690
862
867
TMS
TAU


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
100
0 CPS
H₂O
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

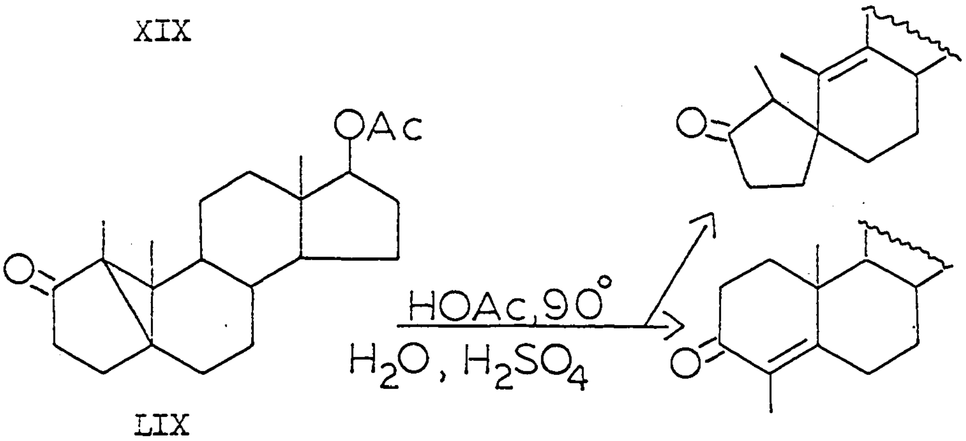

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
100
0 CPS
HOAc
H₂O
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0



XVI



XIX



LIX

more complex set of products as shown by the n.m.r. spectrum (Figure 20, page 74). The upfield region of the spectrum is considerably more complex than that shown by the dark reaction. Very noticeable is the complete lack of the hydroxyl band at 6.93τ. Shaking the sample with D_2O produced absolutely no change in the spectrum, showing the lack of significant amounts of alcohol including L and LI. Thus, L and

LI are shown to be true photoproducts originating directly from XXXIV.

These data leave two alternatives for the production of XLVIII a,b and XLIX during the irradiation of XXXIV. Since they are not derived from the photochemical rearrangements of XXXV, they may be the products of the acid catalyzed rearrangement of XXXV or they may be true photoproducts originating directly from XXXIV. The former explanation is preferred because of the following reasoning. Although a high yield of XXXV is produced from the irradiation of XXXIV in t-butanol, its concentration in aqueous acetic acid must be small because of its acid catalyzed destruction. Hence, the amount of light absorbed by XXXV in the presence of large amounts of XXXIV should also be small and destruction of XXXV via this pathway negligible. One cannot, however, rigorously exclude the efficient photochemical destruction of XXXV (and consequently the production of XLVIII a,b and XLIX from XXXIV via a photochemical path) because of the possibility of energy transfer from XXXIV to XXXV.

The most interesting segment in the study of phenanthrone was carried out in an attempt to explain the stereospecificity of the photochemical rearrangements of some 2-cyclohexenones (see Historical). In 1961 Zimmerman (1, 2) proposed a detailed mechanistic scheme in an attempt to explain the photochemical rearrangements of cross-conjugated cyclohexadienones. Since the appearance of his original communication, he has published several other papers in an attempt to refine and support his mechanistic theories (45, 46). Since the advent of photochemical rearrangements of simple 2-cyclohexenones (21, 22), Zimmerman has adapted his mechanistic scheme to include these also (26, 27, 47). At the time the work to be presented here was begun, Zimmerman had attempted to explain (47) the stereospecific photochemical rearrangement of Δ^4-cholesten-3-one (XV) (21). His mechanistic scheme is shown in Figure 21, page 79. The open circles represent electrons in a heavily 2S-weighted orbital. The "y"s represent electrons in the $2P_y$-oxygen orbital, which lies in a plane perpendicular to the $2P_x$-oxygen orbital used in forming the Pi-bond to carbon. The solid circles represent the Pi-electrons. Four discrete steps are included in this scheme:

a) Promotion of a non-bonding (n) P_y-electron to a Pi-antibonding (π^*) orbital.

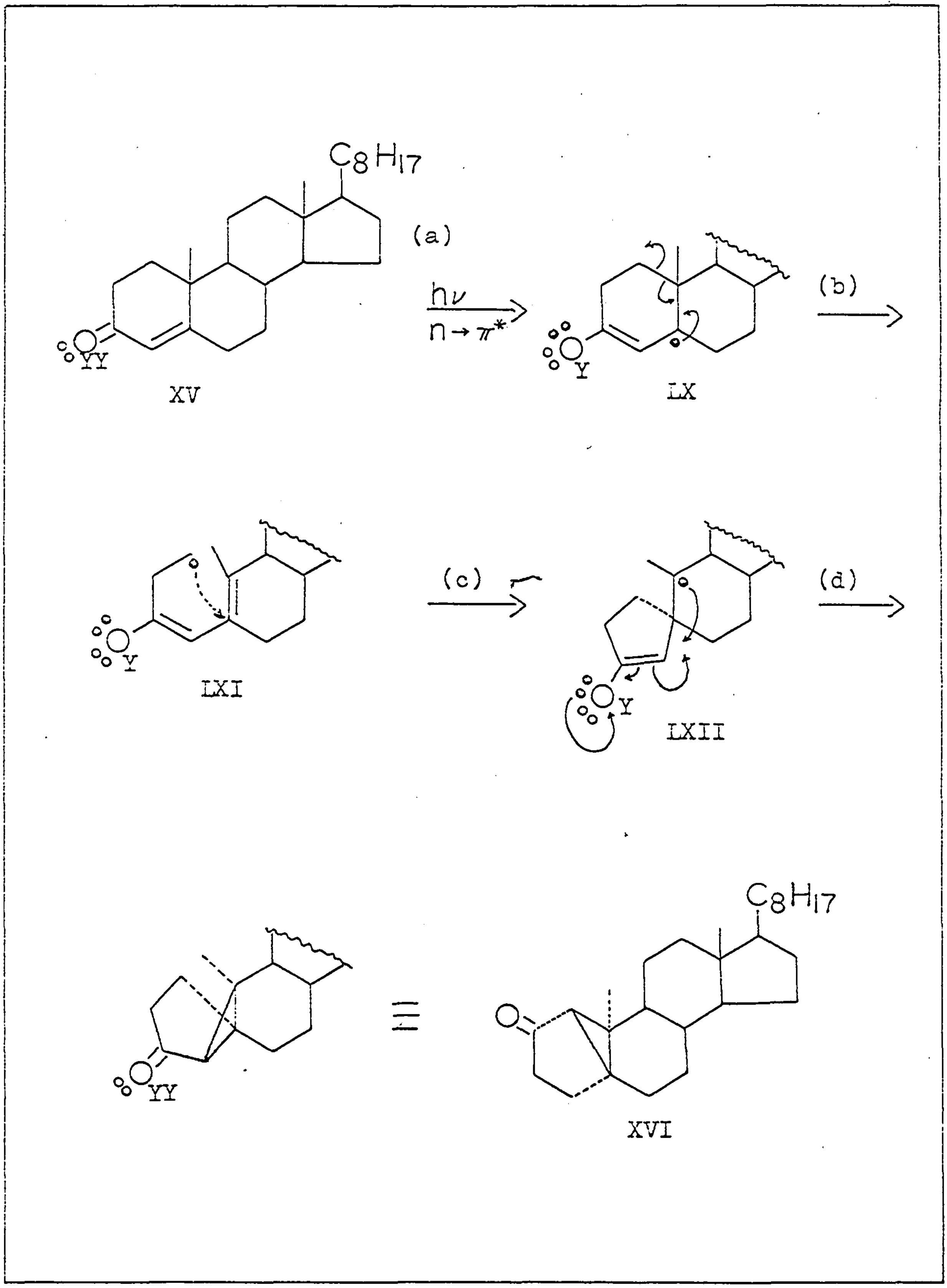
b) Homolytic fission of the 1,10-bond.

c) Intramolecular odd-electron addition to the 5,10-double bond via rearward apprcach.

d) Electron demotion ($\pi^* \rightarrow n$) and 4,10-bond formation.

The stereospecificity of the reaction is attributed to a conformational preference of the side chain in species LXI, which

Figure 21. Mechanistic scheme proposed by Zimmerman


C_8H_{17}
(a)
XV
$h\nu$
$n \rightarrow \pi^*$
LX
(b)
LXI
(c)
LXII
(d)
≡
C_8H_{17}
XVI

leads to preferred rearward attack at C-5. (This explanation carries with it the implication that in the absence of a preferred conformation, rotation about the 4,5-bond will be fast compared to the rate of odd electron addition to C-5). All of the systems which had been investigated up until this time, contained the possibility for a similar conformational preference of the species analogous to LXI.

In order to disprove or support this proposed pathway, a system was investigated which would yield a species analogous to LXI, but which would provide the radical side chain no conformational preference. Such a system is 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV, phenanthrone) and the analogous mechanism is shown in Figure 22, page 82. If a conformational preference of the side chain in LXIV is necessary for stereospecificity, then racemic product (XXXV) should be obtained since LXIV does not afford that preference.

Irradiation of optically pure (see Experimental) phenanthrone (XXXIV d, $[\alpha]_D^{27} = +332^\circ$) in t-butanol gave rise to 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone* (XXXV l, cyclophenanthrone) with $[\alpha]_D^{27} = -40.2^\circ$ and irradiation of XXXIV l with $[\alpha]_D^{27} = -332^\circ$ gave XXXV d with

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*This author wishes to acknowledge Dr. William Welstead's complete structural proof for XXXV (see Figure 23, page 84 for the degradative scheme) and his preliminary irradiations of optically impure XXXIV.

Figure 22. Mechanistic scheme for phenanthrone (XXXIV)

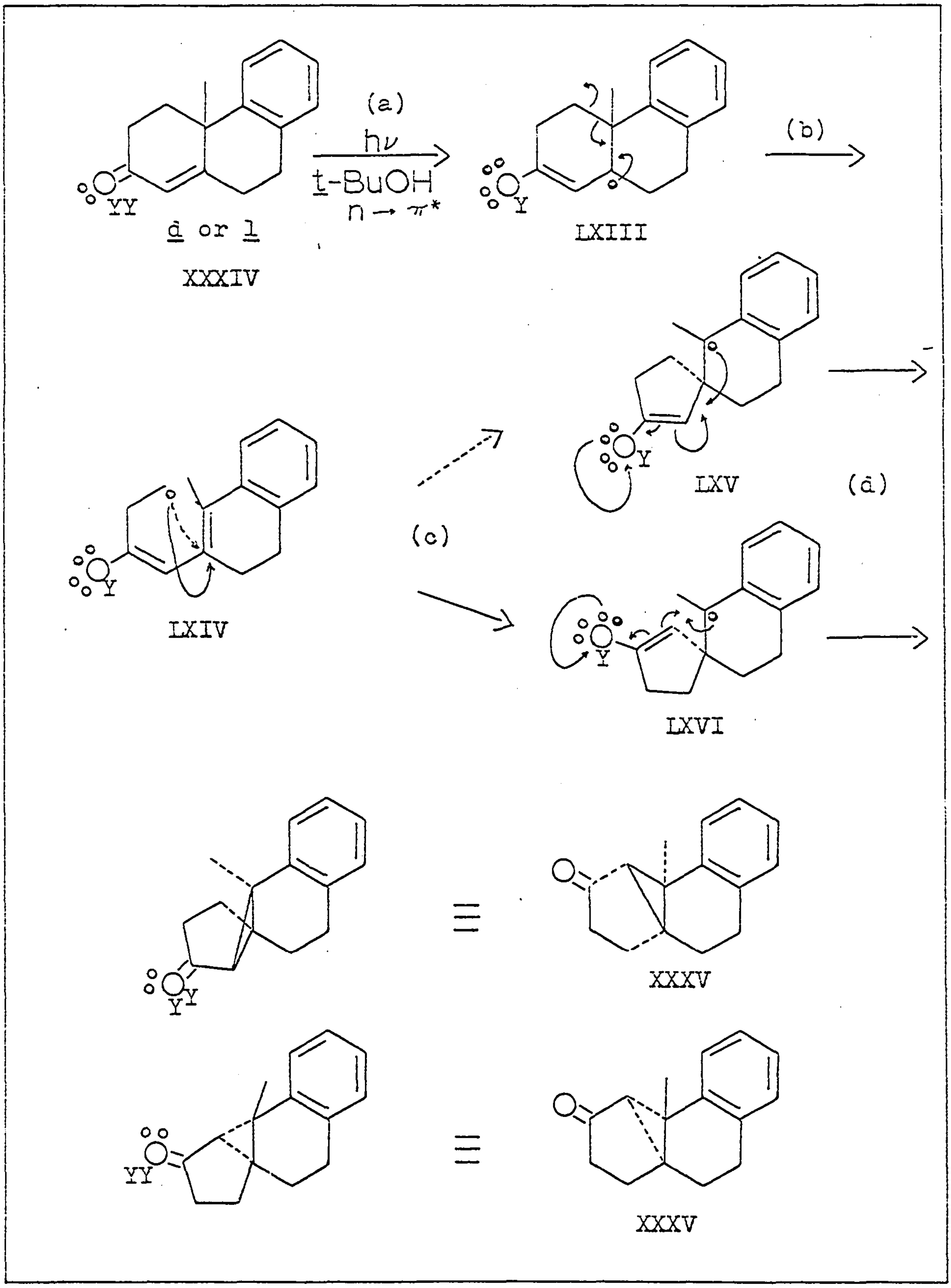
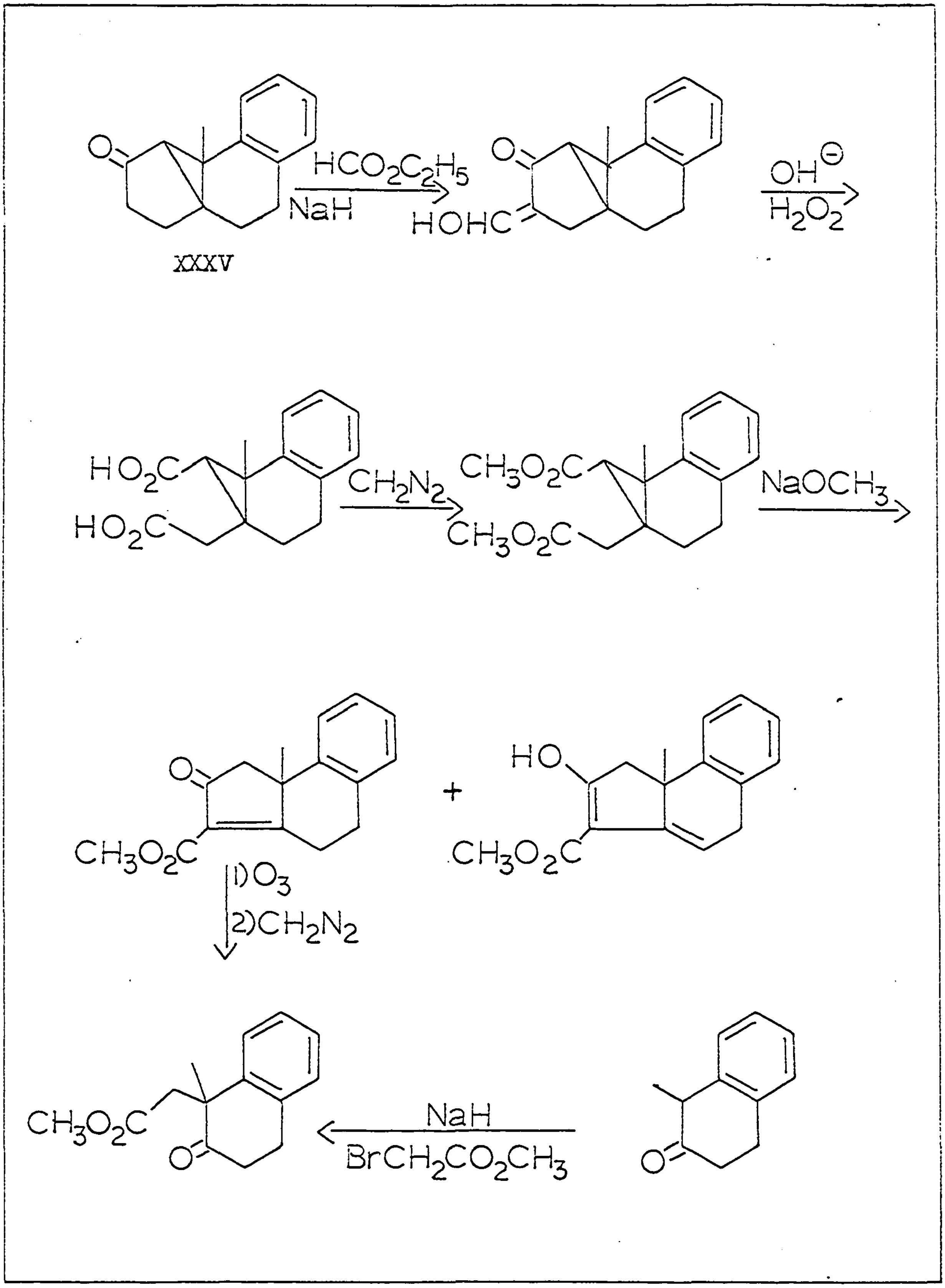

(a)
hν
t-BuOH
n → π*
YY
d or l
XXXIV
Y
LXIII
(b)
LXIV
(c)
LXV
(d)
LXVI
YY
≡
XXXV
YY
≡
XXXV

Figure 23. Degradative scheme for XXXV



XXXV
$HCO_2C_2H_5$
NaH
HOHC
$OH^{\ominus}$
H_2O_2
HO_2C
HO_2C
CH_2N_2
CH_3O_2C
CH_3O_2C
$NaOCH_3$
CH_3O_2C
+
HO
CH_3O_2C
1) O_3
2) CH_2N_2
CH_3O_2C
NaH
$BrCH_2CO_2CH_3$

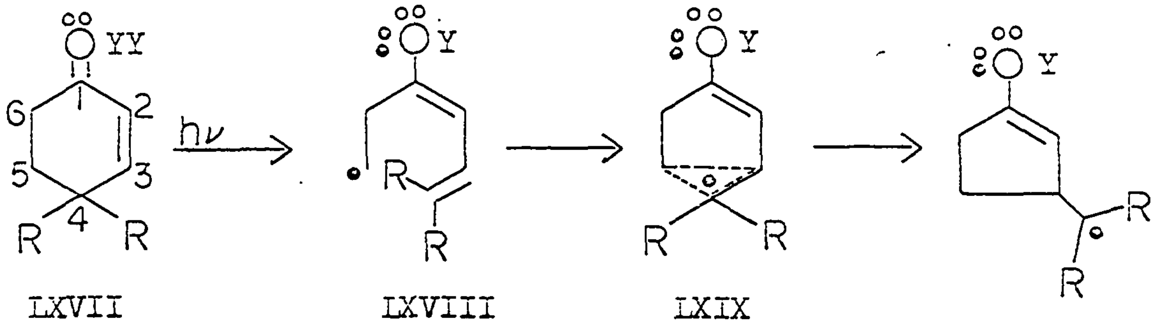
$[\alpha]_D^{27} = +40.9^\circ$. The phenanthrone recovered from each of these reactions had specific rotations of $+323^\circ$ and -3[illegible]° respectively. Optically pure (see Experimental) cyclophenanthrone has specific rotations of -42.3° and $+42.5^\circ$ respectively. Thus the conversion of XXXIV to XXXV proceeds with a degree of stereospecificity in excess of 95%. In view of these results, two mechanistic pictures are possible:

a) The scheme proposed by Zimmerman is essentially correct and species LXIV does exist (although not necessarily as a diradical), but in this case, the stereospecificity of the rearrangement cannot be attributed to a conformational preference of the side chain (this possibility is not excluded in those cases where a preferred conformation does exist however). Rather, 1,5-bond formation must be much faster than attainment of a planar state (in which the molecule becomes symmetrical) and also faster than rotational equilibration about the 4,5-bond which would make frontward and rearward attack at C-5 equally probable.

b) A concerted mechanism is applicable and the species LXIV does not exist.

This author prefers a concerted mechanism since if 1,5-bond formation must necessarily be much faster than attainment of a planar state and rotation about the 4,5-bond, the rate of the reaction is such that it already approaches concertedness (this assumes that attainment of a planar state or rotation about the 4,5-bond is not sterically or electronically hindered so that either of these becomes very slow or impossible).

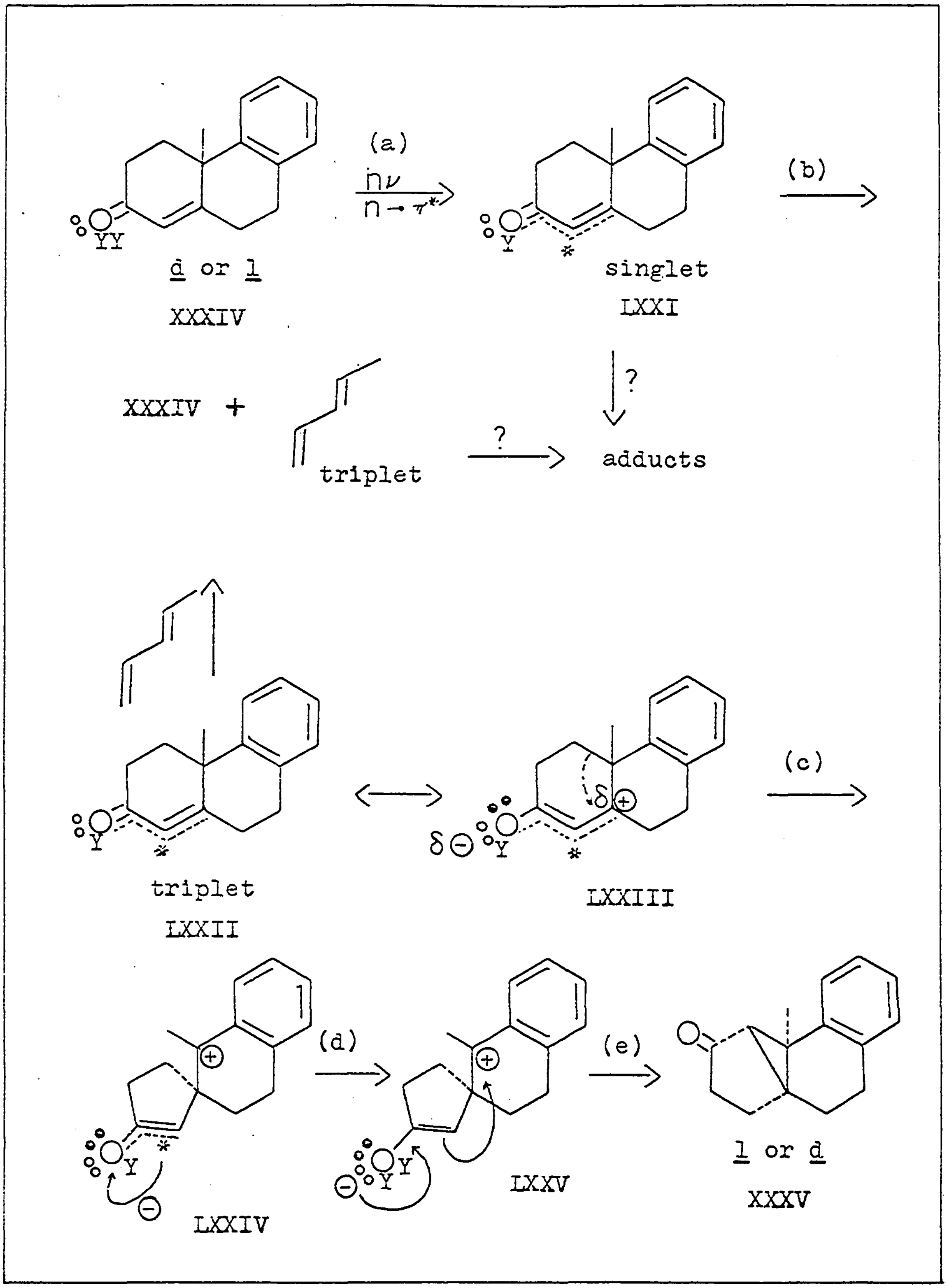
After this work had been in progress for a considerable length of time, Zimmerman published a refined mechanism (27) involving 4,4-dialkyl-2-cyclohexenone (LXVII). This mechanistic picture included a species (LXVIII) analogous to LXIV.



LXVII LXVIII LXIX LXX

He states, however, that although the radical species at C-5 is pictured as completely released, the possibility of an intervening species (LXIX), in which C-5 is not completely released from the remaining Pi-system before bonding to C-3 occurs, definitely exists. This is in fact, admitting the possibility of a concerted bond migration. Since authenticated alkyl migrations of radical species are virtually unknown (48), this author prefers the mechanism shown in Figure 24, page 88. In this scheme, the open and solid circles and "y"s have the same designation as that used by Zimmerman. The * is used to represent the electron in the Pi-antibonding

Figure 24. Proposed mechanistic scheme for phenanthrone (XXXIV)


d or l
XXXIV
(a)
hν
n → π*
singlet
LXXI
(b)
XXXIV +
triplet
?
adducts
?
triplet
LXXII
δ⊖
δ⊕
LXXIII
(c)
LXXIV
(d)
LXXV
(e)
l or d
XXXV

orbital. This scheme includes the following five steps:

a) Promotion of an electron from the P_y-oxygen nonbonding orbital (n) to a Pi-antibonding orbital (π^*). This electron is delocalized over the entire Pi-system, which is pictorially demonstrated by the dotted line. A similar pictorial representation has recently been used by Saltiel (49).

b) Intersystem crossing from the first excited singlet state (LXXI) to the lowest lying triplet state (LXXII) of the molecule. The $\delta\oplus$ and $\delta\ominus$ are used to denote the relative electronic charge in the Pi-bonding orbital system only.

c) Concerted 1,10-bond breakage and 1,5-bond formation.

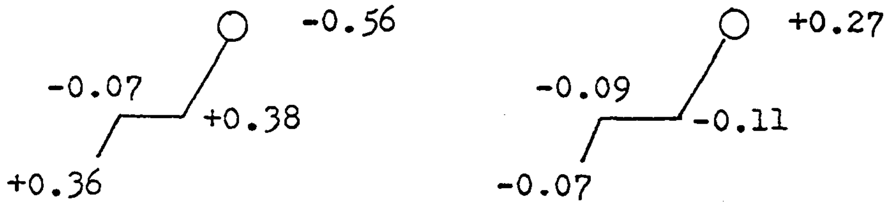
d) Electron demotion of an electron from the Pi-antibonding system to the P_y-oxygen orbital.

e) 4,10-Bond formation via a zwitterionic intermediate.

The triplet LXXII is included in this scheme because Zimmerman has shown by acetophenone sensitization that the triplet state of XXXIV is responsible for the production of XXXV (26). In an attempt to support this, XXXIV was irradiated in the presence of benzophenone, also a known triplet sensitizer (50, 51). This resulted in a complex mixture of unidentified products including reduction products. However, the reaction proved to be sensitized nicely by dibenzothiophene with no side products being formed. This may have been due to true triplet sensitization, but because of the known fluorescence (52) and unknown intersystem crossing efficiency of dibenzothiophene (53), singlet sensitization cannot be rigorously excluded. Irradiation of XXXIV in the presence of piperylene (1,3-pentadiene), a known triplet quencher (54), resulted in the complete absence of XXXV in the reaction products and in the production of photoaddition products between XXXIV and piperylene. These products could arise by the addition of triplet piperylene to ground state XXXIV or/ and by the addition of ground state piperylene to excited singlet LXXI. These two possibilities were arrived at by the following reasoning. Addition of triplet α,β-unsaturated ketone (2-cyclopentenone) to ground state olefin (cyclopentene) has been shown to occur (57). In general, α,β-unsaturated ketones are believed to have triplet state energies near 70 kcal./mole. For example 4,4-diphenyl-2-cylohexenone (XXXVII) has a triplet state energy of 68.5 kcal./mole (27). Ethylene, on the other hand, has a triplet state energy of about 82 kcal./mole (49). Hence, triplet energy transfer from 2-cyclopentenone to cyclopentene is probably endothermic and hence inefficient. However, when 2-cyclopentenone or 2-cyclohexenone is irradiated in the presence of cyclopentadiene, triplet energy transfer from ketone to olefin is very efficient (49), since the transfer is now probably exothermic. If it is assumed that XXXIV has a triplet energy near

70 kcal./mole, transfer of this energy to piperylene will be exothermic (triplet energy of piperylene is 58.8 and 56.9 kcal./mole for <u>trans</u> and <u>cis</u> respectively) (55) and hence probably diffusion controlled (56). However, it has not been shown that triplet diene cannot add to ground state ketone and this cannot be excluded as a possibility. Hence, cycloaddition products can arise indirectly from LXXII. Singlet energy transfer from LXXI to piperylene should be inefficient because of the relative singlet-singlet absorptions of XXXIV (313mμ) and piperylene (224mμ) (58). The addition products can therefore also arise by addition of LXXI to ground state piperylene. One other possibility for the formation of the addition products is the absorption and reaction of a complex between XXXIV and piperylene.

The excited state is shown as being a hybrid of structures LXXII and LXXIII. Brand (59) found that n → π^* excitation of acrolein increases the C-O bond length and causes a considerable redistribution of the Pi-electrons. He has also shown that a greater bond order is associated with the central rather than with the terminal C-C bond. This is reasonable, since on promotion of an electron from a non-bonding orbital which is highly localized on oxygen to a Pi-antibonding orbital which extends over the entire Pi-system, the oxygen becomes electron deficient. It is only reasonable then, that the electrons in the Pi-bonding orbital system are polarized toward oxygen to alleviate this deficiency. Hence, in the Pi-<u>bonding</u> orbital system, the β-carbon maintains a partial positive charge. Also it is reasonable to assume that it is the Pi-<u>bonding</u> orbital system which will be important in bonding. That the β-carbon shows carbonium ion-character is suggested by the addition of water to the double bond of XXXIV during irradiation in acetic acid-water. Solvent addition during photochemical reactions has been shown to occur in the case of 4,4-dimethyl-2-cyclohexenone (see Historical) and 2-cyclooctenone (60). Zimmerman and others (2, 61) have argued that in the n → π* excited state of a ketone, the oxygen becomes electron poor and the carbon skeleton electron rich relative to the ground state. Thus LCAO-MO calculations show (49) the ground and excited state electron distribution to be:



Ground state   n → π*   Excited state

It is therefore argued that a zwitterionic species in which the oxygen is depicted as having a negative and the carbon a positive charge (62, 63) is not a descriptive picture of the excited state. Studies of formaldehyde however, have shown that although the dipole of the n → π* excited state is smaller than that of the ground state, the polarization remains in the same direction, that is, oxygen negative and carbon positive (64).

1,10-Bond breakage with simultaneous 1,5-bond formation gives rise to a species LXXIV, in which a formal positive charge is now localized on C-10, while the negative charge is shown to be delocalized over the remaining Pi-system. Electron demotion ($\pi^* \rightarrow n$) gives LXXV, a ground state zwitterionic species for which ground state resonance structures may be written. It should be pointed out here that irradiation of XXXIV in t-butanol gave a small amount (ca. 1.5%) of XLIX. However, XLIX is also produced by irradiating XXXV in t-butanol, but this, of course, does not exclude a direct photochemical path from XXXIV. In any case, XLIX probably arises from a state similar to LXXIV or LXXV via proton loss; a similar product is produced in the irradiation of 4,4-dimethyl-2-cyclohexenone (see Historical). Also, the irradiation of XXXV in t-butanol produced no detectable amounts of XXXIV, in opposition to the results reported by Jeger (see Historical).

In the mechanistic scheme just described proton donation was not included since the reaction occurs as readily in benzene (see Historical). In any case, if proton donation does in fact occur, it is not clear at what stage this should be invoked.

In conclusion, it is interesting to compare the photochemistry of the cross-conjugated cyclohexadienones (for a review see (65)) with the results which have been given here. The photochemical reactions of cross-conjugated cyclohexadienones in general exhibit four characteristics:

1) The reactions are stereospecific.
2) The reactions are solvent sensitive and the incorporation of solvent (usually water) is common.
3) Alkyl migrations reminiscent of carbonium ion rearrangements are common.
4) The reactions occur with high quantum efficiency ($\Phi \approx 1.0$).

The photochemical reactions of simple α,β-unsaturated ketones, on the other hand, exhibit the following characteristics:

1) The reactions are stereospecific (XXXIV → XXXV).
2) The reactions are solvent sensitive and products resulting from incorporation of solvent are found (L and LI).
3) Alkyl migrations are common (XXXIV → XXXV).
4) The reactions occur with low quantum efficiency ($\Phi \approx 10^{-2}$-10^{-3}) (26).*

Seemingly, the only difference between the photochemical reactions of these classes of compounds rests in their relative

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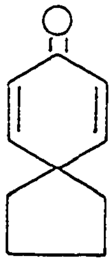
*T. A. Bettig, Department of Chemistry, Iowa State University, Ames, Iowa. Research on 2-cyclohexenones. Private communication. 1965.

quantum efficiencies. It is interesting to speculate that this relatively low efficiency shown by simple 2-cyclohexenones is due to two factors, low efficiency of intersystem crossing and low efficiency in triplet to product conversion. The former could be supported by the ability to trap the singlet LXXI as well as the singlet excited state of 4,4-dimethyl-2-cyclohexenone,* and the inability to trap that of spiro-(4,5)-deca-1,4-diene-3-one (LXXVI).** The latter is supported by the quenching of the triplet LXXII and by the inability to quench the triplet of 4,4-diphenycyclohexadienone with naphthalene (45).



LXXVI

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*T. A. Rettig, Department of Chemistry, Iowa State University, Ames, Iowa. Research on 2-cyclohexenones. Private communication. 1965.

**S. Dominianni, Department of Chemistry, Iowa State University, Ames, Iowa. Research on cross-conjugated cyclohexadienones. Private communication. 1965.

EXPERIMENTAL

Instruments and Methods

All melting points are uncorrected and were measured on a Kofler microscope hot stage equipped with a polarizer.

The ultraviolet spectra were obtained in 95% ethanol solution unless otherwise noted. The spectra were recorded on a Beckman Model DK-2A spectrophotometer made available by a grant (NSF-G14916) from the National Science Foundation.

All infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

The nuclear magnetic resonance spectra were measured on a Varian Associates Model HR-60 or A-60 spectrometer operating at 60 Mc. Spectra obtained with the HR-60 spectrometer were calibrated by the side band technique using tetramethylsilane as internal standard. Chemical shifts are reported as τ-values (66).

All optical rotations were measured at the sodium D line on an O. C. Rudolph & Sons Model 399 polarimeter. All samples were weighed directly into 5 ml. volumetric flasks and diluted with 3 ml. of 95% ethanol delivered by means of a volumetric pipet. Two mls. of solution were then introduced into a jacketed 1 dm. polarimeter tube of 2 ml. capacity. All final rotations were measured at 27° at a concentration of 1 g. of sample per 100 ml. of solvent. All final rotations were determined at 1/10 dilution to determine the validity of reported specific rotations.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York or Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Resolution of Racemic 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone and Racemic 4a-Methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone

Preparation of 2-tetralone

2-Tetralone was prepared by the procedure of Barltrop and Saxton (67) and purified through the bisulfite addition compound (68).

Preparation of 1-methyl-2-tetralone

1-Methyl-2-tetralone was prepared by the procedure of Stork *et al*. (69).

Preparation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV)

Phenanthrone (XXXIV) was prepared by the method of Howell and Taylor (70). Recrystallization from Skelly B with rapid magnetic stirring gave XXXIV as fine crystals, m.p. 89-90° and $\lambda_{max}^{t\text{-}BuOH}$ 313mμ (50), $\lambda_{max}^{95\%\ EtOH}$ 235mμ (17,100) (reported (70) 90°; (71) 90-91°, λ_{max}^{EtOH} 236mμ (17,000); (40) 89-90°, λ_{max} 239mμ (18,000)). The infrared spectrum (Figure 4, page 27) exhibits absorption at 3.30, 3.38, 3.43, 6.03, 6.61, 6.68, 6.90, 7.07, 7.28, 7.35, 7.44, 7.57, 7.62, 7.80, 7.92, 8.08, 8.37, 8.57, 9.23, 9.37, 9.59, 9.83, 10.12, 10.48, 10.68, 10.87, 11.51, 11.95, 12.65, 12.97, 13.18, 13.32, 13.67 and 14.32 μ.

Preparation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone pyrrolidine enamine (XL)

An anhydrous methanol solution of phenanthrone (XXXIV, 3.0 g. in 12 ml.) was heated under nitrogen just to the boiling point. Pyrrolidine (1.3 g.) was added all at once, and a precipitate began to form immediately. After cooling, the product was filtered off and washed with cold methanol. The melting point (107-109°) was unchanged after recrystallization from hexane. The yield of recrystallized product was 3 g. (80%). The infrared spectrum (KBr, 6.09, 6.21μ) and the ultraviolet spectrum ($\lambda_{max}^{abs.\ EtOH}$ 284μ (22,200)) are consistent with XL (28).*

Anal. Calcd. for $C_{19}H_{23}N$: C, 85.98; H, 8.75. Found: C, 85.77; H, 8.65.

Preparation of the d-camphor-10-sulfonic acid salt of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone pyrrolidine enamine (XLI)

To a magnetically stirred, hot acetone solution of the phenanthrone enamine (XL, 11.7 g. in 70 ml.) was added a

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*The author is indebted to Dr. William Welstead for obtaining the physical constants and analysis for the enamine.

hot acetone solution of d-camphor-10-sulfonic acid ($[\alpha]_D^{27}$ = +40°, c 2.5, 95% ethanol; 10.5 g. in 35 ml.). On cooling in ice, the stirred solution soon deposited a yellow solid (XLI, 18.5 g., crop I) which was filtered and washed with cold acetone. Ether (150 ml.) was added to the filtrate, and continued stirring and cooling of this solution gave more of the yellow solid (1.0 g., crop II).

Resolution of the d-camphor-10-sulfonic acid salt of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone pyrrolidine enamine (XLI)

A systematic recrystallization of XLI was carried out in ethyl acetate-methanol solvent. Deposition of crystals was effected by ice cooling of the magnetically stirred solutions. All rotations were obtained using approximately 0.03 g. of salt in 3 ml. of 95% ethanol except in the cases of the final maximum rotations when exactly 0.030 g. was used in 3 ml. of 95% ethanol. The recrystallization scheme is shown in Table 1, page 19.

The salt labeled N-1 in Table 1 proved to be XLI l, m.p. 163-167°. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ EtOH}$ 269mμ (23,000). For the infrared spectrum see Figure 2, page 22, and for the n.m.r. spectrum see Figure 3, page 24.

Anal. Calcd. for $C_{29}H_{39}O_4NS$: C, 69.99; H, 7.90; N, 2.82; S, 6.43. Found: C, 69.66; H, 7.62; N, 2.98; S, 6.61.

The salt labeled O-1 in Table 1 proved to be XLI d, m.p.

167-184°. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ EtOH}$ 269mμ (23,400). The infrared spectrum is shown in Figure 2, page 22, and the n.m.r. spectrum is shown in Figure 3, page 24. Anal. Calcd. for $C_{29}H_{39}O_4NS$: C, 69.99; H, 7.90; N, 2.82; S, 6.43. Found: C, 70.06; H, 8.13; N, 2.59; S, 6.75.

Hydrolysis of the d-camphor-10-sulfonic acid salts of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone pyrrolidine enamine (XLI)

The levorotatory salt XLI 1 (4.2 g.; $[\alpha]_D^{27} = -131°$, c 1.0, 95% ethanol) was dissolved in water (200 ml.), and a dilute solution of aqueous potassium hydroxide (0.5 g. in 100 ml.) was added with stirring. A precipitate formed immediately, and the suspension was allowed to stir at room temperature for five minutes. The mixture was then made acidic to litmus with dilute hydrochloric acid and extracted five times with ether. The combined ether extracts were then washed twice with dilute hydrochloric acid, dilute sodium bicarbonate and saturated sodium chloride solutions. The ether was dried over magnesium sulfate, filtered and removed under reduced pressure, giving rise to a slightly yellow solid (1.7 g.). The solid was dissolved in pentane and treated twice with charcoal. Complete removal of solvent gave phenanthrone XXXIV 1 (1.5 g.; m.p. 64.5-67.5°; $[\alpha]_D^{27} = -325°$, c 1.0, 95% ethanol). Recrystallization of this material from pentane gave XXXIV 1 which had a melting point of 68.0-69.0°

and showed $[\alpha]_D^{27}$ = -332° (c 1.0, 95% ethanol). The infrared spectrum is shown in Figure 4, page 27, and shows absorptions at 3.31, 3.41, 6.05, 6.13, 6.71, 6.91, 6.98, 7.07, 7.25, 7.35, 7.45, 7.55, 7.80, 7.92, 8.08, 8.38, 8.50, 8.63, 8.84, 9.09, 9.22, 9.38, 9.60, 9.75, 9.84, 10.51, 10.64, 10.85, 11.40, 11.59, 11.91, 12.67, 13.14, 13.57 and 14.43 µ.

The same hydrolysis procedure was used for the dextrorotatory salt XLI d (4.3 g.; $[\alpha]_D^{27}$ = +168°, c 1.0, 95% ethanol) and gave crude phenanthrone XXXIV d (1.8 g.; m.p. 64-69°; $[\alpha]_D^{27}$ = +328°, c 1.0, 95% ethanol). Recrystallization of this material from pentane gave XXXIV d with a melting point of 68-69° and $[\alpha]_D^{27}$ = +332° (c 1.0, 95% ethanol). The infrared spectrum is shown in Figure 4, page 27, and is superimposable upon that of XXXIV l.

Formation of racemic 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV d,l) by combination of equal amounts of optically active forms (XXXIV d and XXXIV l)

Phenanthrone ((XXXIV d; 15.71 mg.; $[\alpha]_D^{27}$ = +332°) and (XXXIV l; 15.71 mg.; $[\alpha]_D^{27}$ = -332°)) was weighed out onto the same glassine paper and then brushed into an agate mortar and completely dissolved in ether. After evaporation of the ether, the residue was crushed with an agate pestle. This treatment gave racemic phenanthrone with a melting point of 87-89°. Its infrared spectrum (KBr) was exactly superimposable upon that of genuinely racemic phenanthrone (m.p. 89-90°)

obtained by synthesis.

Synthesis of the pyrrolidine enamine of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone and its subsequent reaction with d-camphor-10-sulfonic acid

Cyclophenanthrone (XXXV, 1.22 g.), pyrrolidine (1.3 ml.), d-camphor-10-sulfonic acid (catalytic amount) and toluene (150 ml.) were refluxed under nitrogen for 29 hours, a Dean-Stark water trap being used for water removal. During this time, an additional 2 mls. of pyrrolidine were added in 0.5 ml. increments. Removal of the solvent under reduced pressure gave rise to a dark brown oil. The infrared spectrum (capillary film) of the oil showed a strong 6.18μ absorption, consistent (28) with the double bond stretching mode of the desired enamine.

The oil was taken up in acetone and d-camphor-10-sulfonic acid (1.34 g.) was added. Cooling of this mixture afforded no crystalline products. Addition of the ether to the acetone solution deposited a brown, gummy solid which was washed with ether and dried under vacuum. The infrared spectrum ($CHCl_3$) showed the 5.77μ carbonyl absorption of a camphoric ketone (36) and the 6.00μ absorption of a carbon-nitrogen double bond characteristic of iminium salts (32). However, attempted recrystallization from ethyl acetate, methanol, ethanol, acetonitrile, acetone and chloroform gave no crystalline products.

Preparation of the d-camphor-10-sulfonic acid salt of pyrrolidine

A solution of d-camphor-10-sulfonic acid in ether-methanol was added to a cooled, stirred solution of pyrrolidine in ether. Filtration of the resulting solid and recrystallization from ethyl acetate gave pyrrolidine d-camphor-10-sulfonate (m.p. 120-122°). The infrared spectrum (KBr) showed the expected (36) absorption bands at 2.93, 3.41, 5.75, 8.25 and 9.60 μ.

Attempted synthesis of the d-camphor-10-sulfonic acid salt of the pyrrolidine enamine of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XLIV) using pyrrolidine d-camphor-10-sulfonate

Cyclophenanthrone (XXXV, 1.0 g.), pyrrolidine d-camphor-10-sulfonate (1.43 g.) and toluene (100 ml.) were refluxed for 16 hours using a Dean-Stark water trap to remove any water which formed in the reaction flask. Removal of the toluene under reduced pressure gave a tan solid (2.18 g.). The infrared spectrum (KBr) showed absorptions at 2.93 and 5.89μ which is consistent (36) with a simple mixture of the two starting materials and is inconsistent with the desired salt XLIV.

Preparation of the perchloric acid salt of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone pyrrolidine enamine (XLV)

The procedure used was that established by Leonard and Paukstelis (32). Cyclophenanthrone (XXXV, 7.7 g.) was dissolved in hot absolute ethanol (45 ml.). To this solution (which was allowed to cool to about 30°) was added pyrrolidine perchlorate (6.4 g.) and two drops of pyrrolidine. After allowing this solution to stand at room temperature for 3 hours, the crystals of XLV (12.5 g., m.p. 177-181°) were filtered off and washed with ethanol. The infrared spectrum (KBr) showed the desired (32) 5.98μ absorption of the carbon-nitrogen double bond and the broad 9.15μ absorption of perchlorate.

Anal. Calcd. for $C_{19}H_{24}O_4NCl$: C, 62.37; H, 6.61; N, 3.83; Cl, 9.69. Found: C, 62.39; H, 6.75; N, 3.69; Cl, 9.64.

Preparation of the potassium salt of d-camphor-10-sulfonic acid

The procedure used was that published by Pope and Gibson (72). To a solution of d-camphor-10-sulfonic acid (73.5 g.) in ethanol-water (1:1, 100 ml.) was added aqueous potassium hydroxide until the solution was basic to litmus. The solution was made acidic to litmus with a small amount of the acid. Removal of the solvent under reduced pressure deposited a solid which was recrystallized from ethanol yielding white needles (72 g., m.p. > 310°).

Preparation of the d-camphor-10-sulfonic acid salt of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone pyrrolidine enamine (XLIV)

The perchloric acid salt of cyclophenanthrone pyrrolidine enamine (XLV, 12.5 g.) was introduced into an Erlenmeyer flask containing absolute methanol (75 ml.) and the potassium salt of d-camphor-10-sulfonic acid (8.9 g.). The flask was then stoppered, and its contents were magnetically stirred for 13 hours at room temperature. The potassium perchlorate produced by exchange was then filtered off, and the methanol was removed under reduced pressure. Addition of acetone (10 ml.) to the clear-colorless residue precipitated more potassium perchlorate, which was filtered off. Removal of the acetone under reduced pressure and the addition of ethyl acetate (3 ml.) to the residue with subsequent cooling and scratching of the solution, produced white crystals of XLIV.

Resolution of the d-camphor-10-sulfonic acid salt of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone pyrrolidine enamine (XLIV)

A systematic recrystallization of XLIV was carried out in ethyl acetate-methanol solvent. Deposition of crystals was effected by ice cooling of the magnetically stirred solutions. All rotations were obtained using approximately 0.03 g. of salt in 3 ml. of 95% ethanol except in the cases of the final maximum rotations when exactly 0.030 g. was used in 3 ml. of 95% ethanol. The recrystallization scheme is shown in

Table 2, page 32.

The salt in Table 2 labeled K-2, proved to be XLIV d, m.p. 128-131°. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ EtOH}$ 268mμ (9,000), 232mμ (8,100) calculated for the monohydrate (see analysis). The infrared spectrum is shown in Figure 6, page 36, and the n.m.r. spectrum is shown in Figure 7, page 38.

Anal. Calcd. for $C_{29}H_{39}O_4NS \cdot H_2O$: C, 67.55; H, 8.02; N, 2.72. Found: C, 67.64; H, 7.94; N, 2.81.

The salt in Table 2 labeled L-1 proved to be XLIV l, m.p. 117-122°. The ultraviolet spectrum showed $\lambda_{max}^{95\%\ EtOH}$ 268mμ (9,500), 232mμ (7,800) calculated for the monohydrate (see analysis). The infrared spectrum is shown in Figure 6, page 36, and the n.m.r. spectrum is shown in Figure 7, page 38.

Anal. Calcd. for $C_{29}H_{39}O_4NS \cdot H_2O$: C, 67.55; H, 8.02; N, 2.72. Found: C, 67.54; H, 7.95; N, 2.71.

Hydrolysis of the d-camphor-10-sulfonic acid salts of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone pyrrolidine enamine (XLIV)

The same procedure was used for the cyclophenanthrone salts as was used for the phenanthrone salts. Hydrolysis of XLIV d ($[\alpha]_D^{27}$ = +38.8°, gave dextrorotatory cyclophenanthrone as a white solid with a melting point of 100-110° and $[\alpha]_D^{27}$ = +39.6° (c 1.0, 95% ethanol). Recrystallization from Skelly B gave cyclophenanthrone (XXXV d) with a melting point of 110-111° and $[\alpha]_D^{27} = +42.5°$ (c 1.0, 95% ethanol). The infrared spectrum is shown in Figure 8, page 40, and shows absorptions at 3.44, 3.51, 5.86, 6.70, 6.79, 6.87, 6.97, 7.07, 7.20, 7.66, 7.84, 8.00, 8.12, 8.25, 8.41, 8.48, 8.72, 8.97, 9.43, 9.65, 9.84, 10.07, 10.45, 10.62, 11.07, 11.82, 12.15, 12.37, 12.82, 13.04 and 13.60 µ.

Hydrolysis of XLIV l ($[\alpha]_D^{27} = 0.00°$) gave levorotatory cyclophenanthrone as a white solid with a melting point of 98-109° and $[\alpha]_D^{27} = -38.0°$ (c 1.0, 95% ethanol). Recrystallization from Skelly B gave cyclophenanthrone (XXXV l) with a melting point of 109.5-111.5° and $[\alpha]_D^{27} = -42.3°$ (c 1.0, 95% ethanol). The infrared spectrum is shown in Figure 8, page 40, and is superimposable upon that of XXXV d.

Formation of racemic 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XXXV d,l) by combination of equal amounts of optically active forms (XXXV d and XXXV l)

Cyclophenanthrone ((XXXV d, 8.50 mg.; $[\alpha]_D^{27} = +42.5°$) and (XXXV l, 8.50 mg.; $[\alpha]_D^{27} = -42.3°$)) was weighed out onto the same glassine paper and then brushed into an agate mortar and completely dissolved in ether. After evaporation of the ether, the residue was crushed with an agate pestle. This treatment gave racemic cyclophenanthrone with a melting point of 85-87°. Its infrared spectrum (KBr) was exactly superimposable upon that of genuinely racemic cyclophenanthrone (m.p. 86-87°) obtained from racemic phenanthrone (XXXIV *d*,*l*).

Photochemistry of 4a-Methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in glacial acetic acid

Phenanthrone (XXXIV, 2.37 g.) was dissolved in glacial acetic acid (500 ml.) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 45 minutes and irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 42 hours the irradiation was terminated, and the acetic acid was removed under reduced pressure at 60° leaving a brown oil. The residue was taken up in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (12 x 4 cm.), 25 ml. fractions being collected. The following solvents were used for elution:

Eluent	Volume used (ml.)
1% ether in Skelly B	200
2% ether in Skelly B	200
3% ether in Skelly B	200
4% ether in Skelly B	200
5% ether in Skelly B	200
10% ether in Skelly B	200
15% ether in Skelly B	200
25% ether in Skelly B	700
35% ether in Skelly B	500
50% ether in Skelly B	700
75% ether in Skelly B	300
100% ether in Skelly B	400

Combination of fractions 34-46 gave an oil (XLVI) which amounted to 20-30 mg. The infrared spectrum is shown in Figure 9, page 44, and the n.m.r. spectrum is shown in Figure 10, page 46. The oil was dissolved in methanol (5 ml.) and treated with benzaldehyde (8 drops) and potassium hydroxide (50 mg.) at steam bath temperature for 0.5 hours. The mixture was then cooled, acidified with hydrochloric acid and extracted with ether. The ether layer was then extracted with sodium bisulfite solution to remove excess benzaldehyde and sodium bicarbonate solution to remove benzoic acid. The ether was then dried over magnesium sulfate and removed under reduced pressure giving rise to a white solid (XLVII), m.p. 119-123°; $\lambda_{max}^{95\% \ EtOH}$ 300.5mμ (16,000), 231mμ(s) (5,500). The infrared spectrum is shown in Figure 9, page 44. Insufficient material was obtained for further characterization. An attempt to repeat the photochemical reaction using an irradiation time of 120 hours failed to produce significant amounts of this compound.

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in aqueous acetic acid

Phenanthrone (XXXIV, 5.0 g.) was dissolved in 75% aqueous acid (300 ml.) and purged with nitrogen for 0.5 hours. The solution was irradiated in a Pyrex vessel using a 550 watt Hanovia high pressure mercury arc lamp. The progress of the irradiation was followed by observing the decay of the 235mμ absorption of the phenanthrone. After 126 hours, the absorbance had fallen from 0.885 to 0.350, while that of a sample kept in the dark for the same period of time in the same solvent remained at 0.877.

The irradiation was terminated at the end of 126 hours, and the reaction mixture was poured into water (1.5 l.) and extracted several times with chloroform. The combined chloroform washings were then washed with sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a brown oil. An n.m.r. spectrum of this oil in benzene showed singlets at 4.15 (presumably the olefinic proton of XXXIV), 8.64, 8.72, 8.78, 8.85 (very strong; presumably the angular methyl group of XXXIV) and 8.96 τ. The spectrum also showed a broad absorption band at 6.65 τ which disappeared on shaking the sample with D_2O. The crude reaction mixture from a separate irradiation of XXXIV in the same solvent was dissolved in carbon tetrachloride and its n.m.r. spectrum recorded. It showed singlets at 4.24 (olefinic proton of XXXIV), 8.47 (angular methyl group of XXXIV), 8.60, 8.65 and 8.79 τ. This spectrum also showed a broad absorption at 6.38 τ which disappeared on shaking the sample with D_2O.

The n.m.r. spectrum of XLVIII a,b in benzene showed singlet methyl absorptions at 8.65 and 8.72 τ, while that of L and LI show singlet methyl absorptions at 8.80 and 8.83 τ.

The n.m.r. spectrum of XLVIII a,b in carbon tetrachloride showed singlet methyl absorptions at 8.62 and 8.67τ.

The crude reaction mixture was taken up in a small volume of benzene and chromatographed on an alumina (Woelm, neutral grade III) column (23 x 4.5 cm.), 50 ml. fractions being collected. The separation proceeded as follows:

Eluent	Volume used
2% ether in Skelly B	500 ml.
4% ether in Skelly B	500 ml.
10% ether in Skelly B	500 ml.
12% ether in Skelly B	500 ml.
15% ether in Skelly B	1000 ml.
20% ether in Skelly B	500 ml.
35% ether in Skelly B	1000 ml.
50% ether in Skelly B	1000 ml.
70% ether in Skelly B	500 ml.
80% ether in Skelly B	500 ml.
100% ether in Skelly B	--

Fraction number	Weight in grams	Product composition
35-42	0.255	.150 g. XLIX + unidentified ketone
43-44	0.070	XXXV
48-68	1.63	XXXIV
108-119	0.985	XLVIII a,b
123-127	0.130	L and LI

The infrared spectrum (capillary film) of fractions 35-42 showed strong absorption at 5.75μ (5-membered ring ketone) and 5.85μ (6-membered ring ketone or acyclic aliphatic ketone). Weak bands at 3.30μ and 11.25μ can be assigned to a terminal methylene group. No other characteristic bands were observable. The n.m.r. spectrum of fractions 35-42 (CCl_4) showed a strong singlet at 8.67τ which is assigned to the ketone giving rise to the 5.85μ band in the infrared spectrum. Also observable in the n.m.r. spectrum are two singlets, 4.60 and 5.15τ, which are assigned to the exo-methylene protons of XLIX.

Thin layer analysis of fractions 43-44 showed XXXV to be present, but no other confirmation of this was obtained.

Fractions 108-119 contained XLVIII a,b. The infrared spectrum is shown in Figure 9, page 44. The n.m.r. spectrum (CCl_4) is shown in Figure 20, page 74. Addition of dimethylsulfoxide to the n.m.r. solution caused the 6.90τ singlet to disappear and a new singlet to appear at 5.13τ, indicating a tertiary alcohol (37).

Combined fractions 123-127 proved to be solid at room temperature. The n.m.r. spectrum ($CDCl_3$) of the crude material showed singlet absorptions at 8.58 and 8.71τ in the ratio of approximately 1:2. These absorptions correspond to LI and L, respectively. Addition of dimethylsulfoxide to the n.m.r. solution caused singlets to appear at 5.18, 5.40 and 5.74τ, the center band being about twice as intense as the others. It is doubtful that the sample contained only L and LI and the appearance of more than two singlets is probably due to impurities. Recrystallization of the mixture from benzene and methanol gave two crystalline products. The first (L) had a melting point of 155-157°. Its infrared and n.m.r. spectra are shown in Figure 16, page 64, and Figure 19, page 71, respectively. The second product (LI) had a melting point of 195-197°. The infrared spectrum is shown in Figure 17, page 66. The n.m.r. spectrum is shown in Figure 19, page 71.

Anal. for L and LI Calcd. for $C_{15}H_{18}O_2$: C, 78.23%; H, 7.88%. Found: C, 78.41%; H, 7.98%; C, 78.61%; H, 8.11%.

Stability check on 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in aqueous acetic acid

A solution of phenanthrone (XXXIV, 0.5 g.) in 75% aqueous acetic acid (30 ml.) was allowed to stand in the dark at room temperature for 141 hours and then worked up in the same manner as the mixture obtained from the irradiation of phenanthrone for 126 hours in 75% aqueous acetic acid. An n.m.r. spectrum (CCl_4) of the crude material was virtually superimposable upon that of pure phenanthrone.

Stability check on 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XXXV) in aqueous acetic acid

A solution of cyclophenanthrone (XXXV, 183 mg.) in 75% aqueous acetic acid (5 ml.) was allowed to stand in the dark at room temperature. Periodically, aliquots (5µl.) of this solution were withdrawn and diluted to 10 ml. with 95% ethanol, and the ultraviolet spectra of the resulting solutions were recorded. The reaction proceeded as follows:

Time (hrs.)	Absorbance (238mμ)
0	.831
22	.689
55	.506
117	.258

A solution of cyclophenanthrone (80 mg.) in 75% aqueous acetic acid (23 ml.) was allowed to stand in the dark at room temperature for 126 hours and then worked up in the same manner as the mixture obtained from the irradiation of phenanthrone (XXXIV) for 126 hours in 75% aqueous acetic acid. The n.m.r. spectrum of the crude mixture is shown in Figure 20, page 74.

Irradiation of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XXXV) in aqueous acetic acid

Cyclophenanthrone (XXXV, 0.8 g.) was dissolved in 75% aqueous acetic acid (230 ml.) and purged with nitrogen for 0.5 hours. The solution was irradiated in a Pyrex vessel using a 550 watt Hanovia high pressure mercury arc lamp for 126 hours. The solution was then worked up in the same manner as the mixture obtained from the irradiation of phenanthrone (XXXIV) for 126 hours in 75% aqueous acetic acid. The n.m.r. spectrum of the crude mixture is shown in Figure 20, page 74.

Dehydration of the spiroketol (XLVIII a,b)

A mixture of the spiroketols (XLVIII a,b, 870 mg.) in pyridine (10 ml.) was cooled under nitrogen to 0°. Phosphorous oxychloride (0.7 ml.) was then added under nitrogen over a period of 5 minutes, and the cold mixture was magnetically stirred for 2 hours. A small volume of the reaction mixture was then removed and analyzed by thin layer chromatography. This showed the reaction to be incomplete and more phosphorous oxychloride (1.5 ml.) was added. The mixture was allowed to stir at room temperature for a total of 100 hours, and was then poured onto cold 10% hydrochloric acid (200 ml.). The water layer was extracted with ether, which, in turn, was extracted with sodium bicarbonate solution and then dried over magnesium sulfate. Removal of the ether under reduced pressure gave a light brown oil (510 mg.). While the last traces of solvent were being removed from this oil by means of a vacuum pump, the oil turned a very dark brown color. This was passed through an alumina (Woelm, neutral grade III) column with benzene. Removal of the benzene under reduced pressure gave a light yellow oil (XLIX, 360 mg., 45%). The ultraviolet spectrum showed $\lambda_{max}^{95\%\ ethanol}$ 245mμ (10,900) and 282mμ (1,200). Its infrared spectrum is shown in Figure 12, page 53, and its n.m.r. spectrum is shown in Figure 10, page 46.

Preparation of the dibenzylidene derivatives (LII and LIII) of keto-olefin XLIX

Keto-olefin (XLIX, 350 mg.), potassium hydroxide (1.75 g.) and freshly distilled benzaldehyde (6 ml.) were heated in methanol (50 ml.) at 80° under nitrogen for 1 hour. The mixture was then poured onto iced, dilute hydrochloric acid and extracted with ether. The ether layer was then extracted several times with sodium bisulfite solution in order to remove excess benzaldehyde. The ether layer was then washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a red-orange oil. This was chromatographed on alumina (Woelm, neutral grade III) using benzene-Skelly B (1:1) as eluent.

The first material to elute (LII) (100 mg.) had a melting point of 128-136° which, when recrystallized from methanol was 136.5-138.5°. The second material to elute (LIII) (300 mg.) had a melting point of 150-165° which, when recrystallized from acetone-methanol was 173-175°. The infrared spectra of the high and low melting isomers are shown in Figure 12, page 53. The n.m.r. spectra are shown in Figure 14, page 59. The ultraviolet spectrum of the low melting isomer showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (30,100) and 239mμ (24,000). The ultraviolet spectrum of the high melting isomer showed $\lambda_{max}^{95\%\ EtOH}$ 347mμ (30,400) and 239 mμ (20,400). Since the high melting isomer contained some residual acetone not removed by drying (5.84μ carbonyl stretching frequency in the infrared spectrum and strong singlet absorption at 7.89τ in the n.m.r. spectrum), the molar extinction values reported for this isomer must be considered minimal.

The ultraviolet spectra of the dibenzylidene derivatives were again recorded after allowing the ethanol solutions used for the first spectra to stand on the laboratory bench for about two weeks. The high melting isomer then showed $\lambda_{max}^{95\% \text{ EtOH}}$ 347mμ (23,900) and 241mμ (20,300). The low melting isomer showed $\lambda_{max}^{95\% \text{ EtOH}}$ 347mμ (24,700) and 241mμ (21,000). These data suggest that the dibenzylidene derivatives are equilibrating to a common mixture, probably photochemically. Anal.: Low melting dibenzylidene derivative. Calcd. for $C_{29}H_{24}O$: C, 89.65; H, 6.23. Found: C, 89.66; H, 6.28. Molecular weight (mass spectrometric): 388 for both isomers.

Ozonolysis of the dibenzylidene derivatives LII and LIII

The low melting (m.p. 136.5-138.5) dibenzylidene derivative LII (50 mg.) was dissolved in ethyl acetate (50 ml.) and ozonized at Dry Ice-acetone temperatures. The solution turned a deep lavender color on the introduction of excess ozone. This solution was allowed to stand at room temperature until it became colorless. Then, 30% hydrogen peroxide solution (2 ml.) and water (5 ml.) were added, and the mixture was stirred at room temperature for 24 hours. The ethyl acetate layer was then washed with water several times and then with potassium iodide solu~~tion~~. Removal of the iodine from the ethyl acetate layer was accomplished with sodium thiosulfate solution. The ethyl acetate was then washed with water and saturated sodium chloride solution and dried over magnesium sulfate. Removal of solvent under reduced pressure gave an oil (10 mg.) which was taken up in ethanol (5 ml.) and treated with 2,4-dinitrophenylhydrazine reagent (73, 3 ml.). A precipitate formed within 30 seconds. This was filtered off (10 mg.) and had a melting point of 235-238°. This derivative proved to be the 2,4-dinitrophenylhydrazone of benzaldehyde. Its infrared spectrum (KBr) was superimposable upon that of the authentic 2,4-dinitrophenylhydrazone of benzaldehyde, m.p. 238-241° (reported (73) 237°).

All of the wash solutions used in the neutral workup were acidified (pH=2) and extracted with methylene chloride. The organic layer was then extracted with sodium bicarbonate solution, which was then acidified and extracted with methylene chloride. The organic phase was then dried over magnesium sulfate and evaporated under reduced pressure, leaving a solid residue (10 mg.). This was taken up in ethanol (5 ml.) and treated with 2,4-dinitrophenylhydrazine reagent (2 ml.). After approximately 24 hours had passed a precipitate finally appeared (5.8 mg., m.p. 143-150°). This was taken up in chloroform and passed through a celite-bentonite (1:3) column with chloroform. A solid was obtained (5.1 mg.) which was recrystallized from ethyl acetate-ethanol to give a 2,4-dinitrophenylhydrazone (2.7 mg., m.p. 163-165°) whose infrared spectrum was superimposable upon that of synthetic LV.

See Figure 15, page 62, for a comparison. A second crop of this derivative was obtained (1.0 mg.; m.p. 162-164°).

The same procedure was carried out on the high melting (m.p. 173-175°) dibenzylidene derivative LIII (80 mg.), but a smaller yield (0.3 mg.) of the 2,4-dinitrophenylhydrazone derivative (m.p. 163-165°) was obtained. It, too, had an infrared spectrum (KBr) superimposable upon that of synthetic LV.

Preparation of 3,4-dihydro-1(2H)-naphthalenone-2-acetic acid (LIV)

α-Tetralone (12.2 g.) was added over a period of 0.5 hours (under nitrogen) to a stirred mixture of benzene (150 ml.), sodium hydride (2.1 g.) and ethyl formate (7.5 g.). After a period of one hour at room temperature the mixture had to be cooled because of foaming. When the foaming had subsided, a light-brown, voluminous precipitate had formed. After a period of 3.5 hours at room temperature, the contents of the flask had set to a solid, light-brown mass. More benzene (75 ml.) was added to the reaction flask to facilitate stirring of the contents. Then methyl bromoacetate (13 g.) in benzene (50 ml.) was added over a period of one hour. The mixture was allowed to stir at room temperature for 11 hours and then refluxed for 2 hours. At this time a small volume of the tan-colored reaction mixture was removed and mixed with water. The water remained at a neutral pH. Addition of more sodium hydride to the reaction flask caused its contents to turn bright red. Addition of methyl bromoacetate discharged this color. Alternate addition of sodium hydride and methyl bromoacetate was continued until the reaction mixture was no longer red and showed a basic reaction with water. The excess base was then destroyed by the careful addition of methanol and finally ice-water. The contents were heated on a steam bath for 2 hours (enough sodium hydroxide was added to maintain basic conditions), cooled, and acidified. The mixture was extracted with benzene which in turn was extracted with sodium bicarbonate solution. This was acidified and extracted with benzene which was dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a solid (6.0 g.) which was recrystallized from ether-hexane to give a solid with a melting point of 107-109° (reported (74) 106-108°; (75) 109-110°). The infrared spectrum (KBr) showed strong absorption at 3-4µ (carboxyl), 5.87µ (carboxyl), and 5.92µ (conjugated carbonyl).

Preparation of the 2,4-dinitrophenylhydrazone of 3,4-dihydro-1(2H)-naphthalenone-2-acetic acid (LV)

2,4-Dinitrophenylhydrazine reagent (73, 20 ml.) was added to a solution of 1-tetralone-2-acetic acid (LIV, 300 mg.) in 95% ethanol (25 ml.). After 19 hours the crystals were filtered off and washed with ethanol. A considerable amount of the solid (260 mg.) would not dissolve in chloroform and was filtered off, m.p. 242-246°. The infrared spectrum (KBr) showed strong absorption at 5.86μ and medium absorption at 3-4μ indicating that this was the 2,4-dinitrophenylhydrazone of the acid. This compound was not further characterized.

The material which was soluble in chloroform was passed through a celite-bentonite (1:3) column using chloroform as the eluent. Removal of solvent from the eluent gave an orange solid (230 mg.), m.p. 162-164°. This was recrystallized twice from ethyl acetate-ethanol to give the 2,4-dinitrophenylhydrazone of the ester LV. The infrared spectrum is shown in Figure 15, page 62.

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.25; H, 4.89. Found: C, 58.14; H, 5.04.

Preparation of 1,10a-oxido-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrone (LVI)

A slightly modified version of a procedure published by Plattner *et al*. (76) was used for the epoxidation. Phenanthrone (XXXIV, 2.0 g.) was dissolved in methanol (300 ml.) which was then cooled to about 20° while being flushed with nitrogen. Hydrogen peroxide (30%, 15 ml.) and 4 N sodium hydroxide (15 ml.) were simultaneously added to the stirred solution over about 5 minutes. The yellowing mixture was stirred for approximately 10 hours at 0-5° and then allowed to come to room temperature. Stirring was continued for another 14 hours. At the end of this time the solution was colorless and a white solid had precipitated (the solid apparently was a type of peroxide salt which was very soluble in water and insoluble in ether; it decomposed violently on a melting point block). The contents of the flask were poured into 1.5 l. of water, and this solution was then extracted with ether. The combined ether layers were dried over magnesium sulfate and evaporated under reduced pressure leaving an oil (1.37 g.) which solidified on standing. Chromatography of the solid on alumina (Woelm, neutral grade III) using Skelly B-benzene (1:1) as eluent gave two products; the first (30 mg.) an oil and the second (1.1 g.) a solid. An n.m.r. spectrum of the solid material showed no olefinic absorptions and its infrared spectrum showed only 5.85μ carbonyl absorption. Its large melting point range and apparent inability to crystallize from hexane indicated that it was a mixture of epoxides, although thin layer analysis showed only one spot. No further purification of the solid was attempted.

Preparation of 2,10a-dihydroxy-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (LVII)

Epoxyphenanthrone (LVI, 1.1 g.) was added in small portions to a slurry of lithium aluminum hydride (0.2 g.) in ether (80 ml.). After addition was complete, the mixture was allowed to stir overnight. Moist sodium sulfate was added to the reaction mixture to destroy excess reducing agent and the mixture was filtered. Removal of the ether under reduced pressure gave a non-crystalline solid (1.16 g.), presumably a mixture of the expected diols LVII. No attempt was made to characterize the mixture.

Preparation of 4a-methyl-10a-hydroxy-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrone (L and LI)

The oxidizing reagent was prepared according to the procedure of Poos *et al.* (77). Chromic oxide (1.0 g.) was added in small portions to cooled pyridine (10 ml., 15-20°). To this mixture was added a solution of 2,10a-dihydroxyphenanthrone (LVII, 1.16 g.) in pyridine (10 ml.). The mixture was allowed to stand at room temperature for 24 hours and was then poured into ice water (400 ml.). The water was extracted with benzene-ether (1:1), filtration through celite being used to break emulsions. The organic phase was then extracted with cold 2% hydrochloric acid until the wash water remained acidic. The organic phase was then extracted with sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a solid (0.9 g.) with a wide melting range (m.p. 132-165°). Fractional crystallization first from methanol and then from benzene gave two crystalline products. The first had a melting point of 156-158°. Its infrared spectrum is shown in Figure 16, page 64. Its n.m.r. spectrum was identical to that of the keto-alcohol L obtained from the irradiation of phenanthrone

(XXXIV) in aqueous acetic acid. The second crystalline product had a melting point of 195-198°. Its infrared spectrum is shown in Figure 17, page 66. The amount of material isolated was insufficient for an n.m.r. spectrum.

Irradiation of levorotatory 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV 1)

Phenanthrone (XXXIV 1, 435 mg., $[\alpha]_D^{27} = -332°$) was dissolved in t-butanol (240 ml., distilled once from sodium) in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and then irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 6 hours the irradiation was terminated, and the t-butanol was removed under reduced pressure leaving an oily residue. The residue was taken up in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (4 x 15 cm.), 50 ml. fractions being collected. The separation proceeded as follows:

Eluent	Fraction number	Product composition (infrared analysis)
2% ether in benzene	1-12	nil
2% ether in benzene	13-25	XXXV
5% ether in benzene	26-29	XXXV
5% ether in benzene	30-31	XXXIV and XXXV
5% ether in benzene	32-54	XXXIV

Fractions 13-29 were combined and the solvent completely removed by means of a vacuum pump. The crude solid cyclophenanthrone weighed 210 mg. and showed $[\alpha]_D^{27} = +41.3°$ (c 1.0, 95% ethanol). Treatment of a pentane solution of this solid with charcoal and complete solvent removal gave cyclophenanthrone (XXXV d, 205 mg.) with $[\alpha]_D^{27}$ = +40.9 (c 1.0, 95% ethanol). The infrared spectrum (KBr) was superimposable upon that of cyclophenanthrone (XXXV d, $[\alpha]_D^{27}$ = +42.5°) obtained by resolution through its enamine salt.

Fractions 32-54 were combined and the solvent completely removed by means of a vacuum pump. The crude, solid phenanthrone weighed 210 mg. and showed $[\alpha]_D^{27}$ = -317° (c 1.0, 95% ethanol). Treatment of a pentane solution of this solid with charcoal and complete solvent removal gave phenanthrone (XXXIV l, 200 mg.) with $[\alpha]_D^{27}$ = -318° (c 1.0, 95% ethanol). The infrared spectrum (KBr) was superimposable upon that of phenanthrone (XXXIV l, $[\alpha]_D^{27}$ = -332°) obtained by resolution through its enamine salt.

A second similar experiment was carried out, using a longer irradiation time. Phenanthrone (XXXIV l, 430 mg.; $[\alpha]_D^{27}$ = -332°) was dissolved in t-butanol (200 ml., distilled once) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for one hour and then irradiated with a 550 watt Hanovia high pressure mercury arc lamp. The course of the reaction was followed by withdrawing about 2 ml. of solution and measuring its rotation in a 1 dm. polarimeter tube. The following shows the course of the reaction:

Time (hrs.)	Rotation (degrees)
0	-0.734
7.5	-0.343
18.5	-0.033

After 18.5 hours the irradiation was terminated, and the *t*-butanol was removed under reduced pressure leaving an oily residue. The residue was taken up in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (2 x 15 cm.), 10 ml. fractions being collected. The separation proceeded as follows:

Eluent	Fraction number	Product composition (infrared analysis CCl_4)
benzene	1-29	nil
benzene	30-34	XLIX (5.72μ carbonyl)
benzene	35-101	XXXV (5.82μ carbonyl)
2% ether in benzene	102-110	XXXV
10% ether in benzene	111-114	XXXV
10% ether in benzene	115-116	nil
10% ether in benzene	117-123	XXXIV (5.98μ carbonyl)
10% ether in benzene	124-127	nil

Fractions 35-114 were combined in pentane and treated twice with charcoal. Complete removal of solvent under reduced pressure gave cyclophenanthrone (XXXV *d*) with a melting point of 91-109.5° and $[\alpha]_D^{27} = +41.0^\circ$ (c 1.0, 95% ethanol). The solid was again dissolved in pentane and treated with charcoal. Complete removal of solvent gave XXXV *d* (130 mg.) with a melting point of 105-111° and $[\alpha]_D^{27} = +41.0^\circ$ (c 1.0, 95% ethanol). Its infrared spectrum (KBr) was superimposable upon that of cylophenanthrone (XXXV *d*, $[\alpha]_D^{27} = +42.5^\circ$) obtained by resolution through its enamine salt.

Fractions 117-123 were combined in pentane and treated twice with charcoal. Complete removal of solvent under reduced pressure gave slightly yellow phenanthrone (XXXIV l, 23 mg.) with a melting point of 57-66° and $[\alpha]_D^{27} = -318°$ (c 0.8, 95% ethanol). The infrared spectrum (KBr) was superimposable upon that of phenanthrone (XXXIV l, $[\alpha]_D^{27} = -332°$) obtained by resolution through its enamine salt.

Fractions 30-34 were combined to give a small amount (10-20 mg.) of material which exhibited a 5.72μ carbonyl absorption in its infrared spectrum (CCl_4), characteristic (36) of a five-membered ring ketone. The n.m.r. spectrum (CCl_4) exhibited a one proton multiplet at 2.35-2.64τ and a three proton multiplet at 2.77-3.04τ. Two sharp singlets were present at 4.56 and 5.10τ. There was no absorption between 8.23 and 8.67τ, the region characteristic of the angular methyl groups of phenanthrone (XXXIV) and cyclophenanthrone (XXXV). These data are consistent with the spectral properties of XLIX.

Irradiation of dextrorotatory 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV d)

Phenanthrone (XXXIV d, 332 mg.; $[\alpha]_D^{27} = +332°$) was dissolved in t-butanol (240 ml., distilled once from sodium) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and then irradiated with a 550 watt Hanovia high pressure mercury arc lamp.

After 5 hours the irradiation was terminated, and the t-butanol was removed under reduced pressure leaving an oily residue. The residue was taken up in a small volume of benzene and chromatographed on silica gel using the same technique as was used for the 6 hour irradiation of XXXIV l.

The crude cyclophenanthrone (XXXV l, 125 mg.) showed $[\alpha]_D^{27} = -38.7^\circ$ (c 1.0, 95% ethanol). Treatment of a pentane solution of this solid with charcoal and complete solvent removal gave XXXV l (112 mg.) with $[\alpha]_D^{27} = -40.2^\circ$ (c 1.0, 95% ethanol). Its infrared spectrum (KBr) was superimposable upon that of cyclophenanthrone (XXXV l, $[\alpha]_D^{27} = -42.3^\circ$) obtained by resolution through its enamine salt.

The crude recovered phenanthrone (XXXIV d, 180 mg.) showed $[\alpha]_D^{27} = +320^\circ$ (c 1.0, 95% ethanol). Treatment of a pentane solution of this solid with charcoal and complete solvent removal gave XXXIV d (160 mg.) with $[\alpha]_D^{27} = +323^\circ$ (c 1.0, 95% ethanol). Its infrared spectrum (KBr) was superimposable upon that of phenanthrone ($[\alpha]_D^{27} = +332^\circ$) obtained by resolution through its enamine salt.

A second similar experiment was carried out, using a longer irradiation time. Phenanthrone (XXXIV d, 575 mg.; $[\alpha]_D^{27} = +332^\circ$) was dissolved in t-butanol (290 ml., distilled once) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and irradiated for 18.5 hours. The reaction mixture was chromatographed on silica gel using the same technique as was used for the 18.5 hours irradiation of XXXIV l.

The fractions containing cyclophenanthrone were combined in pentane and treated twice with charcoal. Complete removal of solvent under reduced pressure gave cyclophenanthrone (XXXV l, 153 mg.) with a melting point of 97-110° and $[\alpha]_D^{27} = -40.5°$ (c 1.0, 95% ethanol). The infrared spectrum (KBr) was superimposable upon that of cylophenanthrone (XXXV l, $[\alpha]_D^{27} = -42.3°$) obtained by resolution through its enamine salt.

The fractions containing phenanthrone were combined in pentane and treated twice with charcoal. Complete removal of solvent under reduced pressure gave phenanthrone (XXXIV d, 5 mg.) with a melting point of 53-64° and $[\alpha]_D^{27} = +288°$ (c 0.08, 95% ethanol). The infrared spectrum (KBr) was superimposable upon that of phenanthrone (XXXIV d, $[\alpha]_D^{27} = +332°$) obtained by resolution through its enamine salt.

From this irradiation was also obtained a small amount of material which exhibited an infrared spectrum and n.m.r. spectrum consistent with XLIX. This material is apparently identical (with the possible exception of being enantiomers) with that obtained from the 18.5 hour irradiation of XXXIV l.

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in t-butanol

This irradiation was used as a standard for comparison with the irradiations of XXXIV in the presence of dibenzothiophene and benzophenone. Phenanthrone (XXXIV, 487 mg.) was dissolved in *t*-butanol (230 ml., distilled once from sodium) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 4 hours the irradiation was terminated, and the *t*-butanol was removed under reduced pressure leaving an oily residue. The residue was dissolved in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (12 x 4 cm.), 50 ml. fractions being collected.

The fractions containing cyclophenanthrone (XXXV, infrared analysis) were combined and the solvent completely removed by means of a vacuum pump. The crude cyclophenanthrone weighed 180 mg. The solid was dissolved in Skelly B, treated once with charcoal and allowed to crystallize. This treatment gave 153 mg. of XXXV (m.p. 86-87°, m.m.p. 86-87°).

The fractions containing phenanthrone (XXXIV) were combined and the solvent completely removed by means of a vacuum pump. The crude phenanthrone weighed 300 mg. Recrystallization from Skelly B gave 266 mg. of XXXIV (m.p. 89-90°, m.m.p. 89-90°).

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in t-butanol in the presence of dibenzothiophene

This irradiation immediately followed the one used for a standard. The same lamp and irradiation vessel were used for both. Phenanthrone (XXXIV, 487 mg.) and dibenzothiophene (1.0 g., m.p. 99-100°) were dissolved in t-butanol (230 ml., distilled once from sodium) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 4 hours the irradiation was terminated, and the t-butanol was removed under reduced pressure. The residue was dissolved in a small volume of benzene and chromatographed on silica gel (Baker Analyzed Reagent) column (12 x 4 cm.), 50 ml. fractions being collected. The separation proceeded as follows:

Eluent	Fraction number	Product composition
benzene	1	nil
benzene	2-7	dibenzothiophene
2% ether in benzene	8-16	nil
2% ether in benzene	17-31	XXXV
2% ether in benzene	32	nil
5% ether in benzene	33-34	nil
5% ether in benzene	35-51	XXXIV
15% ether in benzene	52-57	nil
50% ether in benzene	58-66	nil

The appropriate fractions were combined and the solvent completely removed by means of a vacuum pump. This treatment gave crude dibenzothiophene (1.01 g.), cyclophenanthrone (270 mg.) and phenanthrone (210 mg.). Recrystallization of these materials from Skelly B gave 1.0 g. of dibenzothiophene (m.p. 99-100°), 233 mg. of cyclophenanthrone (m.p. 86-87°, m.m.p. 86-87°) and 183 mg. of phenanthrone (m.p. 88-90°, m.m.p. 89-90°).

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in t-butanol in the presence of benzophenone

This irradiation immediately preceded the one used for a standard. The same lamp and irradiation vessel were used for both. Phenanthrone (XXXIV, 487 mg.) and benzophenone (4.18 g., m.p. 47-48°) were dissolved in *t*-butanol (230 ml., distilled once from sodium) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 4 hours the irradiation was terminated, and the *t*-butanol was removed under reduced pressure. The residue was dissolved in benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column. The fractions showing 5.82μ carbonyl absorptions in the infrared spectra (CCl_4) were combined to give an oil (275 mg.) which could not be crystallized from ethanol or hexane. Thin layer analysis showed several spots, none of which appeared to be cyclophenanthrone (XXXV).

Aside from benzophenone, the only crystalline product obtained showed absorptions at 2.88, 3.27, 3.35, 6.69, 6.89 and 8.48 μ in its infrared spectrum ($CHCl_3$). No absorption assignable to a carbonyl group was present.

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in *t*-butanol

This irradiation was used as a standard for comparison with the irradiation of XXXIV in the presence of piperylene. Phenanthrone (XXXIV, 500 mg.) was dissolved in *t*-butanol (300 ml.) which was contained in a Pyrex irradiation vessel. The solution was purged with nitrogen for 0.5 hours and irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 4 hours the irradiation was terminated, and the *t*-butanol was removed under reduced pressure leaving an oily residue. The residue was dissolved in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (12 x 4 cm.), 50 ml. fractions being collected.

The fractions containing cyclophenanthrone (XXXV, infrared analysis) were combined and the solvent completely removed by means of a vacuum pump. The crude cyclophenanthrone weighed 138 mg. The crude phenanthrone collected in like manner weighed 340 mg.

Irradiation of 4-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in *t*-butanol in the presence of 1,3-pentadiene (piperylene)

This irradiation immediately preceded the one used for a standard. The same lamp and irradiation vessel were used for both. Phenanthrone (XXXIV, 500 mg.) was dissolved in *t*-butanol (300 ml.) which was contained in a Pyrex irradiation vessel. After the solution was purged with nitrogen for 0.5 hours, a mixture of *cis*- and *trans*-piperylene (500-600 mg., not exact because of transfer and evaporation losses) was added. The solution was then irradiated with a 550 watt Hanovia high pressure mercury arc lamp. After 4 hours the irradiation was terminated, and the solvent was removed under reduced pressure leaving an oily residue. The residue was dissolved in a small volume of benzene and chromatographed on a silica gel (Baker Analyzed Reagent) column (12 x 4 cm.), 50 ml. fractions being collected. The separation proceeded as follows using increasing ratios of benzene/Skelly B.

Fraction number	Product composition (infrared analysis, CCl_4)
5-11	5.80μ
13-15	5.83μ
17-18	5.87μ
19-20	5.80 and 5.87μ
21-35	5.78μ
36-37	5.82 and 5.97μ
38-	5.97μ

Fractions 5-11 contained only a small amount of oil (20-30 mg.) whose n.m.r. spectrum (CCl_4) showed absorptions of aromatic protons (3.0 τ), olefinic protons (5.0 τ) and aliphatic protons (7.0-9.5 τ) in a ratio of about 2.5:1.0:21. A very strong absorption band appeared at 8.60 τ.

Fractions 13-15 also contained only a small amount of oil (20-30 mg.) whose n.m.r. spectrum (CCl_4) showed absorptions of aromatic protons (3.0 τ), olefinic protons (4.7 τ) and aliphatic protons (6.9-9.1 τ) in a ratio of about 1.0:1.0:4.3. All absorption bands were extremely broad and complex.

Fractions 17-18 also contained only a small amount of oil (20-30 mg.) whose n.m.r. spectrum (CCl_4) showed absorptions of aromatic protons (2.9 τ), olefinic protons (4.5 τ) and aliphatic protons (6.8-9.0 τ) in a ratio of about 2.3:1.0:10.

Fractions 21-35 contained about 230 mg. of oil whose n.m.r. spectrum (CCl_4) showed absorptions of aromatic protons (2.5-3.2 τ), olefinic protons (4.4-4.7 τ) and aliphatic protons (6.5-9.2 τ) in a ratio of about 3.8:1:16. The infrared spectrum (CCl_4) showed strong absorption bands at 3.40 and 5.80μ and several medium to weak absorption bands which could be assigned to various double bond absorptions.

The fractions following 38 contained a total of 205 mg. of crude, solid phenanthrone.

Irradiation of 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XXXV) in t-butanol

This experiment was run in order to determine the origin of the keto-olefin XLIX. Cyclophenanthrone (XXXV, 463 mg.) was dissolved in t-butanol (230 ml., distilled once from sodium) and purged with nitrogen for 0.5 hours. The solution was irradiated in a Pyrex vessel with a 550 watt Hanovia high pressure mercury arc lamp. The progress of the irradiation was followed by the decay of the 238mμ absorption band (25μl of sample diluted to 5 ml.) of XXXV and proceeded as follows:

Hours of irradiation	Absorbance λ_{max}^{EtOH} 238mμ	Absorbance λ_{min}^{EtOH} 226mμ
0	.518	.390
5	.525	.401
19	.529	.453
29	.456	.395
42	.380	.352
54	.355	.357

The irradiation was terminated after 54 hours, and the solvent was removed under reduced pressure. The residue was then dissolved in chloroform, and the solvent was removed under reduced pressure. This process was repeated several times in order to remove t-butanol. An infrared of this material ($CHCl_3$) showed a very broad carbonyl absorption (5.70-5.95μ) and weak bands at 6.15 and 6.23μ. A medium intensity band was present at 11.06μ, possibly due to a terminal methylene group. The n.m.r. spectrum ($CHCl_3$) showed a sharp, low intensity singlet at 4.48 and a broad absorption band at 4.82-5.27τ, which would mask any other weak absorption in this area.

The mixture was chromatographed as usual on silica gel. Combined fractions 26 and 27 (10 mg.) showed 5.72μ and 5.82μ carbonyl absorptions in the infrared spectrum (CCl_4). An n.m.r. spectrum (CCl_4) showed two singlet absorptions at 4.54 and 5.08τ. These data are compatable with impure XLIX. Starting material XXXV was also obtained from the chromatography (220 mg. crude).

Irradiation of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) in t-butanol

This experiment was run in order to determine the origin of keto-olefin XLIX. Phenanthrone (XXXIV, 2.0 g.) was dissolved in *t*-butanol (230 ml., distilled once from sodium) and purged with nitrogen for 0.5 hours. The solution was irradiated in a Pyrex vessel with a 550 watt Hanovia high pressure mercury arc lamp. The irradiation was terminated after 45 hours, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform, and the solvent was removed under reduced pressure. This process was repeated several times in order to remove *t*-butanol. An n.m.r. spectrum ($CHCl_3$) of the crude material showed small spikes at 4.14 (vinyl hydrogen of XXXIV), 4.47 and 4.94τ. The last two spikes can be attributed to the exo-methylene protons of XLIX.

Chromatography of the crude mixture on silica gel as usual, gave crude phenanthrone (120 mg.), crude cyclophenanthrone (XXXV, 720 mg.) and a small amount of material whose n.m.r. spectrum (CCl_4) showed sharp singlets at 4.55 and 5.10τ. These can be assigned to XLIX.

That some XLIX might be formed from XXXV on the silica gel column is of no consequence since absorptions due to the exo-methylene protons of XLIX can be seen in the crude reaction mixture before chromatography. It should be pointed out that the vinyl hydrogen absorption of XXXIV appears at 4.14τ (authentic sample) in chloroform while in carbon tetrachloride it appears at 4.25τ (authentic sample). A similar shift is seen for the exo-methylene protons of XLIX.

SUMMARY

Complete resolution of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (XXXIV) and 4a-methyl-1,4,4a,9,10,10a-hexahydro-4,10a-cyclo-3(2H)-phenanthrone (XXXV) has been accomplished by a novel method involving iminium salts.

The irradiation of optically pure phenanthrone (XXXIV) in t-butanol gave good yields of XXXV with an optical purity in excess of 95%. Preliminary quenching and sensitization experiments were carried out in an attempt to identify the reactive state in the conversion of XXXIV to XXXV. Based on these results, a mechanistic interpretation of this transformation is given as well as a comparison to existing interpretations of similar systems. A second photoproduct (XLIX) produced in low yields has also been identified.

Irradiation of phenanthrone (XXXIV) in aqueous acetic acid produced two photoproducts (L and LI) which had incorporated a molecule of water. Three secondary products (XLVIII a,b and XLIX) were also produced by the acid catalyzed rearrangement of XXXV. Complete structure proofs are given for these five compounds.

A brief comparison of the photochemistry of cyclic α,β-unsaturated ketones and cross-conjugated cyclohexadienones is given.

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