

PHOTOCHEMICAL REARRANGEMENT OF 3-KETO-
4-CARBOXY-9-METHYL- $\Delta^{1,4}$ -HEXAHYDRONAPHTHALENE
AND RELATED COMPOUNDS

A THESIS

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GLOSSARY OF ABBREVIATIONS

DDQ	2,3-Dicyano-5,6-dichlorobenzohydroquinone
EMD	Exact mass determination
glc	Gas liquid chromatography
Hz	Hertz
ir	Infrared
nm	Nanometer
nmr	Nuclear magnetic resonance
ppm	Parts per million
SE-30	Silicone gum rubber (methyl)
TMS	Tetramethylsilane
uv	Ultraviolet

SUMMARY

The primary purpose of this research was to investigate the effects of electron withdrawing groups on the course of photochemical rearrangements of bicyclic cross-conjugated cyclohexadienones. More specifically, the photochemical reactions of dienones having carboxy and carbomethoxy substituents on the chromophore were investigated. In work previously reported by Caine, DeBardleben, and Dawson (1) it was found that electron withdrawing substituents on the C-2 position of 3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene favored photochemical rearrangements to 5/7-fused hydroazulene structures. The specific goal of this research was to compare the effects of the C-2 and C-4 substituted chromophores, particularly with respect to formation of 5/7-fused structures versus spiro compounds.

Two model dienones, 3-keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (I) and 3-keto-4-carbomethoxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (II) were investigated in various media. Compound I was irradiated in anhydrous dioxane to produce 6-methylspiro [4.5]-deca-3,6-dien-2-one (III) in 48% yield. Irradiation of I in aqueous acetic acid resulted in a 42% yield of 1 β -carboxy-6 β -hydroxy-6 α -methyl-spiro[4.5]-deca-3-en-2-one lactone (IV). In both irradiations, considerable polymeric material was produced, starting material was recovered, but no hydroazulene compounds were detected. Attempts to recover better yields of III and IV by longer irradiation times resulted only in production of more polymer. Irradiation of I in anhydrous methanol resulted in the formation of a

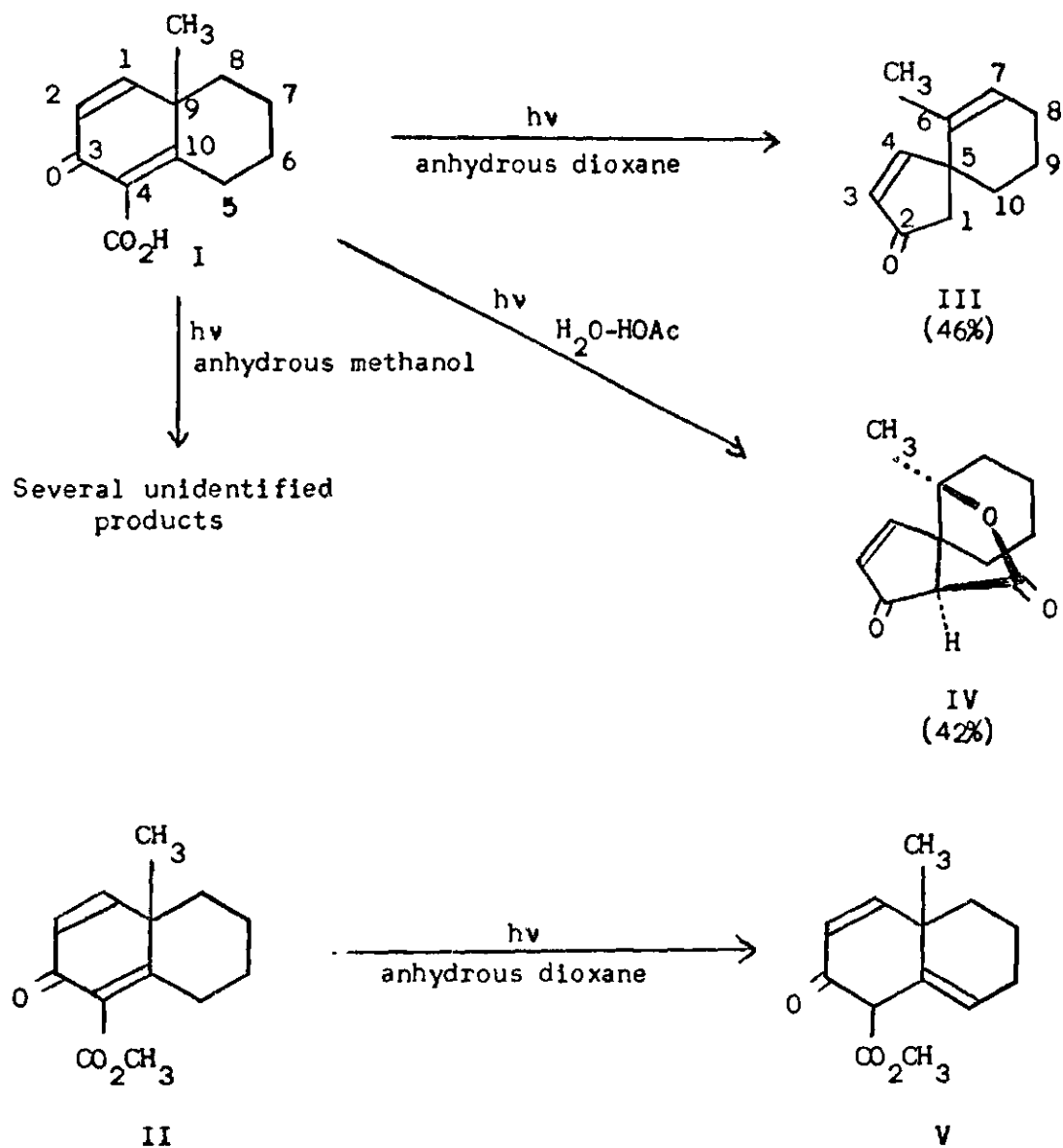
mixture of several unidentified products.

Irradiation of II in anhydrous dioxane resulted in formation of a single compound as determined by glc. Attempts to recover and identify the photoproduct resulted only in recovery of II leading to the conclusion that II photochemically deconjugated to give 3-keto-4-carbomethoxy-9-methyl- $\Delta^{1,10}$ -hexahydronaphthalene (V) which reconstituted during isolation procedures. Analysis of the crude photoproduct by nmr showed some evidence to support this conclusion.

There was no evidence for any 5/7-fused hydroazulenones being formed from irradiation of the C-4 substituted chromophores showing a marked difference from the photochemical directing effect of the C-2 substituted analogs. This can best be explained by consideration of the electron withdrawing effects of the substituents in determining the mode of cleavage taken by the mesoionic cyclopropyl intermediates which generally can form lumiproducs or rearrange to form spiro or hydroazulene ketones. Chart I shows a summary of photochemical results.

Chart I*

Summary of Photochemical Results



*Numbering presented in Chart I is that reflected throughout this thesis.

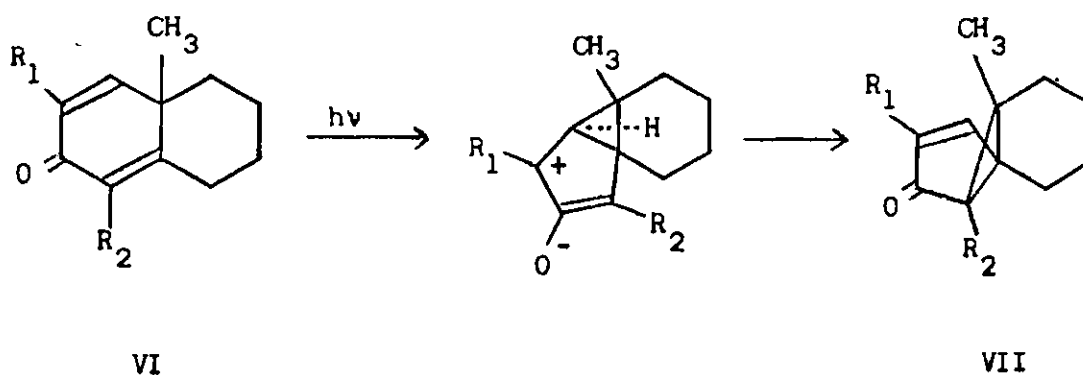
CHAPTER I

INTRODUCTION

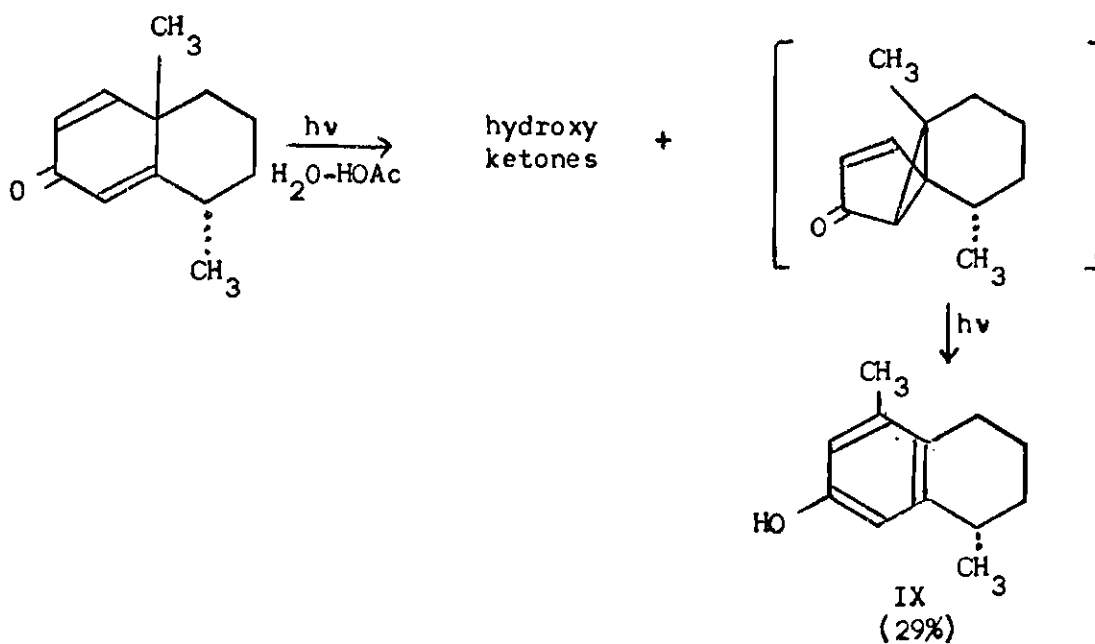
A great deal of interest has been generated in organic photochemical reactions within the past several years, chiefly due to their stereospecificity and utility in natural products synthesis. Irradiation by ultraviolet light often causes complex rearrangements in organic molecules which cannot be effected easily, if at all, by thermal methods. Natural products chemists are particularly interested in photochemical rearrangements of cross-conjugated cyclohexadienones as they are of great synthetic value in steroid chemistry. The first concerted effort in this field was by Barton (2) in studies involving the sesquiterpene α -santonin. Irradiation of α -santonin in neutral media led to a cyclopropyl lumiprodut which underwent further reaction by acid catalyzed ring opening to a 5/7-fuzed ring system upon treatment with aqueous acetic acid. As illustrated by recent comprehensive reviews on cyclohexadienone photochemistry (3-5), it has subsequently been found that almost all compounds having the cyclohexadienone chromophore exhibit analogous behavior to give lumiproduts, 5/7-fuzed systems, spiro compounds, and phenols.

The exact mechanism of cyclohexadienone rearrangements are presently unproved, however it is widely accepted that a zwitterionic intermediate is formed which in neutral media forms a lumiprodut (cyclopropyl ketone) or in aqueous acidic media, captures a proton to

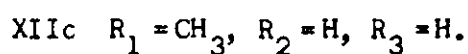
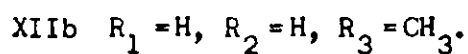
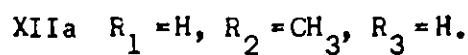
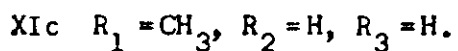
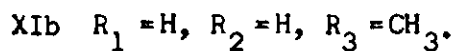
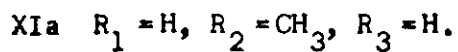
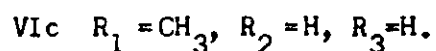
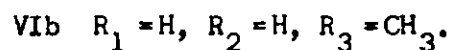
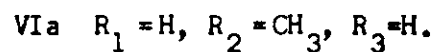
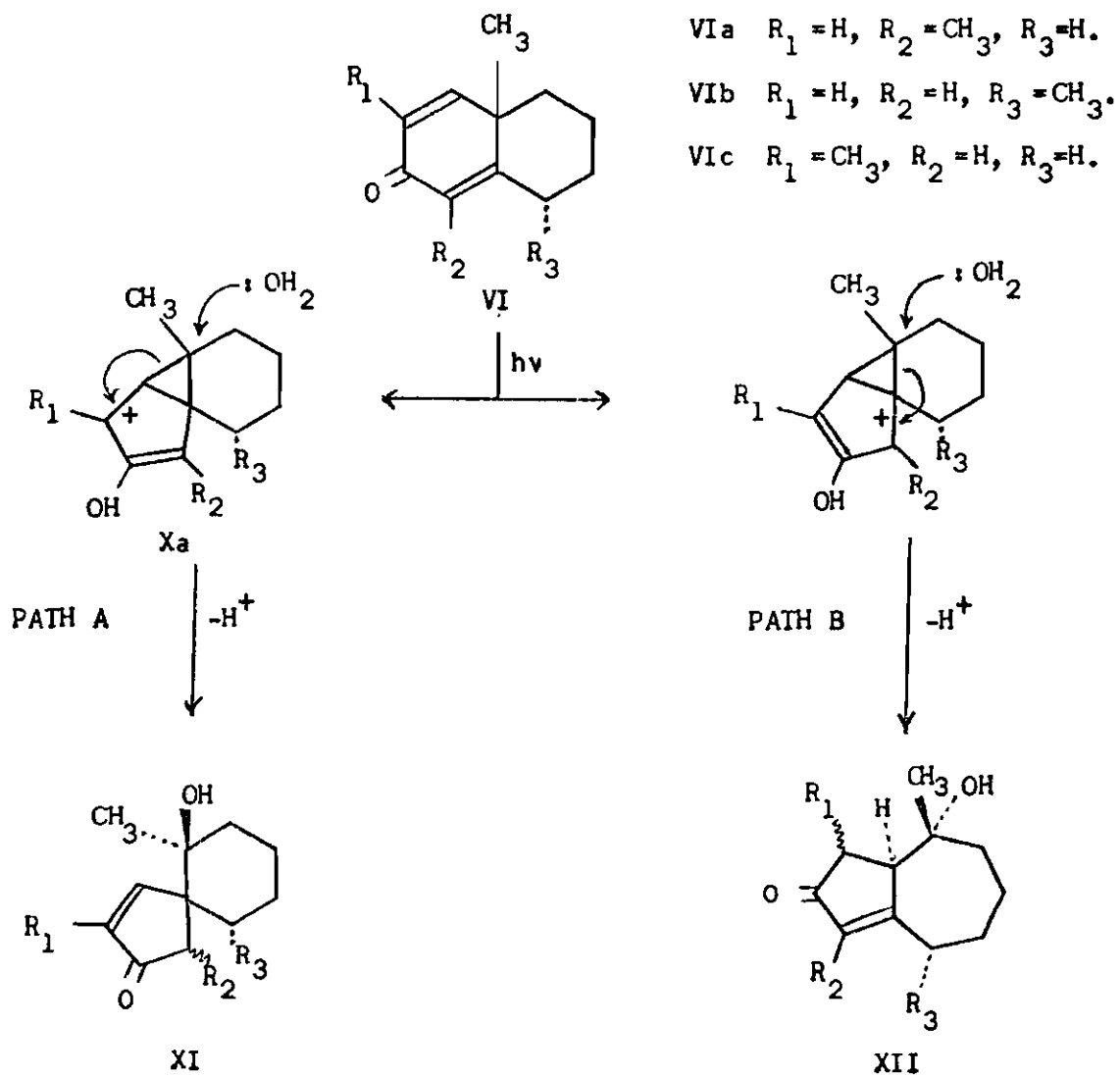
give a mesoionic species and ultimately a hydroxy ketone. The pathway by which the mesoionic species is formed is generally accepted as that proposed by Zimmerman and Schuster (6). As summarized by Kropp (7), cyclohexadienones of type VI in neutral media form the zwitterion intermediate and the cyclopropyl ketones of type VII.



The cyclopropyl ketones are photochemically labile and are usually isolated only as secondary products. Even in aqueous media some cyclopropyl ketone is formed as illustrated in the case of dienone VIII which gives phenol IX in 29% yield (8).



In aqueous acidic solvents cyclohexadienones of type VI are generally converted to spiro compounds of type XI or hydroazulenones such as XII.

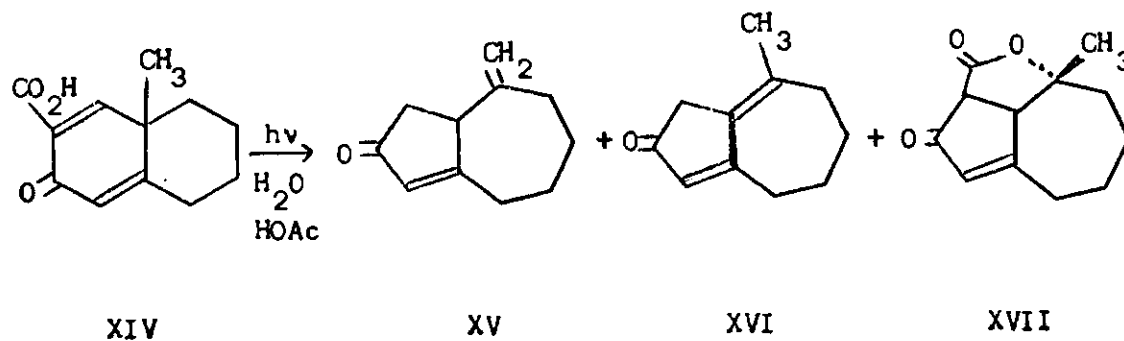


Through their inductive effect electron donor substituents at C-4 tend to stabilize species Xb resulting in a preponderance of XII. The model dienone VIa was irradiated and gave the hydroazulenone XIIa in 80% yield with no spiro compound being reported (9). Likewise, α -santonin gives the 5/7-fused hydroxy ketone as the major product in 30% yield (2). When the substituent in question is methyl as in VIa and α -santonin, hyperconjugation as well as induction may play an important part in stabilization of the mesoionic species (7).

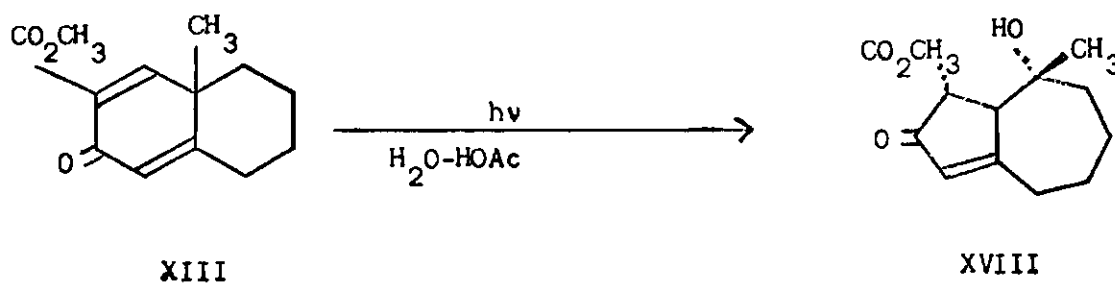
In the absence of a substituent at C-4, the relative amount of spiro product obtained is increased at the expense of the hydroazulenone. Dienone VIb irradiated in aqueous acetic acid at room temperature gives hydroazulenone XIIb in 19% yield and spiro hydroxy ketone XIb in 16% yield (8).

Presence of an electron donor at C-2 favors formation of species Xa and consequently XI. Dienone VIc on irradiation in aqueous acetic acid give spiro hydroxy ketone XIc in 48-51% yield with no detectable amount of hydroazulenone XIIc being formed (10).

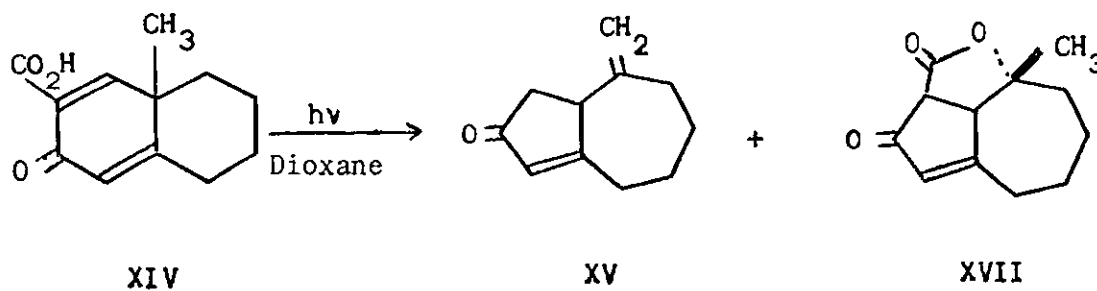
Conversely, an electron withdrawing substituent at C-2 stabilizes Xb and favors formation of the hydroazulenone product. Caine and DeBardleben (1) studied the photochemistry of 2-carbomethoxy-3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (XIII) and the analogous acid XIV. Upon irradiation in aqueous acid, XIV gave the hydroazulenone products XV, XVI, and XVII in five, seven and six percent yields respectively.



In aqueous acid the ester XIII gave hydroazulenone XVIII in 67% yield.



In neutral media, acid XIV afforded the hydroazulene ketone XV in 67% yield and the lactone XVII in 16% yield.



In all the above cases there were no spiro hydroxy ketones isolated. An electron withdrawing group at C-4 should favor development of the charge at C-2 in the mesoionic species resulting in a preponderance of the spiro product. This thesis is a report of the

investigation of the effect of C-4 substituted carboxy and carbomethoxy cyclohexadienones on photochemical rearrangements. Although the results of this research are expected to be of limited synthetic value, formation of predominantly spiro compounds would lend considerable support to the mechanistic theory of the photochemically generated cyclopropyl mesoionic species.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Whenever feasible, reactions were conducted under a nitrogen atmosphere established using an apparatus similar to that described by Johnson (11). All inorganic chemicals used were commercially available reagent grade. All liquid organic reagents and solvents except ether were purified according to procedures described by Fieser (12) and distilled prior to use. Ether, anhydrous and USP, was purchased commercially. All anhydrous solvents were stored over 3A, 4A, or 5A molecular sieves as applicable (13). Anhydrous sodium sulfate was used as a drying agent in ether solutions during reaction workups. Removal of solvents in vacuo was accomplished using a Buchi Rotavapor rotary evaporator. Column chromatographies employed Grace grade 923, 100-200 mesh silica gel in the ratio of 25 g silica gel to one gram of mixture.

A Hanovia 450-Watt high pressure mercury lamp in either an all Pyrex or all quartz apparatus similar to that described by Kropp and Erman (8) was the light source for all irradiations. A slow stream of prepurified dried nitrogen was bubbled through the solution prior to and during all irradiations to deoxygenate and agitate the solution.

Infrared spectra were obtained using a Perkin-Elmer Model 457 recording spectrophotometer. Solution spectra were obtained using 0.1 mm sodium chloride cells. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60D nuclear magnetic spectrometer. Tetramethylsilane was used as an internal standard and chemical

shifts are reported in ppm downfield from TMS. The abbreviations s, d, d of d, t and m refer to singlet, doublet, doublet of doublets, triplet, and multiplet respectively. Ultraviolet spectra were obtained using a Cary Model 14 recording spectrophotometer with one centimeter balanced cells, 95 percent ethanol as solvent. Mass spectral data were obtained on a Varian Associates Model M-66 medium resolution mass spectrometer with a 70 electron volt source. Gas chromatographic analyses were accomplished using a Perkin-Elmer Model 881 flame ionization gas chromatograph using a 6 foot by 1/8 in. stainless steel column packed with 10 percent K-20M Carbowax on 60/80 Chromasorb W HMDS with a temperature program of 100 to 200°C at 12 degrees per minute or a 6 foot by 1/8 in. stainless steel column packed with 10 percent SE-30 on 80/100 Chromasorb W HMDS with a temperature program of 100 to 225°C at 12 degrees per minute or a 6 foot by 1/8 in. stainless steel column packed with 10 percent SE-30 on 80/100 Chromasorb W HMDS with a temperature program of 100 to 225°C at 12 degrees per minute. Preparative gas chromatography was performed on an Aerograph Model A-90P Manual Temperature Programmer Gas Chromatograph equipped with a thermal conductivity detector using a 3 ft by 1/4 in. stainless steel column packed with 15 percent 20M Carbowax on acid washed firebrick at a temperature of 190°C.

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Boiling points are uncorrected. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

CHAPTER III

EXPERIMENTAL

3-Keto-9-methyl- Δ^4 -octahydronaphthalene (XXIV)

Compound XXIV was prepared by a modification of the method of Ross and Levine (14). Methyl vinyl ketone (46.0 g, 0.65 mole) in 400 ml of anhydrous ether was added dropwise over a four hr period to a stirred solution of 2-methylcyclohexanone (146.0 g, 1.30 mole) and ethanolic potassium hydroxide (20.0 g, 0.5 mole, in 60 ml of absolute ethanol) in 600 ml of anhydrous ether maintained at 0°. The mixture was stirred at 0° for an additional two hr, allowed to warm to room temperature and stirred overnight. The mixture was added to an equal volume of water which was then acidified with 40 ml of glacial acetic acid. The aqueous layer was separated and washed with three 200-ml portions of ether. The ether layers were combined, washed with two 200-ml portions of water and one 200-ml portion of saturated brine solution and dried over sodium sulfate. Evaporation of the solvent in vacuo followed by fractional vacuum distillation of the dark viscous residue yielded 47.0 grams (44%) of XXIV at 82-83/0.25 mm [lit. (15) b.p. 82-84/0.5 mm]. VPC analysis (Carbowax column) showed one compound, shown by ir and nmr to be the desired bicyclic ketone.

3-Keto-4-carbomethoxy-9-methyl- Δ^4 -octahydronaphthalene (XXV)

Compound XXV was prepared by the general procedure of Wenkert (16). A 1000-ml three-neck flask fitted with dropping funnel, variable distilling

head, mechanical stirrer, thermometer, and nitrogen inlet tube was charged with 11.2 g (0.25 mole) of 53.4% sodium hydride/mineral oil and 500 ml of dry 1,2-dimethoxyethane. Compound XXIV (47.0 g, 0.28 mole) was added rapidly with stirring. The solution was stirred at room temperature overnight and solvent was removed by distillation until the remaining volume was approximately 200 ml. The solution was cooled to room temperature and 1000 ml of ether was added. Carbon dioxide dried through concentrated sulfuric acid and a calcium chloride drying tube was allowed to bubble through the solution for 1.25 hr while maintaining a solution temperature of 0-3° by use of an ice bath. To the cold reaction mixture was added 500 ml of 10% sodium hydroxide solution and stirring was continued for 15 min. The solution was washed with three 500-ml portions of ether to remove unreacted starting materials. The solution was acidified to pH 2-3 with 3:1 hydrochloric acid and stirred vigorously for 30 min to hasten removal of carbon dioxide. The solution was extracted with three 100-ml portions of ether. The ether layers were combined and poured slowly into a stirred solution of diazomethane (ca. 10.5 g, 0.25 mole) in 500 ml of ether maintained at 0° in an ice-salt bath (the diazomethane was freshly prepared from Dupont EXR-101, N,N'-Dimethyl-N,N'-dinitroso-terephthalamide, 70% in mineral oil, according to instructions issued by the manufacturer). The cold mixture was stirred for 30 min and the excess diazomethane destroyed by slowly adding dilute hydrochloric acid. The layers were separated and the organic layer washed with two 500-ml portions of saturated sodium bicarbonate and one portion of saturated brine. The ether solution was dried, the solvent removed in vacuo to yield 26.2 g (63%) of a yellow

oil. Analysis by glc (Carbowax) showed one compound, retention time 10.6 min. Distillation yielded 25.2 g of XXV as a pale yellow liquid, b.p. 123-127°/1.5 mm. Cooling to -78° caused crystallization of XXV, m.p. 77.5 - 78.5°; ir (film) 1672 (α,β -unsat ketone), 1616 (conj alkene), 1737 (α,β -unsat ester), 1448, 1234, and 1027 cm^{-1} ; nmr (CCl_4) δ 1.28 (s, 3H, 9- CH_3), 1.50 - 2.00 (m, 8H, 1-, 6-, 7-, 8- CH_2), 2.12 - 2.62 (m, 4H, 2-, 5- CH_2), 3.69 (s, 3H, 4- COCH_3); mass spectrum (70eV) m/e 222 (M^+), 190 ($\text{M}^+ - \text{CH}_3\text{OH}$), 162 ($\text{M}^+ - \text{HCO}_2\text{CH}_3$), EMD 222.12674 (Calcd: 222.12549).

In a related experiment the 3-carboxy enone (XXV) was prepared by omitting the diazomethane step in the preceding synthesis. Starting with 22.5 g (0.50 mole) of 53% sodium hydride/mineral oil dispersion and 93.0 g (0.55 mole) of XXIV, the Wenkert procedure was followed up to the point preceding addition to diazomethane. At that point solvent was removed in vacuo at room temperature until the remaining volume was ca. 50 ml. On lowering the temperature to 0°, colorless needle crystals precipitated which were suction filtered and washed with cold ether to yield 20.2 g (19%) of XXV; m.p. 61 - 62.5° with rapid decarboxylation at 72° (decarboxylation occurred slowly at room temperature with approximately 5% decarboxylation after four months storage as determined by nmr); ir (CHCl_3) 1690 (α,β -unsat ketone), 1607 cm^{-1} (conj alkene); nmr CDCl_3 δ 1.33 (s, 3H, 9- CH_3) 1.57 - 2.11 (m, 8H, 1-, 6-, 7-, 8- CH_2), 2.43 - 3.50 (m, 4H, 2-, 5- CH_2).

3-Keto-4-carbomethoxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (II)

Compound II was prepared by the method of Tuller (17), A 5000-ml three-neck flask fitted with mechanical stirrer, variable takeoff distilling head, and nitrogen inlet tube was flame dried and charged with 22.2 g

(0.20 mole) of freshly sublimed selenium dioxide, 3000 ml of t-butyl alcohol (freshly distilled over sodium t-butoxide) and 10 ml of glacial acetic acid. The mixture was stirred with warming until all the selenium dioxide had dissolved and a solution of 11.5 g (0.05 mole) of XXVI in 500 ml of t-butyl alcohol was added. The reaction mixture was stirred at reflux for three days and 3000 ml of solvent were removed by distillation. The remaining suspension was cooled to 0° and filtered through a fritted glass funnel to remove metallic selenium. The filtrate was concentrated in vacuo and the residue dissolved in 500 ml ether, cooled to 0° and filtered through fritted glass to remove unreacted selenium dioxide. The filtrate was stirred well with 200 ml of saturated sodium carbonate solution and solid sodium carbonate was added slowly with stirring until evolution of carbon dioxide ceased. The mixture was filtered with suction and the filter cake washed well with ether. The layers were separated and the aqueous layer extracted with two 100-ml portions of ether. The combined ethereal extracts were washed with water, dried, and concentrated in vacuo. The dark viscous oil was fractionally distilled to give 7.80 g (55%) of an orange oil, glc analysis (SE-30) showing one compound, dienone II, retention time 10.2 min. Decolorization with activated charcoal in methanol followed by cooling to -78° yielded light yellow crystals of II; m.p. 53.5 - 54.5°; ir (film) 1733 (α,β -unsat ester), 1661 (α,β -unsat ketone), 1532 (conj alkene) and 1608 (conj alkene), 1321, 1236, 1038, and 843 cm^{-1} ; nmr (CCl_4) δ 1.29 (s, 3H, 9- CH_3), 1.41 - 2.06 (m, 6H, 6-, 7-, 8- CH_2), 2.18 - 2.58 (m, 2H, 5- CH_2), 3.75 (s, 3H, 4- CO_2CH_3), 6.10 and 6.77 (AB quartet, $J_{AB} = 10$ Hz, 2H, 1-, 2-CH); uv max (95% EtOH) 241 nm ($\epsilon = 15,400$); mass spectrum (70eV) m/e 220 (M^+),

188 (M^+-CH_3OH), 161 ($M^+-CO_2CH_3$), EMD 220.10890 (Calcd: 220.10985).

Anal: Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32.

Found: C, 70.96; H, 7.44

In a related experiment an attempt was made to synthesize dienone I directly from the carboxy enone XXV. The preceding procedure was followed except acidification with acetic acid and subsequent neutralization with sodium carbonate were omitted and the reaction mixture was maintained at 65° rather than reflux to minimize decarboxylation. The crude product was not distilled as was II but instead was treated with activated charcoal, taken up in 200 ml of ether and extracted with three 50-ml portions of saturated sodium bicarbonate solution. The combined basic extracts were acidified to pH 2-3 with 3:1 hydrochloric acid. The mixture was cooled and extracted with three 100-ml portions of ether. The organic layers were combined, concentrated in vacuo to ca. 20 ml precipitating light yellow crystals which were suction filtered and washed with cold ether yielding 4.28 g (29%) of a compound believed to be the carboxy trienone 3-keto-4-carboxy-9-methyl- $\Delta^{1,4,5}$ -tetrahydronaphthalene (XXVIII). An extensive study of this compound to determine structure was not undertaken; however nmr data was consistent with the proposed structure; nmr δ 1.38 (s, 3H, 9- CH_3), 1.62 - 2.09 (m, 2H, 8- CH_2), 6.45 and 7.10 (AB quartet, $J_{AB} = 10$ Hz, 2H, 1-,2-CH), 7.92 and 8.10 (d of t, $J = 2$ Hz, 1H, 5-CH).

3-Keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (I)

A 500 ml flask fitted with a variable takeoff distilling head, nitrogen inlet and magnetic stirrer was charged with 9.0 g (0.041 mole) of II, 200 ml of 10% aqueous sodium bicarbonate solution (0.25 mole) and

200 ml of methanol. The suspension was maintained at 50°C with stirring for three days, 250 ml of solvent were removed by distillation at atmospheric pressure, 200 ml of water was added, and solvent again removed by distillation until the remaining volume was ca. 200 ml. The solution was extracted with three 200-ml portions of ether, the ether layers combined and concentrated *in vacuo* to yield 2.60 g (29%) of an oil, shown by glc to be 95% starting ester II. The aqueous layer was acidified to pH 2-3 with 3:1 hydrochloric acid and extracted with three 100-ml portions of ether. The ether layers were combined and concentrated *in vacuo* to yield 6.46 g (79.5%) of dienone acid I as a semi-solid material.

Recrystallization from ether yielded amber crystals, m.p. undetermined (decomposed slowly at temperatures exceeding 90°); ir (CHCl₃) 1731 (α,β-unsat carboxylic acid), 1655 (α,β-unsat ketone), 1600 (conj alkene), 1321, 1136, 980, and 845 cm⁻¹; nmr (CDCl₃) δ 1.34 (s, 3H, 9-CH₃), 1.47-2.70 (m, 7H, 6-, 7-, 8-CH₂ and 5-CH), 3.21-3.64 (m, 1H, 5-CH), 6.33 and 7.00 (AB quartet, J_{AB} = 10 Hz, 2H, 1-, 2-CH), 10.02 (s, 1H, 4-COOH); uv max (95% EtOH) 240 nm (ε = 13,900); mass spectrum (70eV) m/e 162 (M⁺-CO₂, no molecular ion), EMD (on M⁺-CO₂) 162.10499 (Calcd: 162.10439).

Anal: Calcd for C₁₂H₁₄O₃: C, 69.88; H, 6.84.

Found: C, 70.08; H, 7.01.

Analysis of I by glc (Carbowax) showed two peaks of equal intensity on the flame ionization instrument (PE881), retention times of 7.1 and 9.0 min. On the thermal conductivity instrument (A-90P) the second peak was larger than the first (10:1). The second peak was collected and determined by ir and nmr to be 3-keto-9-methyl-Δ^{1,4}-hexahydronaphthalene; ir (film) 166 (α,β-unsat ketone), 1628 and 1606 (conj alkene), 1270,

1162, 943, and 883 cm^{-1} ; nmr (CCl_4) δ 2.25 (s, 3H, $-\text{CH}_3$), 1.36-2.05 (m, 6H, 6-,7-,8- CH_2), 2.22-2.62 (m, 2H, 5- CH_2), 5.93 (s, 1H, 4-CH), 6.03 and 6.77 (AB quartet, $J_{AB} = 10\text{ Hz}$, 2H, 1-,2-CH).

Irradiation of 3-Keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthylene (I)
in Anhydrous Dioxane

A solution of 0.96 g (0.0047 mole) of I in 250 ml of anhydrous dioxane was irradiated for 25 min using an all quartz probe. The solvent was removed in vacuo, glc analysis (Carbowax) showing two minor peaks (starting material) and a major peak, retention time 7.4 min. The residue was taken up in ca. 20 ml of ether precipitating a white flocculent material which was filtered off to afford 0.12 g (13%) of a base soluble, polymeric substance which showed no well defined spectral characteristics. The ethereal filtrate was extracted with three 20-ml portions of saturated sodium bicarbonate and one 20 ml portion of saturated brine. The basic aqueous solutions were combined, acidified and treated in the usual manner to yield 0.32 g (33%) of material, shown by nmr to be primarily starting acid I but containing some polymer. The ether solution was concentrated in vacuo to yield 0.47 g (48%) of 6-methylspiro [4,5]-deca-3,6-diene-2-one (III). Analysis by glc (Carbowax) showed one compound, retention time 7.4 min. Distillation using a Hickman microstill gave III, b.p. $109-111^\circ/0.25\text{ mm}$; ir (film) 1712 (α,β -unsat ketone), 1662 (non-conj alkene), 1645 (conj alkene), 1584, 1442, 1181, and 797 cm^{-1} ; nmr (CCl_4) δ 1.54 (d, 3H, 6- CH_3), 1.60-2.15 (m, 6H, 8-,9-,10- CH_2), 2.00 and 2.38 (AB quartet, $J_{AB} = 18.5\text{ Hz}$, 2H, 1- CH_2), 5.57 (m, 1H, 7-CH), 6.06 and 7.31 (AB quartet, $J_{AB} = 5.5\text{ Hz}$, 2H, 3-,4-CH); uv max (95% EtOH) 218

nm ($\epsilon = 0,200$); mass spectrum (70eV) m/e 162 (M^+), 147 ($M^+ - CH_3$), EMD 162.10615 (Calcd: 162.10439).

Anal: Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70

Found: C, 81.28; H, 8.90.

Irradiation of 3-Keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (I)
in Aqueous Acetic Acid

A solution of 1.02 g (0.0049 mole) of I in 250 ml of 45% aqueous acetic acid was irradiated for 30 min using an all quartz probe. The solution was washed into a 1000 ml round bottom flask, frozen at -78° , and the solvent removed by lyophilization to yield a light yellow semi-solid material. The mixture was taken up in 100 ml of ether and 0.28 g (27%) of polymeric material was taken off by filtration. The ether solution was extracted with three 100-ml portions of saturated sodium bicarbonate solution and one 100-ml portion of saturated brine. The basic extracts were combined, acidified, and worked up in the usual manner to yield 0.18 g (19%) of a semi-solid material shown by glc and nmr to be a mixture of acetic acid, starting acid I, and polymer. The ether solution was concentrated in vacuo to yield a yellow oil. Recrystallization in ca. five ml of carbon tetrachloride afforded 0.41 g (42%) of white, spherical crystals of 1 β -carboxy-6 β -hydroxy-6 α -methylspiro[4.5]-deca-3-en-2-one lactone (IV), m.p. 125.5-126.0 $^\circ$; ir ($CHCl_3$) 1769 (γ -lactone), 1711 (α,β -unsat ketone), 1672 (non-conj alkene), 1382, 1176, 1069, 954 cm^{-1} ; nmr ($CDCl_3$) 1.15 (s, 3H, 6- CH_3), 1.52 - 2.70 (m, 8H, 7-, 8-, 9-, 10- CH_2), 3.38 (d, $j = 1.5$ Hz, 1H, 1-CH), 6.17 (d, $J = 5.5$ Hz, 1H, 3-CH), 7.53 and 7.62 (d of d, $J = 1.5$ Hz, 1H, 4-CH); uv max (95% EtOH) 223 nm ($\epsilon = 8,400$);

mass spectrum (70eV) m/e 206 (M^+), 162 ($M^+ - CO_2$), EMD 206.09295 (Calcd: 206.09421).

Anal: Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84.

Found: C, 69.94; H, 7.00.

Attempted Irradiation of 3-Keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydro-naphthalene (I) in Anhydrous Methanol

Several attempts were made to isolate and identify products from the irradiation of I in anhydrous methanol. In each case, ca. 0.25 g of I was dissolved in 250 ml of anhydrous methanol (dried by distillation over magnesium hydroxide/magnesium methoxide) and irradiated for periods of time varying from 15 min to 3 hr employing both Pyrex and quartz filters. In each case the reaction was monitored by withdrawing five ml samples at 15 min intervals, concentrating the solution in vacuo, and analyzing by glc. Using the Pyrex filter, a gradual disappearance of I and an appearance of six significant peaks was noted. Using the quartz filter the same phenomenon was noted only proceeding more rapidly. Analysis of the crude product by nmr showed several C-9 methyl absorptions (δ 1.3 - 1.8), several smaller absorptions in the methoxy region (δ 3.5 - 4.0) and poorly defined peaks in the vinyl region. Attempts to isolate products by column chromatography failed to produce any compound pure enough to be identified. No attempt was made to separate the photo-products by preparative gas chromatography due to the number and proximity of peaks.

Irradiation of 3-Keto-4-carbomethoxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (II) in Anhydrous Dioxane

Attempts to derive products from the non-sensitized irradiation of

II in anhydrous dioxane using both Pyrex and quartz filters failed. A solution of 1.08 g (0.0049 mole) of II and 2.68 g (0.0147 mole) of benzophenone in 250 ml of dry dioxane were irradiated for three hours using a Pyrex filter. The reaction was followed by glc analysis (SE-30, five ml aliquots withdrawn at 15 min intervals) which showed gradual disappearance of II with appearance of two major peaks at 13.4 and 18.5 min and several minor peaks. The photolysis mixture was concentrated in vacuo to yield 1.86 g of a residue which was chromatographed on 50 g of silica gel. Elution with 500 ml hexane, 500 ml 9:1, 3:1, and 1:1 hexane-ether, and 500 ml ether afforded 0.97 g of white crystals, 0.75 g of a light yellow oil shown by nmr to be II, and 0.08 g of an unidentified mixture. The white crystals (m.p. in excess of 300°) gave nmr absorptions in the aromatic and $-OCH_2$ regions only and are believed to be a photoproduct of the solvent and sensitizer. Analysis of the crystals by glc (SE-30) showed one compound, retention time 18.5 min. Analysis of the 0.08 g mixture by glc showed no peak at 13.4 min. It is assumed the dienone deconjugated photochemically to give 3-keto-4-carbomethoxy-9-methyl- $\Delta^{1,10}$ -hexahydronaphthalene (V) and re-conjugated on the chromatography column. This assumption is substantiated by nmr analysis of the crude product which shows a poorly resolved triplet at δ 4.50, $J = 10$ Hz (5-CH), and a singlet at δ 6.12 (4-CH). (No attempt was made to isolate V by preparative gas chromatography.)

Attempted Synthesis of 3-Keto-4-carboethoxy-9-methyl- Δ^4 -octahydro-naphthalene (XXIII)

Synthesis of XXIII was attempted by a modification of the Nazarov procedure (18) as suggested by Heathcock (19). Ethyl β -ethoxy-propionyl

acetate (XXI) (20 g, 0.106 mole) in 100 ml of dry benzene was added dropwise over a period of one hr to 12.0 g (0.106 mole) of 2-methylcyclohexanone (XXII) and 0.4 g (catalytic amount) of β -naphthalene sulfonic acid in 400 ml of dry benzene in a three-neck one-liter flask equipped with a Dean-Stark tube, condenser, mechanical stirrer, and nitrogen inlet tube. The mixture was stirred at reflux temperature for three days without collection of water in the Dean-Stark tube. The solvent was removed in vacuo and the crude material taken up in 200 ml ether which was then extracted with three 50-ml portions of saturated sodium bicarbonate, one 50-ml portion of water and one of saturated brine. The ethereal solution was dried (sodium sulfate) and solvent removed in vacuo. Analysis by nmr showed the presence of starting materials only.

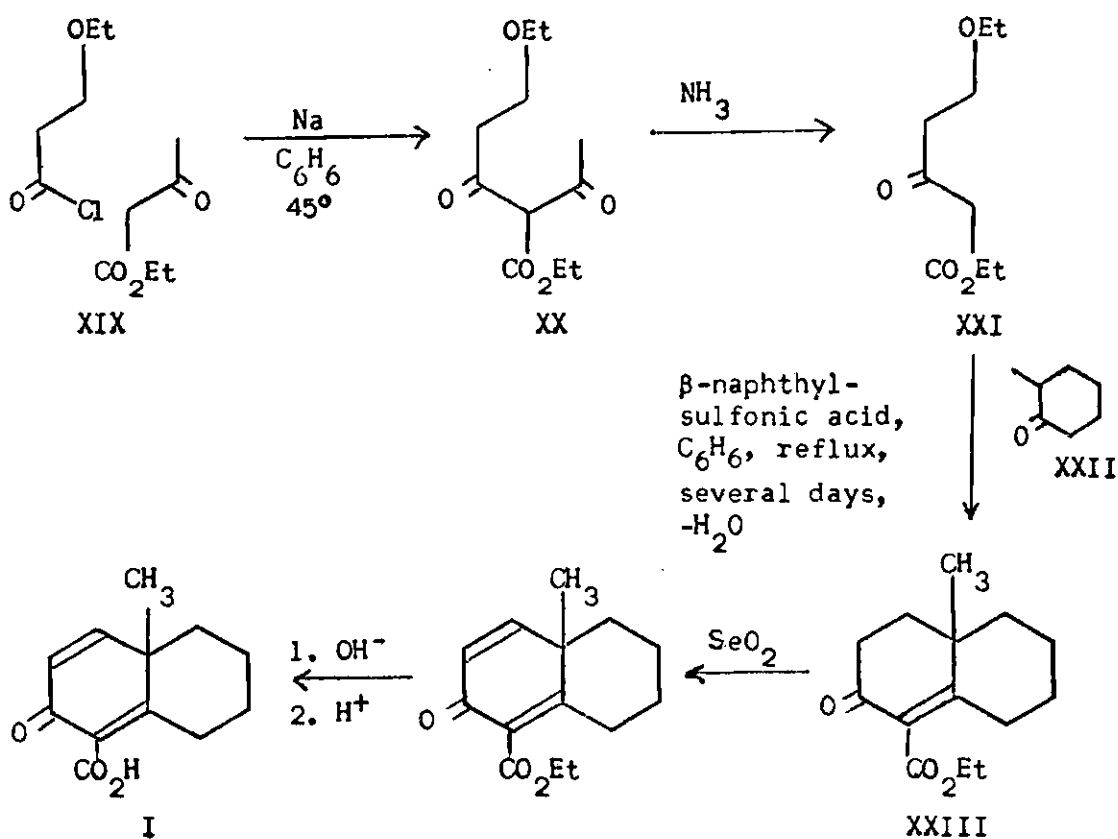
CHAPTER IV

DISCUSSION OF RESULTS

Although the photochemistry of 3-keto-4-carboxy-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (I) is of primary interest in this research, it is also worthwhile to discuss the synthetic procedures involved in obtaining the carboxy dienone.

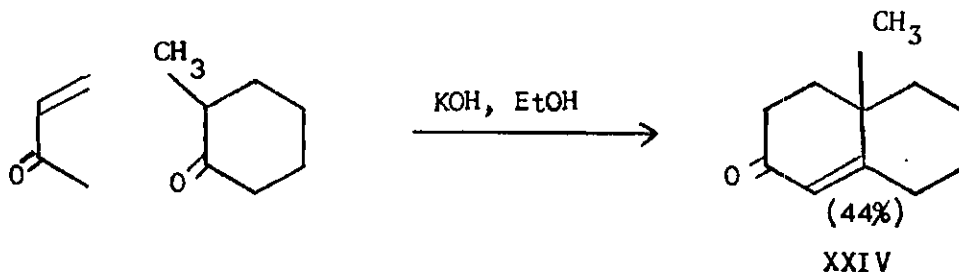
An attempt was initially made to synthesize I by the method outlined in Chart II.

Chart II

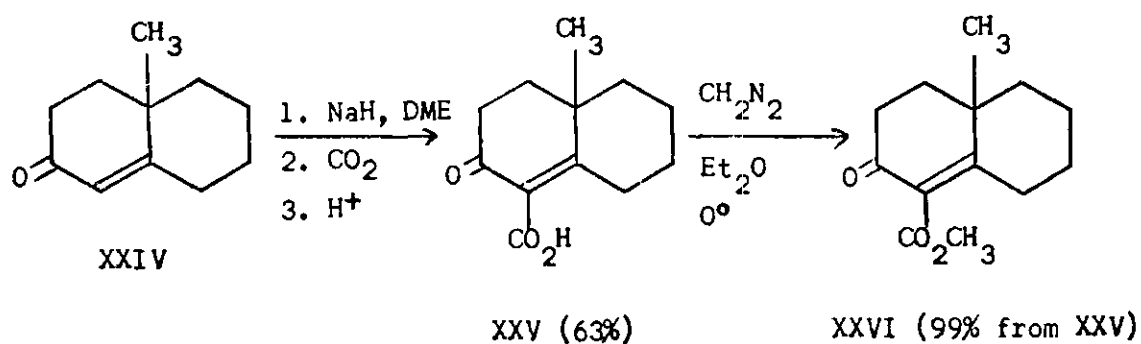


The β -ethoxypropionyl chloride (XIX) was prepared by the general procedure of Leslie and Henze (20) in 84% yield, b.p. 69°/31 mm. Compound XXI was prepared from XIX through intermediate XX (not isolated) by the procedure of Wenkert (21) in 40% yield, b.p. 31-34/0.50 mm. Synthesis of XXIII was attempted by a modification of the Nazarov procedure (18) as suggested by Heathcock (19). An equimolar mixture of XXI and 2-methylcyclohexanone (XXII) and a catalytic amount of β -naphthylsulfonic acid was refluxed in benzene under a nitrogen atmosphere for three days. Standard workup failed to yield XXIII in detectable amounts. Another attempt using xylene as solvent also failed.

Starting material for the synthesis of I was 3-keto-9-methyl- Δ^4 -octahydronaphthalene (XXIV) prepared according to the method of Ross and Levine (14) with slight variation in reaction time. The 44% yield of XXIV was slightly better than that reported by Ross and Levine (35-40%) but slightly less than the 50% reported by Caine and DeBardeleben (1) for the preparation of XXIV using equimolar amount of 2-methylcyclohexanone and methyl vinyl ketone rather than a two fold excess of the cyclohexanone. In each preparation of XXIV approximately 75% of the 2-methylcyclohexanone was recovered during fractional distillation and 30% of the methyl vinyl ketone was recovered as a volatile polymer (solidifying to a brittle plastic at room temperature) while approximately 15% remained as a non-volatile residue.

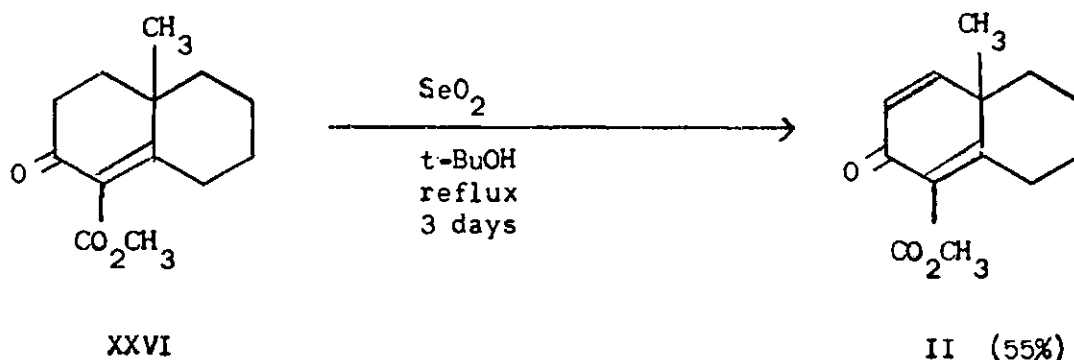


3-Keto-4-carbomethoxy-9-methyl- Δ^4 -octahydronaphthylene (XXVI) was prepared from XXIV by the general procedure of Wenkert (16). The best overall yield received in three runs was 63% with the yield determining step found to be the carboxylation as opposed to the esterification. The intermediate acid XXV was isolated in 65% yield in one preparation. Pure crystals of the acid were dissolved in ether and allowed to react with diazomethane at 0° affording an essentially quantitative yield of XXVI. Although special care was taken to avoid presence of protonic impurities in the media which would have lowered the yield in the carboxylation step, it was not found possible to improve the yield of XXVI.



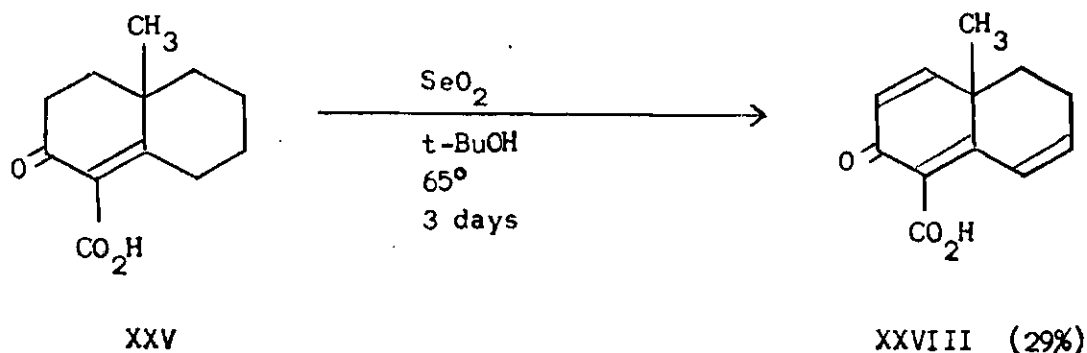
Various methods were tried for the conversion of XXVI to its dienone analog II, with none being better than that described by Tuller (17). Oxidation by DDQ failed to produce II in detectable quantities. The Tuller method utilizes a large excess (eight equivalents) of selenium dioxide and resulted in a 55% yield of the desired product. Preparations using four equivalents of selenium dioxide produced lower yields, seven percent in one case. The Tuller method calls for trituration with hot hexane to extract the dienone from the crude reaction mixture. This

method was tried and produced II containing much less amorphous selenium than II isolated by distillation of the crude mixture due to the tendency of selenium to sublime at high temperatures. However, the trituration technique significantly lowered the yield of II and it was found advantageous to accept the higher yields at the expense of having to remove selenium by techniques other than trituration. Column chromatography (elution with large amounts of 10:1 hexane-ether) proved successful in removing selenium but was more time consuming than the simple technique of treatment with activated charcoal in boiling methanol. This technique produced II sufficiently pure to be crystallized in ether-hexane and recrystallized from ether.



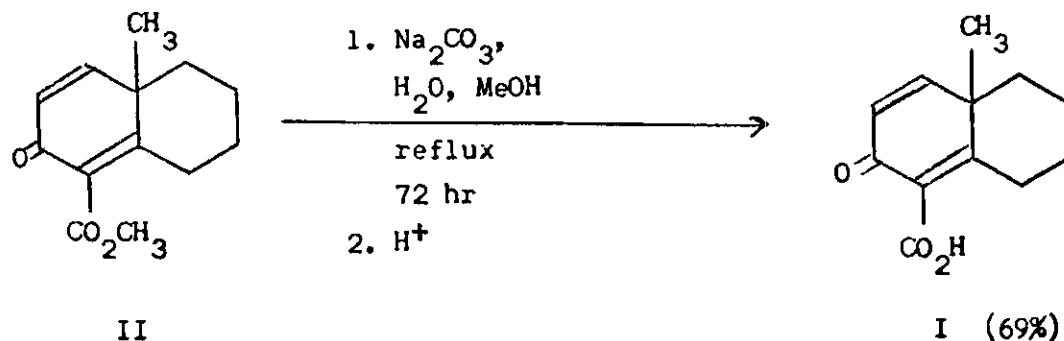
Although conversion of ester dienone II to the acid dienone I would appear to be a straightforward base hydrolysis, difficulty was encountered in obtaining I in sufficient yields to make the process synthetically feasible. The first attempt involved reaction of II with excess sodium bicarbonate in 20% aqueous methanol with stirring for 24 hr at room temperature. Workup involved extraction of the reaction mixture with ether followed by acidification to pH 2-3 using dilute hydrochloric acid and extraction of dienone acid with ether. This method

produced I in less than five percent yield with 80% recovery of starting material. The same procedure repeated at reflux temperature gave a seven percent yield. Attempts were made using one equivalent and an excess of 10% sodium hydroxide in aqueous methanol and ethanol at room temperature and at reflux for 24 hr periods with the best yield being 11%. One attempt was made using excess lithium iodide in refluxing collidine which had been found by Krakower, Brown, and Fried (22) to be a good method for the hydrolysis of base stable esters. This procedure failed to produce I in detectable amounts. Attempted oxidation of 3-keto-4-carboxy-9-methyl- Δ^4 -octahydronaphthalene (XXVII) to acid I using eight equivalents of selenium dioxide resulted in a 29% conversion to a compound believed to be 3-keto-4-carboxy-9-methyl- $\Delta^{1,4,5}$ -tetrahydronaphthalene (XXVIII). Selective hydrogenation of XXVIII was not attempted. Another attempt using two equivalents of selenium dioxide produced no dienone acid and a lower yield of trienone XXVIII.

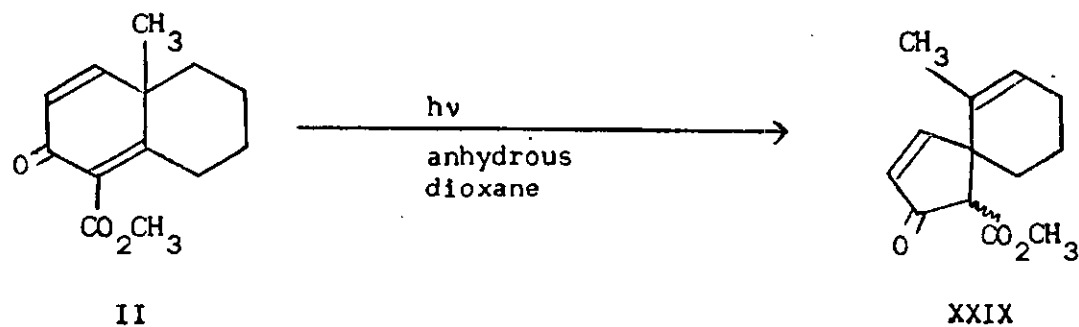


The procedure giving the best yield of I was that initially tried reacting crystalline ester II with sodium carbonate (10% in aqueous methanol) and allowing the reaction to proceed for 72 hr rather than the shorter period, with removal of all methanol by distillation prior

to initial extraction with ether. This procedure resulted in a 69% yield of I with 29% recovery of ester II. Trace amounts of selenium also degraded the yield of I as indicated by the difference noted in using crystalline II (69% yield) and II purified only by decolorization with activated charcoal (39% yield).

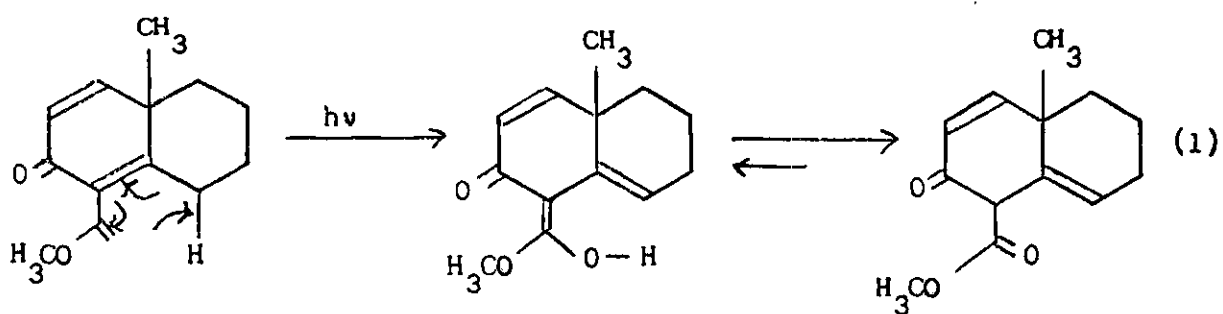


From the irradiation of II in anhydrous dioxane one would expect the main product to be the spiro compound XXIV.

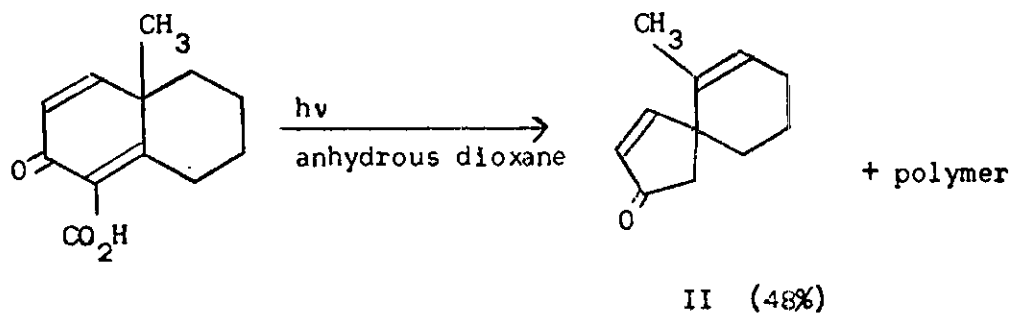


Compound XXIX was not detected in any of the irradiations of II as noted by the absence of a multiplet in the $\delta 5.5$ vicinity of the nmr spectrum corresponding to the C-7 hydrogen. Photolysis of II for up to three hours using both Pyrex and quartz filters failed to produce any new peaks on glc (SE-30 and Carbowax) analysis. Scheffer and Boire (23) had noted that the direct (singlet) photochemical reaction of certain α, β -

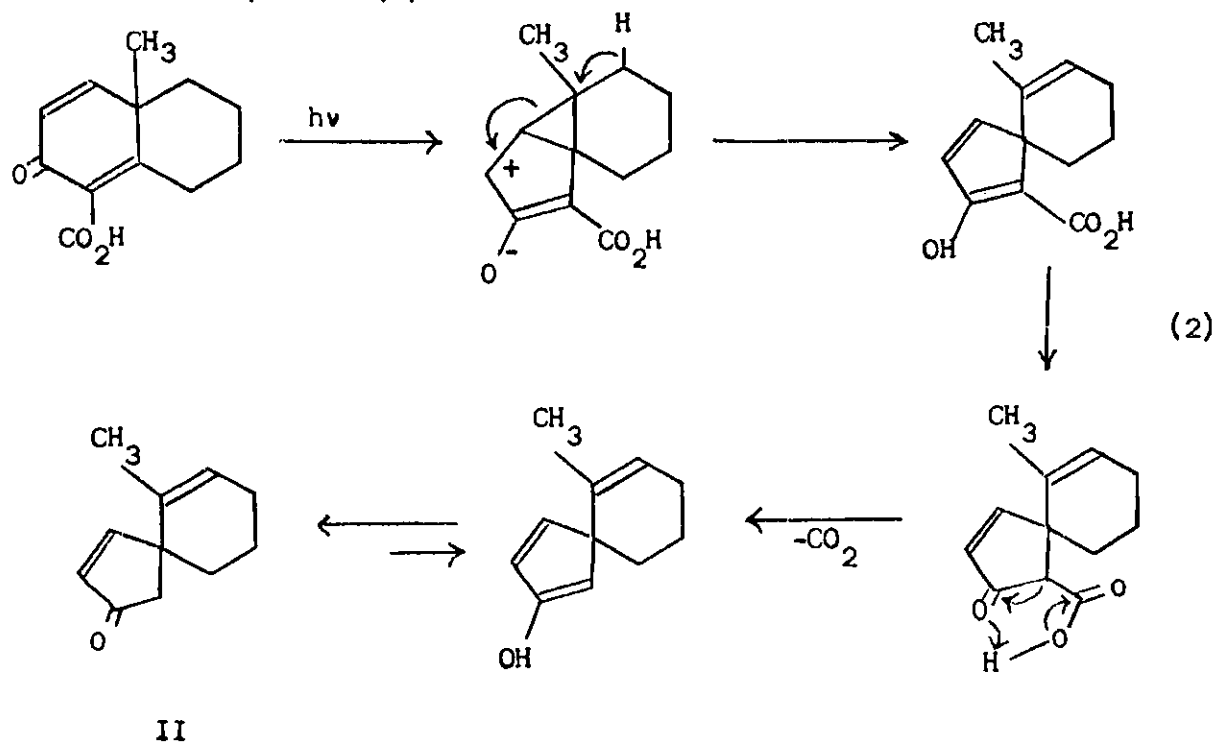
unsaturated esters is likely to be deconjugation of the double bond to the β,γ -position whereas sensitized (triplet) reactions may completely avoid this phenomenon. It was thought that this may apply in the direct photolysis of II in that it might be undergoing deconjugation in the photochemical reaction and reisolmerizing during the glc analysis and preparation of the nmr sample. Therefore a sensitized (triplet) photolysis was attempted, hopefully to avoid the possible isomerization problem. However, this attempt failed in that there was still no evidence of XXIX or any other rearranged photoproduct in the crude mixer. Furthermore, there was even more evidence that the ester was indeed isomerizing photochemically as noted by appearance of a new peak on glc analysis coupled with disappearance of starting material. Analysis by nmr gave indications of the C-4 and C-5 protons present in the deconjugated system. Attempts to isolate XXIX failed, apparently because it is isomerized on the chromatography column. A simplified mechanism for the isomerization of II is in Equation (1):



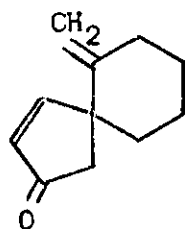
Irradiation of I in anhydrous dioxane produced spiro ketone III in 48% yield with recovery of starting material and considerable polymer.



Formation of the spiro ketone III can be rationalized through the mechanism in Equation (2):

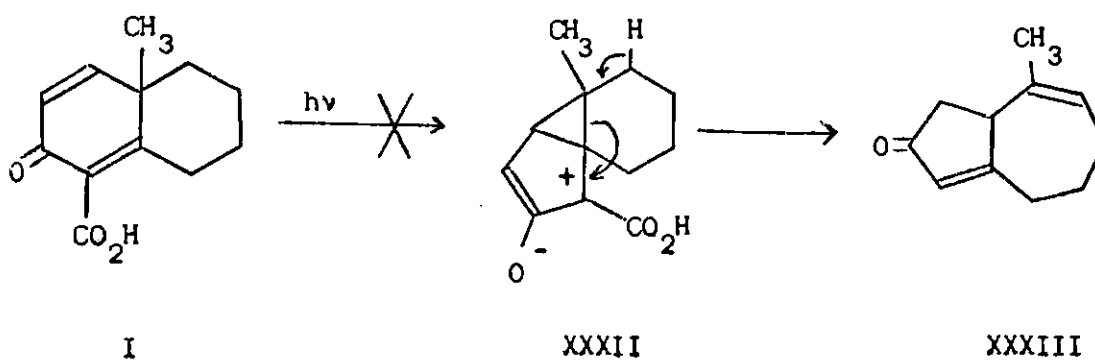


There was no indication that lumi product was present in the final reaction mixture, however this does not preclude the fact that lumi-product may have been present at one time during the reaction and underwent cleavage so as to give dienone III. There was no indication of formation of isomer XXXII containing an exocyclic double bond.



XXXII

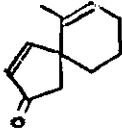
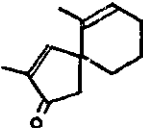
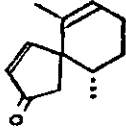
The absence of any hydroazulenone XXXIII as a product of irradiation of I in inert media clearly illustrates the dominance of zwitterionic species XXX over XXXII due to destabilization of the positive charge in XXXII by the electron withdrawing carboxyl substituents.



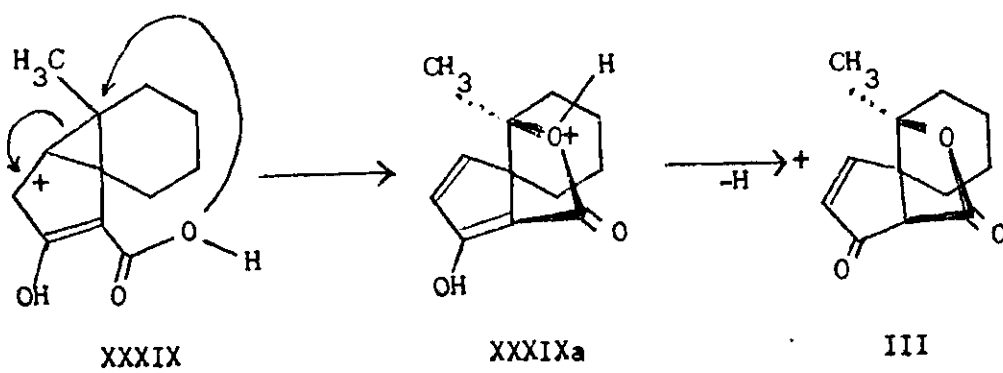
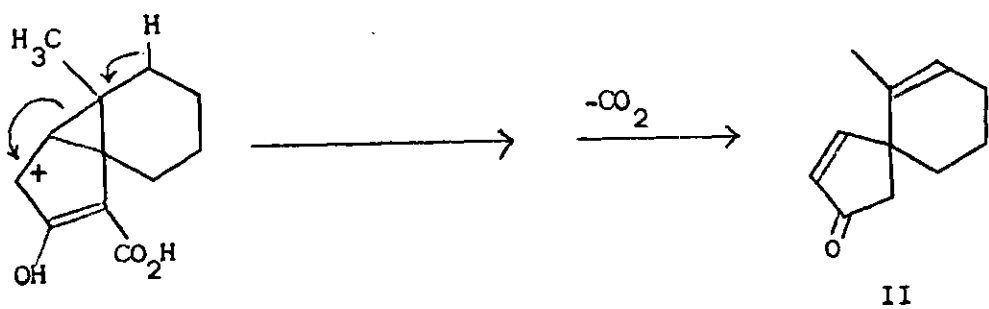
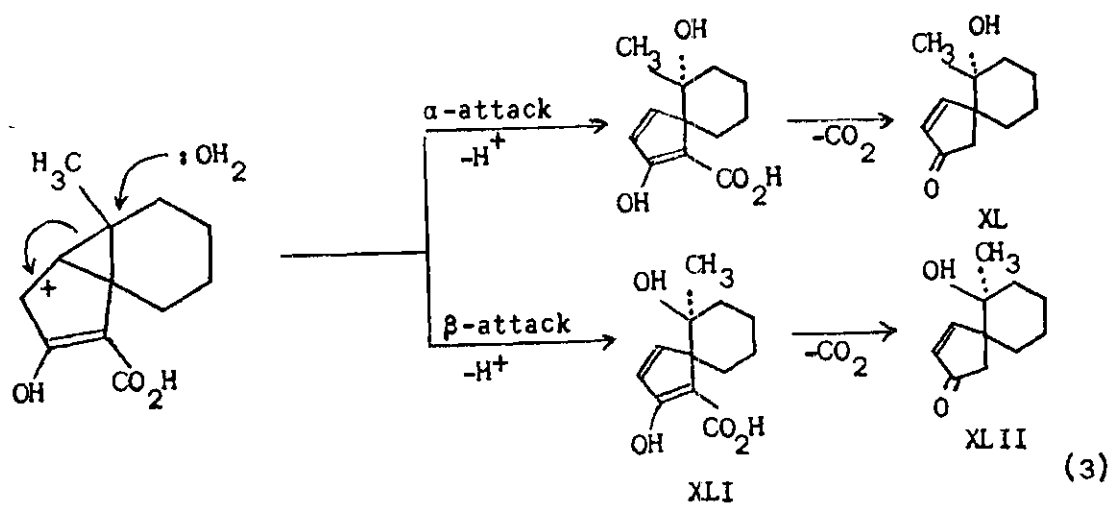
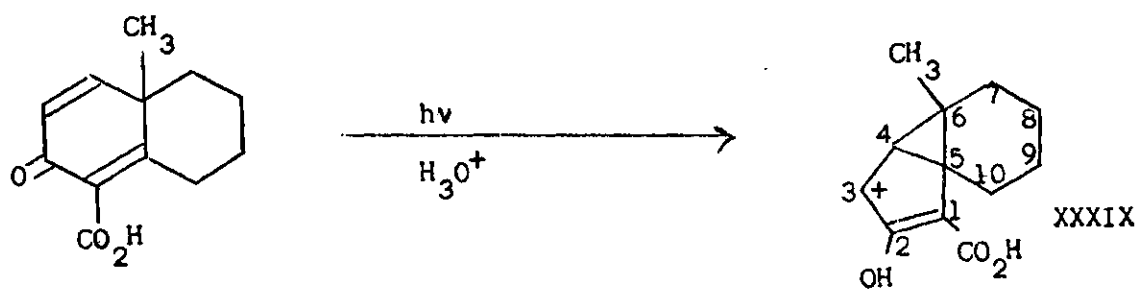
The physical and spectral properties of III conform closely to those observed by Kropp (24) for the 3-methyl and 10-methyl analogs as shown in Chart III following:

Chart III

Comparison of III and Analogous Compounds

Compound			
B.P.	109-111°/0.25 mm	119-120°/0.30 mm	87-88°/0.25 mm
ir (max)	1712, 1662, 1645 cm ⁻¹	1700, 1661, 1639 cm ⁻¹	1712, 1689 1587 cm ⁻¹
uv (max)	218 nm, ε = 9,200	229 nm, ε = 10,400	223 nm, ε = 8,800
nmr			
3,4-CH	δ6.06 and 7.31, 2d, J = 5.5		δ6.22 and 7.46, 2d, J = 5.5
6-CH ₃	δ1.54, d, J = 2	δ1.48, m, J = 2	δ1.52, s
1-CH ₂	δ2.00 and 2.38, 2d, J = 18.5	δ2.14 and 2.54, 2d, J = 18.5	δ2.28 and 2.42, 2d, J = 18.5
7-CH	δ5.57, m	δ5.56, m	δ5.62, m

Irradiation of I in aqueous acidic media would be expected to give hydroxy ketones XL and XLII, dienone II, or lactone III depending on the mechanism of opening the cyclopropyl intermediate XXXIX as demonstrated in Equation (3).



Formation of XL by nucleophilic attack from the α -Face is unlikely as steric hindrance would necessitate considerable carbonium ion character at C-6. The mechanism shown in Equation (3) for formation of lactone III is one of two possibilities, the other being lactonization by loss of water from XLI. Examination of models shows that considerable stretching of the 4-6 bond is required to bring the carboxyl group within bonding distance of C-6 and that XXXIXa is a severely strained species. However, this species could still be in the excited state with bond lengths and angles distorted. It could also be that the transition state for the formation of III lies closer to the bond breaking (4-6) state than to the formation of the oxygen bond to C-6. Considering these arguments one might expect lactone III to also be formed in neutral media, which is not the case. One must therefore consider the alternative, lactonization of XLI. Caine and DeBardeleben (1) disclaimed such a route for lactone formation during photolysis of the 2-carboxy analog because (1) it would require lactonization to compete with decarboxylation and (2) lactone was formed in inert media. Reaction workup by Caine and DeBardeleben entailed removal of solvent in vacuo which would indeed favor decarboxylation. However, the method employed in this research was lyophilization which might allow lactonization rather than decarboxylation. Considering the absence of lactone as a product of inert media photolysis, formation of lactone III from species XLI seems more logical than a simple concerted attack of the carboxyl group at C-6 as indicated in Equation (3).

In the initial irradiation of I in aqueous acetic acid, the crude product was first analyzed by glc (Carbowax). The presence of four

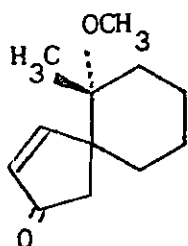
major peaks (in addition to those representing starting material) indicated an nmr of the crude sample might not be informative. Therefore, without any spectral examination, the crude material was chromatographed after extraction with base to remove polymer and unreacted starting material. Column chromatography resulted in isolation of some polymer, lactone IV, and small amounts of dienone III (six percent). On subsequent runs the crude sample was first analyzed by nmr and in each case found to be relatively pure lactone and contained no dienone III.

Analysis of crystalline lactone IV by glc (Carbowax) showed four peaks in the ratios and retention times corresponding to those noted previously for the crude photo-product. Apparently the lactone is primarily (60%) degraded to dienone III on the Carbowax column (retention time 7.4 min) with other peaks possibly representing spiro lactone IV, hydroxy acid XLI, and hydroxy ketone XLII. Likewise, the lactone was degraded on the chromatography column to give dienone III with no isolation of XLI or XLII. Once it was determined that column chromatography degraded the lactone, purification of the photoproduct on subsequent irradiations consisted of extraction with base to remove polymer and unreacted starting material and crystallization from carbon tetrachloride. Analysis of the crude material from which no more lactone could be crystallized showed lactone present by no indication of III, XLI, or XLII, or any hydroazulenone compounds.

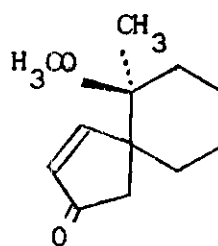
The spectral properties of lactone IV were consistent with the proposed structure. The 1769 cm^{-1} ir absorption is strongly indicative of the γ -lactone. The low field doublet of the AB quartet in the nmr spectrum is assigned to the C-4 proton. The peaks of this doublet show

splitting, ca. 1.5 Hz, presumably because of long range coupling through an "M" arrangement with the C-1 proton which also shows the ca. 1.5 Hz splitting. This same phenomenon was noted by Smith, *et al.*, (24) in the nmr spectrum of 4,4,6-trimethylcyclohex-2-enone and by Wiemann, Risse and Casals (25) in the case of 4,4-dimethylcyclohex-2-enone.

Irradiation of I in anhydrous methanol would be expected to give methoxy ketones XLIII and XLIV as well as dienone III through mechanisms already presented in Equation (3).



XLIII



XLIV

A complex mixture was obtained upon irradiation of I in anhydrous methanol which may have contained III, XLIII, XLIV and other compounds. The crude mixture was never separated thoroughly enough to isolate and identify products.

Both model dienones I and II proved to be very inactive photochemically. Carboxydienone I produced photochemically rearranged products only upon irradiation using a quartz filter and then with production of considerable polymer. Yields were high enough, however, to make the procedure synthetically appealing. Carbomethoxy dienone II failed to produce photochemically rearranged products and would be of little synthetic value. The ability of carboxy dienone I to produce spiro[4.5]-systems with no substituents on the 5-membered ring makes it

a logical precursor for such systems. Although spiro products were isolated in good yield by Kropp (26), the reaction directing substituent was the electron donating methyl at C-3 (on the spiro compound), an entity found in few natural products and one which is difficult to remove.

CHAPTER V

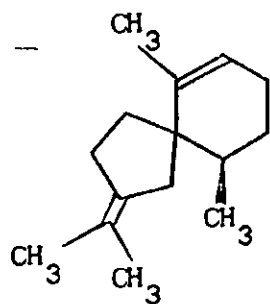
RECOMMENDATIONS

Further study should be conducted on the compound believed to be the trienone acid 3-keto-4-carboxy-9-methyl- $\Delta^{1,4,5}$ -tetrahydronaphthalene to prove its structure and investigate selective hydrogenation (catalytic hydrogenation at atmospheric pressure) as a possible synthetic route to dienone acid I.

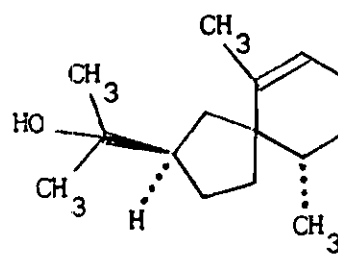
Study should be continued on the photochemistry of I in anhydrous methanol with more vigorous attempts made to isolate and identify methoxy ketones XLIII and XLIV.

An attempt should be made to isolate the deconjugated ester V by preparative gas chromatography and further studies made of the photochemical behavior of II upon irradiation at various wavelengths in sensitized (triplet) and non-sensitized (singlet) reactions.

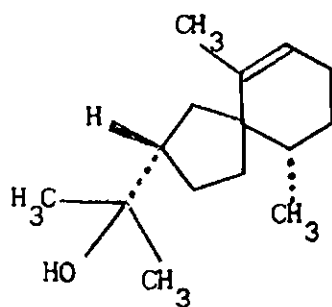
Finally, the synthetic value of the photochemistry elaborated by this research should be thoroughly investigated. Specifically, the photochemistry of compounds such as carboxy dienone I in neutral media should be investigated as a possible step in the synthesis of natural products such as β -vetivone (XLV), hinesol (XLVI), and agarospirol (XLVII).



XLV



XLVI



XLVII

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