

A STUDY OF THE
PHOTOCHEMICAL REARRANGEMENTS OF
2-METHOXY-3-KETO-9-METHYL- $\Delta^{1,4}$ -HEXAHYDRONAPHTHALENE

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PHOTOCHEMICAL REARRANGEMENTS OF
2-METHOXY-3-KETO-9-METHYL- $\Delta^{1,4}$ -HEXAHYDRONAPHTHALENE

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GLOSSARY OF ABBREVIATIONS

bp	boiling point
cm ⁻¹	wave numbers (ir spectrum)
EMD	exact mass determination (mass spectrum)
eV	electron volt
glc	gas-liquid chromatography
Hz	Hertz (cycles per second, nmr spectrum)
ir	infrared
J	coupling constant (nmr spectrum)
m+	molecular ion (mass spectrum)
m/e	mass to charge ratio (mass spectrum)
mp	melting point
nm	nanometers (millimicrons, uv spectrum)
nmr	nuclear magnetic resonance
tlc	thin layer chromatography
uv	ultraviolet
ε	extinction coefficient (uv spectrum)

SUMMARY

The principal goal of this research was to further investigate the photochemical rearrangement of the cross-conjugated cyclohexadienone, 2-methoxy-3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (1). Dawson (7) reported the formation of 2-methoxy-3-keto-6 α -methyl-6 β -hydroxy[4.5]spirodecene-1 (13) in 35 per cent yield from irradiation of dienone 1 in 45 per cent aqueous acetic acid. Irradiation of 1 in anhydrous dioxane gave not only the expected lumiprodukt, 2-keto-3-methoxy-10 α -methyltricyclo[4.4.0.0^{1,5}]dec-3-ene (2), but another produkt identified as the tricyclic enone 8-methyl-1-methoxy-4,5,6,7,8,8 α -hexahydro-1 α -cyclo-2(1H)-azulenone (3) along with a small amount of the phenol 4. Compounds 2 and 3 were formed in 31 and 27 per cent yield, respectively.

After its isolation from the photolysis mixture by careful column chromatography, the tricyclic enone 3 was hydrogenated in the presence of palladium on carbon. The resulting dihydro derivative (5) was subjected to nmr analysis using various concentrations of a europium shift reagent. An unsuccessful attempt was made to convert the tricyclic ketone 5 into a compound of known structure.

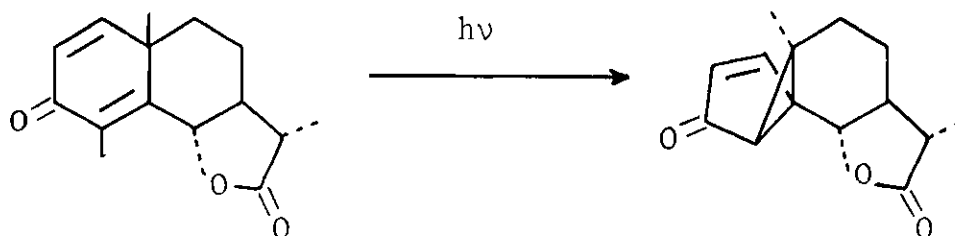
The lumiprodukt 2 was transformed into the 3-keto-tricyclodecane 9 by the following sequence of steps: sodium

borohydride reduction of 2 followed by acylation of the resulting alcohol gave the acetoxy compound 7 in 83 per cent yield. Hydrolysis of the enol ether function of 7 gave the tricyclic α -acetoxy ketone 8. Lithium-ammonia reduction of 8 afforded the ketone, 3-keto-10 α -methyltricyclo[4.4.0.0^{1,5}]decane 9. This latter product should be a useful material in connection with studies on the mechanism of cyclohexadienone photochemical rearrangements.

CHAPTER I

INTRODUCTION

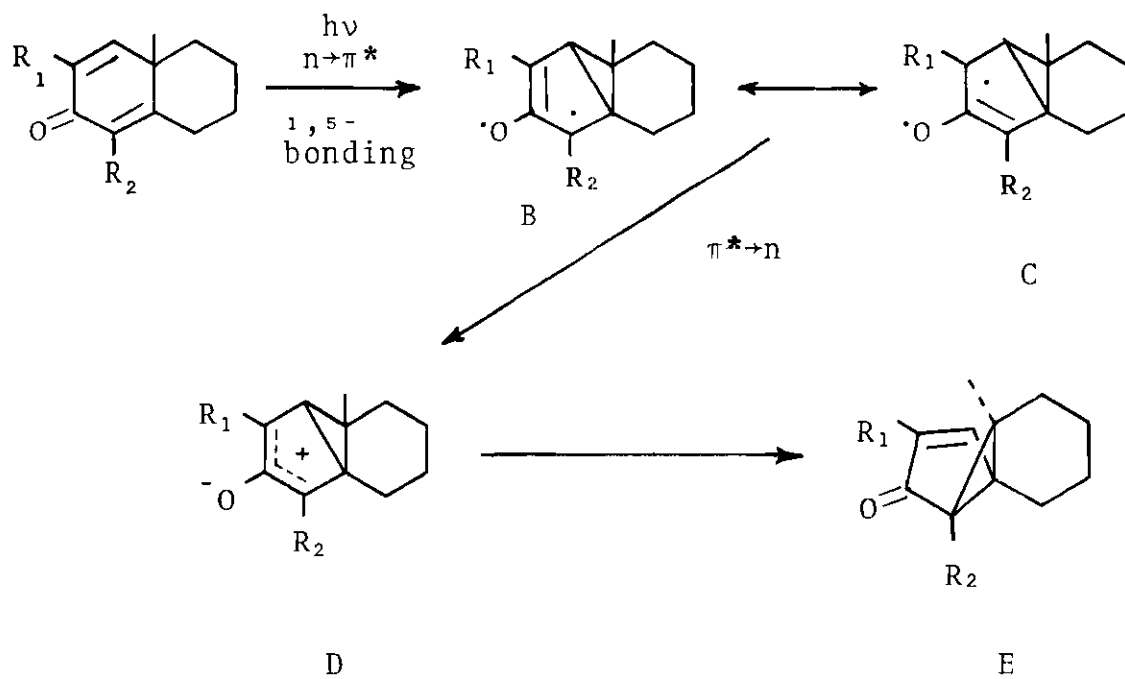
In recent years much interest has been generated in the field of organic photochemistry primarily because of the stereospecificity of photochemical reactions and their utility in organic synthesis. Of particular interest to natural products chemists are the photochemical rearrangements of cross-conjugated cyclohexadienones. Barton (1) initiated this interest during his investigation of the photochemistry of the naturally occurring sesquiterpene α -santonin. Irradiation of α -santonin in neutral media led to the bicyclo[3.1.0]hexane derivative known as lumisan-tonin:



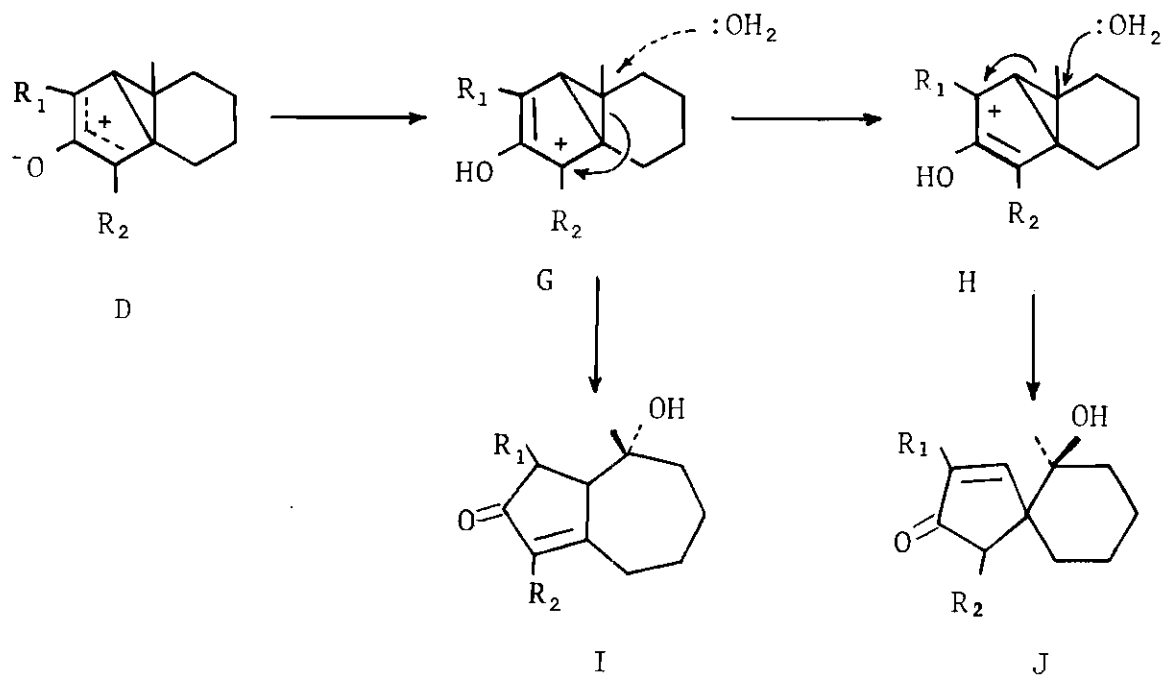
As illustrated by recent reviews (2-4), it has been found that almost all compounds possessing the cyclohexa-dienone chromophore exhibit analogous behavior when irradi-

ated with ultraviolet light.

Although still unproven the zwitterionic species D proposed by Zimmerman and coworkers (5) is widely accepted as the key intermediate in the cyclohexadienone photochemical rearrangement. According to Zimmerman (5) there is first an $n \rightarrow \pi^*$ electronic transition to the singlet state of the dienone followed by intersystem crossing to give the triplet excited state. 1,5-Bonding occurs next to form the diradical represented by resonance structures B and C. $\pi^* \rightarrow n$ Demotion produces the zwitterion D, which in neutral media, normally undergoes a 1,4-sigmatropic rearrangement to form the lumipproduct E.

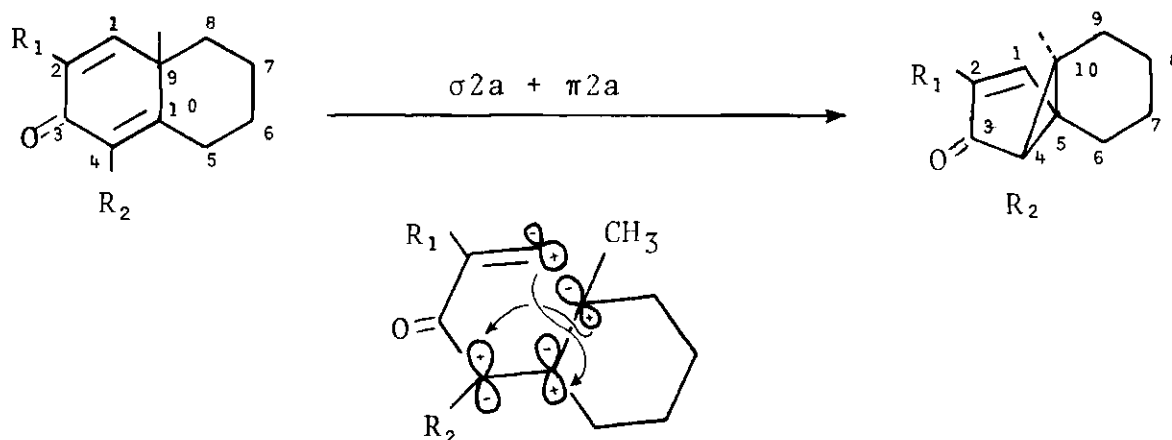


In acidic media the zwitterion D is protonated forming the mesoionic species represented by resonance extremes G and H. Attack by solvent results in either the spiro ring system J or the 5/7-fused ring system I. It should be noted that the electronic characteristics of substituents R_1 and R_2 have an important role in the course of the reaction. Substituents R_1 and R_2 determine which structure, G or H, contributes more to the total structure of the mesoionic species and therefore the mode of solvent attack, ultimately determining the nature of the products.



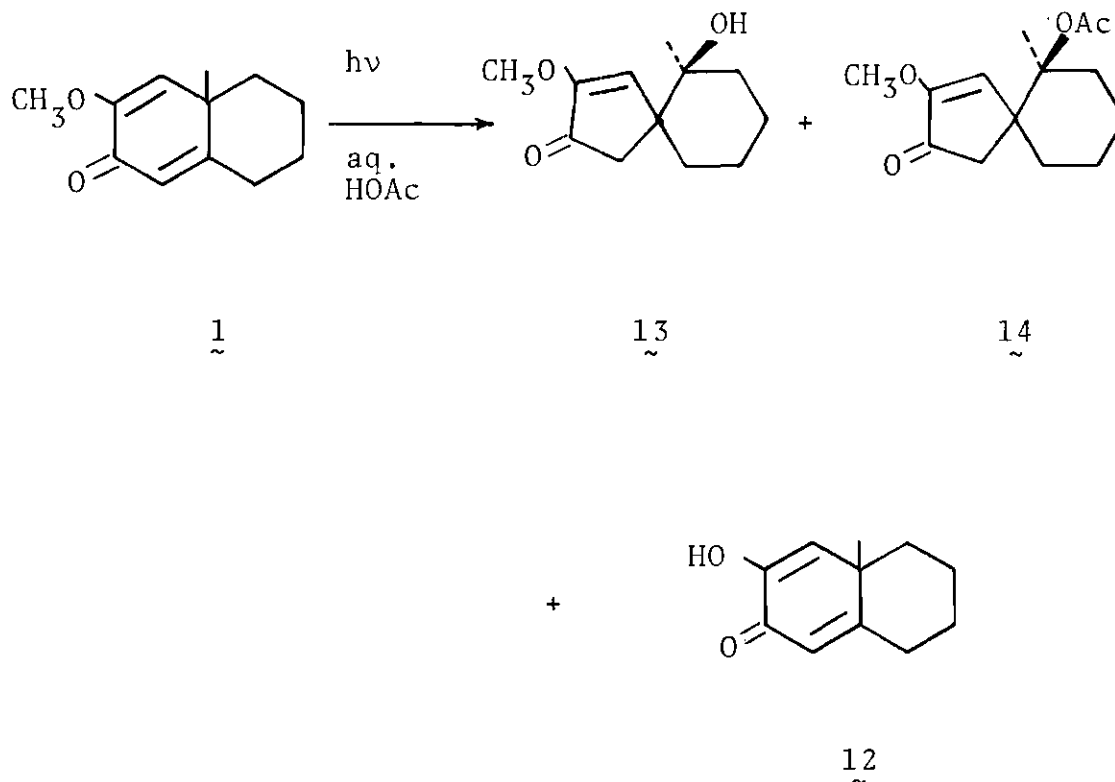
Woodward and Hoffman (6) consider the cyclohexadienone photochemical rearrangement to be a concerted $[\sigma 2a + \pi 2a]$ cycloaddition. According to these workers (6)

anataara facial addition of the 1,9-bond to the 4,10-bond and inversion of configuration at C-9 occurs in the excited state to form the corresponding lumiprodukt:



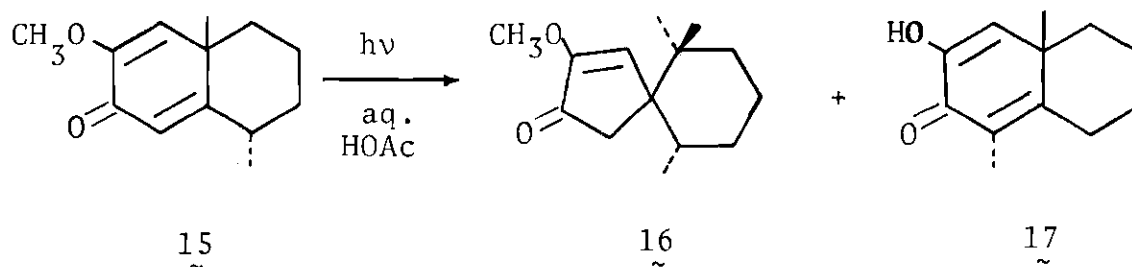
Unfortunatly the Zimmerman mechanism leads to precisely the same products as would be obtained by a concerted process. Either mechanism remains a possibility.

The dienone under investigation, 2-methoxy-3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (1) was first studied by Dawson (7). After obtaining 1 in a four step synthesis, he irradiated the dienone in aqueous acetic acid. The expected spiro hydroxy enone 13 was isolated, but only in a 35 per cent yield. A considerable amount of the disphenol 12 was also recovered along with a small amount (3 per cent) of 14.

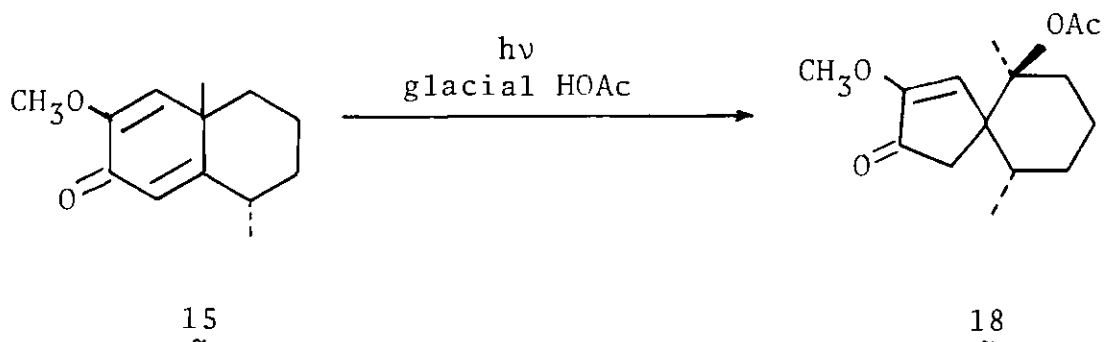


The low yield of photoproduct $\underset{\sim}{13}$ was chiefly due to light promoted hydrolysis of the starting material to give mainly $\underset{\sim}{12}$.

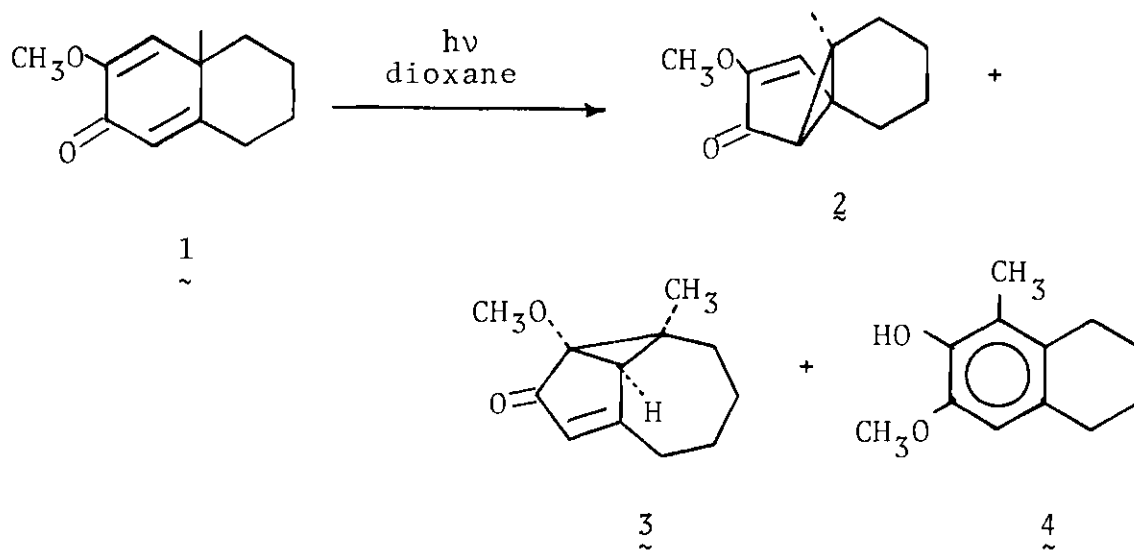
A similar dienone, 2-methoxy-3-keto-5,9-dimethyl- $\Delta^{1,4}$ -hexahydronaphthalene ($\underset{\sim}{15}$), was converted into the corresponding photoproduct $\underset{\sim}{16}$ in a 28 per cent yield. Again, most of the products were hydrolyzed starting material ($\underset{\sim}{17}$).



Ingwalson (8), in his synthesis of (\pm) - α -vetispiene, improved the yield of 18 to 90 per cent by irradiating the dienone 15 in glacial acetic acid, thereby reducing the amount of hydrolysis.

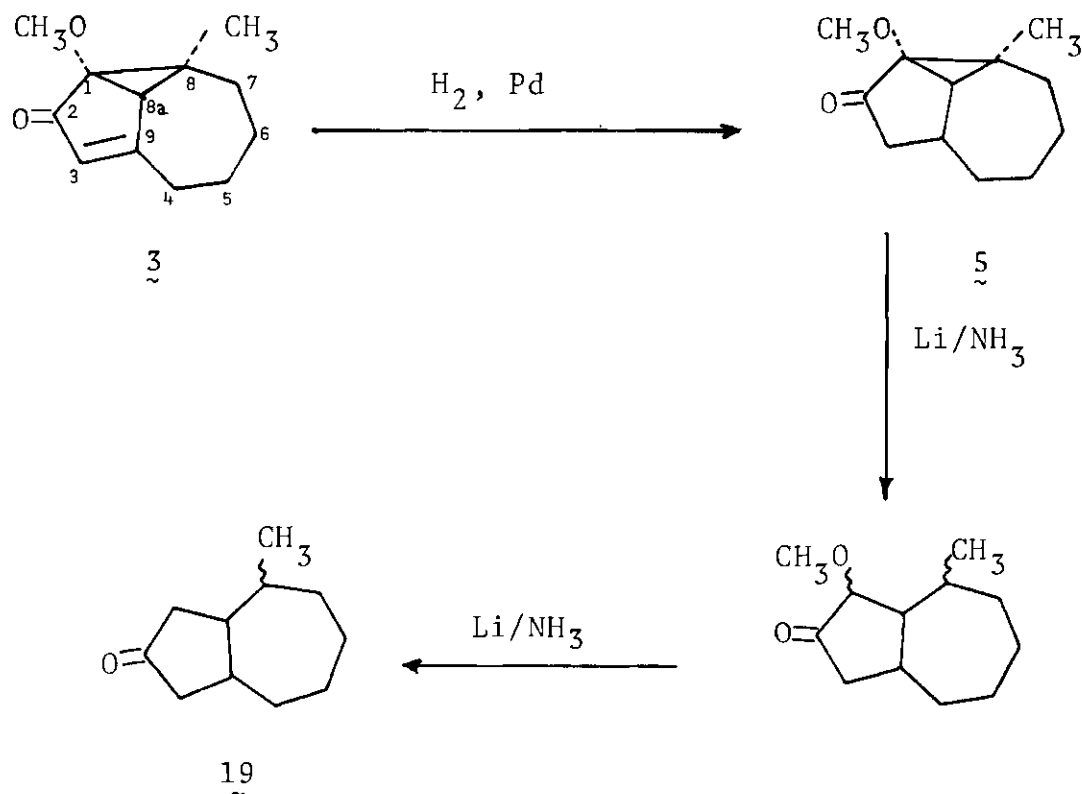


Dienone 1 was first irradiated in neutral media by Chao (9). When irradiated in anhydrous dioxane 1 gave the expected lumipproduct 2 along with a small amount of phenol 4 and a third product, an isomer of 2, which was not iden-



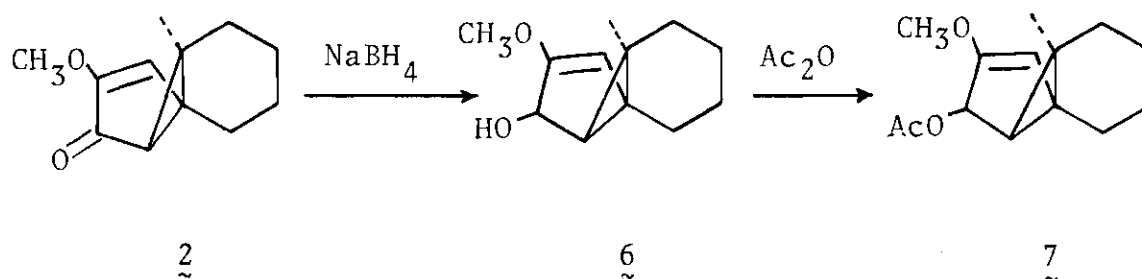
tified. The spectral properties of the unknown product suggested that it might be compound 3. In this work efforts were made to confirm this structure.

Compound 3 was first hydrogenated in the presence of a palladium catalyst and the product 5 was subjected to nmr analysis using a europium shift reagent. The saturated tri-cyclic ketone 5 was subjected to several transformations in a further effort to characterize the compound, but these transformations proved to be unsuccessful. Compound 5 was first treated with lithium-ammonia solution to open the cyclopropyl ring in conjugation with the carbonyl group. A second lithium-ammonia reduction in the presence of ethanol

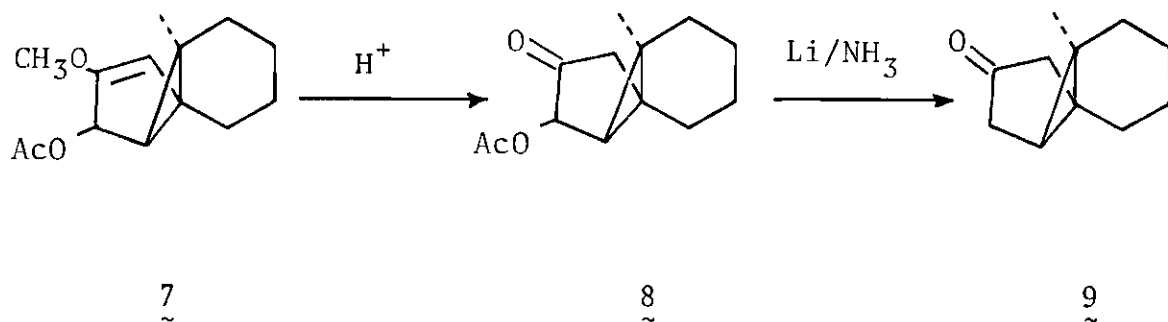


was performed on the resulting product, which should have removed the α -methoxy group and afforded the azulene 19, a compound of known structure (10). Unfortunately, no conclusive results were obtained from these reactions. The transformation was repeated except the second time the reaction was conducted in one step. Compound 5 was added to an excess of lithium dissolved in anhydrous ammonia then ethanol was added. Again, no positive results were obtained from the reaction.

Since the structure assigned to compound 2 was not entirely conclusive, efforts were made to confirm this structure. It was decided to convert the lumiproduct 2 into the tricyclic ketone 9. This transformation would not only help confirm the structure of 2, but also the product 9 would be a valuable precursor for future mechanistic studies. Compound 2 was reduced with sodium borohydride which afforded the alcohol 6 in almost quantitative yield. Treatment of 6 with acetic anhydride in dry pyridine gave the ester 7 in 83 per cent yield.



The next step in the sequence was to reductively remove the acetate group then hydrolysis of the enol ether function would give the desired ketone. Unfortunately, the reductive cleavage of the ester proved to be unsuccessful; treatment of 7 with lithium-ammonia solution afforded a number of products. The spectral properties of the crude material indicated that neither starting material nor any of the simple reduction products were present. The reduction was repeated using calcium in ammonia, but similar results were obtained. Since reductive cleavage of the ester in 7 could not be successfully accomplished, another approach was tried. Hydrolysis of the enol ether function was accomplished successfully without affecting the ester in compound 7. Next the α -acetoxy ketone 8 was reduced smoothly with lithium-ammonia solution to give the desired tricyclic ketone 9.



CHAPTER II

INSTRUMENTATION AND EQUIPMENT

When a nitrogen atmosphere was required for a reaction, an apparatus similar to that described by Johnson (11) was used. All organic solvents except ether and hexane were purified according to the procedures described by Fieser (12). Removal of solvents in vacuo was accomplished by using a Büchi Rotary Evaporator. Anhydrous sodium sulfate was used as a drying agent during workup of the reactions. A Hanau 7-watt low pressure mercury arc lamp, which furnished more than 90 per cent emission at 2537 Å was employed in the irradiation experiments. Solutions were deoxygenated and agitated prior to and during irradiation with a slow stream of dry nitrogen. Chromatography columns were prepared using Grace Grade 923 100-200 mesh silica gel in the ratio of approximately 25 g of silica gel to 1 g mixture. Catalytic hydrogenations were performed using a Parr low pressure hydrogenation apparatus.

Ultraviolet spectra were obtained with a Beckman DB-GT recording spectrophotometer, using 95 per cent ethanol as the solvent and 1-cm balanced cells. Infrared spectra were obtained using a Perkin-Elmer model 457 recording spectrophotometer; 0.1 mm sodium chloride cells were used. Nuclear magnetic resonance spectra were obtained on a Varian Asso-

ciates Model A-60D or a T-60 Nuclear Magnetic Resonance Spectrometer. Tetramethylsilane was used as an internal standard and chemical shifts are reported downfield from it. The abbreviations m, s and d are used for multiplet, singlet and doublet, respectively. Mass spectral data were obtained using a Varian Associates Model M-66 medium resolution mass spectrometer with a 70 electron volt source or a Hitachi Perkin-Elmer RMU-7L high resolution mass spectrometer with an 80 electron volt source. Glc analyses were performed using a Perkin-Elmer model 881 flame ionization gas chromatograph. A 6 foot by 1/8 inch stainless steel column, packed with 10 per cent K-20 Carbowax on 60/80 chromasorb W HMDS, with a temperature program from 100° to 200° at 12 degrees per minute was used throughout the work. Preparative glc was performed using an Aerograph model A-90P manual temperature program gas chromatograph. Melting points were determined on a Fisher Johns apparatus and are uncorrected.

CHAPTER III

EXPERIMENTAL

3-Keto-9-methyl- Δ^4 -octahydronaphthalene (10)

Compound 10 was prepared by the general method of Ross and Levine (13). Methyl vinyl ketone (50 g, 0.7 mole) in 300 ml ether was added dropwise over a 3 hr period to a stirred solution of 2-methylcyclohexanone (112.2 g, 1.0 mole), ethanolic potassium hydroxide (6.0 g, 0.1 mole in 20 ml of absolute ethanol) and 500 ml of ether. After the addition was complete, the reaction mixture was stirred for 1 hr at 0°, allowed to warm to room temperature and stirred for an additional 12 hr. After the addition of an equal volume of water, 30 ml of glacial acetic acid was added to the reaction mixture. The aqueous layer was separated and washed with two 200-ml portions of ether. The ether extracts were combined, washed with two 200-ml portions of saturated brine solution and dried (Na_2SO_4). Evaporation of the solvent in vacuo followed by vacuum distillation of the residue gave 57.40 g (49%) of 10: bp 82-83°/0.25 mm [Lit. (13) bp 82-84°/0.5 mm].

2-Methoxy-3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (1)

Following the method of Seebach (14), a 3000-ml three-

neck flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer was flame dried while being swept with dry nitrogen. Next the flask was charged with 1100 ml of glacial acetic acid and 100 ml of acetic anhydride. After heating the solution for 1 hr, lead tetraacetate (246 g, 0.55 mole) and 3-keto-9-methyl- Δ^4 -octahydronaphthalene (60 g, 0.37 mole) were added and the mixture was stirred for 24 hr at 70-80° under a nitrogen atmosphere. Most of the acetic acid was removed by distillation at aspirator pressure. Water (600 ml) was added and the mixture was thoroughly extracted with three 150 ml portions of ether. The combined ether extracts were cautiously neutralized with solid sodium bicarbonate, washed with saturated brine solution and dried (Na_2SO_4). The solvent was removed in vacuo to leave a dark brown oil which was not purified but used directly in the next step. Compound 11 exhibited the following properties: ir (CCl_4) 1735 (ester C=O), 1655 (α,β -unsaturated C=O) and 1618 cm^{-1} (conjugated C=C); nmr (CCl_4) δ 1.23 (s, 3H, 9- CH_3), 2.01 (s, 3H, 2-COOC CH_3) and 5.06 (s, 1H, 4-CH).

The procedure of Rao and Axelrod (15) was employed for the preparation of compound 1. The keto acetate 11 prepared as described above was dissolved in 1200 ml of methanol and placed in a 3-l flask equipped with a gas dispersion tube. A solution of potassium hydroxide (20 g, 0.35 mole) in 100 ml of water was added, the mixture was stirred for a few minutes and a thin stream of air was allowed to bubble

through the solution for 24 hr. Most of the methanol was removed in vacuo; water was added to the residue and the mixture was washed with three 150-ml portions of ether. The aqueous layer was acidified with dilute hydrochloric acid and extracted with three 100-ml portions of ether. The combined ether extracts were washed with two 100-ml portions of saturated brine solution, dried (Na_2SO_4) and the ether removed in vacuo. The residue, a dark brown oil which crystallized on standing, was not further purified, but was dissolved in 750 ml of dry t-butyl alcohol and stirred under nitrogen. A solution of potassium metal (5 g, 0.13 mole) in 150 ml of dry t-butyl alcohol was added in a thin stream. The reaction mixture, which turned a brilliant red-orange color, was stirred for 30 min at which time methyl iodide (40 g, 0.28 mole) in 100 ml of dry t-butyl alcohol was added in a thin stream. The reaction mixture was heated at reflux for 30 min. Most of the solvent was then removed by distillation. Water (500 ml) was added to the residue and the mixture was thoroughly extracted with five 100-ml portions of ether. The combined ether extracts were dried (Na_2SO_4) and the solvent removed in vacuo leaving a brown oily residue which crystallized on standing. Recrystallization from ether gave 9.4 g (16% yield from 10) of 1, mp 106-107° [Lit (7) mp 106.5-107°]. The spectral properties exhibited by 1 were identical with those in the literature (7).

Irradiation of 2-Methoxy-3-keto-9-methyl- $\Delta^{1,4}$ -
hexahydronaphthalene (1)

Compound 1 (2.5 g, 0.013 mole) was dissolved in 200 ml of freshly distilled anhydrous dioxane and irradiated for 4 hr using a Hanau NK 6/20 mercury arc lamp. The solution was deoxygenated and agitated for 10 min prior to and during the irradiation by use of a slow stream of dry nitrogen. Analysis of the crude photomixture by glc (carbowax column) using acetophenone as an internal standard showed in addition to starting material, two new major compounds 2 and 3 formed in 31 and 27 per cent yield, respectively. Compound 4 was formed in less than two per cent yield. The solvent was removed in vacuo and the residue, a light red colored oil, was subjected to chromatography on 60 g of silica gel previously washed in dry acetone. Elution with 3 l of 1 per cent ether in hexane afforded 15 fractions, each consisting of various concentrations of the photoproducts 2, 3, and 4. Fractions 3-6 were combined to give a mixture of the photoproducts enriched in 2, and subjected to chromatography on 25 g of silica gel. Elution with 1.5 l of 1 per cent ether in hexane afforded 0.53 g of pure material identified as 2-keto-3-methoxy-10 α -methyltricyclo [4.4.0.0^{1,5}]dec-3-ene (2) by the following properties: uv max (95% EtOH) 238 nm(ϵ 7, 238), 282 nm(ϵ 2, 215); ir (CHCl₃) 1695 (α, β -unsaturated C=O) and 1618 cm⁻¹ (conjugated C=C); nmr (CCl₄) δ 1.13 (s, 3H, 10 α -CH₃), 1.65 (s, 1H, 1-H),

3.61 (s, 3H, 3-OCH₃), 6.07 (s, 1H, 4-CH); mass spectrum 70 eV m/e 192 (m⁺), EMD 192.116 (calculated 192.115). Fractions 9-14 were combined which gave a mixture enriched in 3. Chromatography of the mixture using 20 g of silica gel and eluting with 2 l of 1 per cent ether in hexane afforded 0.28 g of pure 3 identified as 8 α -methyl-1 α -methoxy-4,5,6,7,8,8 α -hexahydro-1 β -8-cyclo-2(1H)-azulenone having the following properties: uv max (95% EtOH) 240 nm(ϵ 5, 471); ir (CCl₄) 1695 (α,β -unsaturated C=O) and 1592 cm⁻¹ (conjugated C=C); nmr (CCl₄) δ 1.25 (s, 3H, 8 α -CH₃), 2.43 (s, 1H, 8-CH), 3.43 (s, 1H, 1-OCH₃) and 5.50 (s, 1H, 3-CH); mass spectrum 70 eV m/e 192 (m⁺), 177 (m⁺-CH₃), EMD 192.114 (calculated 192.115). Compound 4 was isolated by combining fractions 1 and 2 from the initial chromatography and subjecting the mixture to chromatography on 3 g of silica gel. Elution with 50 ml of 1 per cent ether in hexane afforded 0.008 g of pure 4 having the following spectral properties: ir (CHCl₃) 3535 (-OH), 1590 and 1480 cm⁻¹, nmr (CCl₄) δ 2.08 (s, 3H, Ar-CH₃), 3.68 (s, 3H, -OCH₃) and 6.57 (s, 1H, Ar-H).

8 α -Methyl-1 α -methoxy-3,4,5,6,7,8,8 α ,9-octahydro-
1 β ,8-cyclo-2(1H)-azulenone (5)

The tricyclic ketone 3 (0.400 g, 0.002 mole) was dissolved in 50 ml of 95 per cent ethanol and 0.1 g of palladium on carbon (10 per cent) was added. The solution was shaken for 2.5 hr in a Parr low pressure apparatus at 40 psi.

The solution was filtered three times to remove the catalyst and the solvent was removed in vacuo. The residue, 0.395 g (0.002 mole) of a dark yellow oil, exhibited the following spectral properties: ir (CHCl_3) 1715 cm^{-1} (C=O), nmr (CCl_4) δ 1.19 (s, 3H, $8\alpha\text{-CH}_3$), 2.17 (s, 1H, $8\alpha\text{-H}$), 3.33 (s, 3H, 1-OCH_3); mass spectrum 70 eV m/e 194 (m+), 179 (m+- CH_3); EMD 194.131 (calculated 194.132).

Deuterium Exchange of $8\alpha\text{-Methyl-}1\alpha\text{-methoxy-}3,4,5,6,7,8,8\alpha,9\text{-octahydro-}1\beta,8\text{-cyclo-}2(1\text{H})\text{-azulenone}$ (5)

Compound 5 (0.075 g, 0.0039 mole) in 0.5 ml of dry dioxane was added to 1.5 ml of a 5 per cent solution of NaOD prepared by dissolving sodium (0.13 g) in 5 g of deuterium oxide. Deuterium oxide (1.5 ml) was added and the solution was refluxed for 20 hr under a nitrogen atmosphere. The solution was cooled and extracted with two 10 ml portions of ether. The ether extracts were combined and the solvent was removed in vacuo. The residue was subjected to a second deuterium exchange by using the same procedure described above. The combined ether extracts from the second exchange were dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was shown by mass spectral analysis to contain greater than 95 per cent of the dideutero derivative 5a.

Attempted Reduction of $8\alpha\text{-Methyl-}1\alpha\text{-methoxy-}3,4,5,6,7,8,8\alpha,9\text{-octahydro-}1\beta,8\text{-cyclo-}2(1\text{H})\text{-azulenone}$ (5)

Ammonia (40 ml, freshly distilled from sodium) was

collected in a 100 ml round bottom flask equipped with a nitrogen atmosphere, a magnetic stirrer, a dropping funnel and a cold trap condenser filled with dry ice-acetone. Freshly cut lithium wire (0.052 g, 0.0076 mole) was added and the mixture was stirred for 30 min. Compound 5 (0.46 g, 0.0024 mole) in dry t-butyl alcohol (0.178 g, 0.0024 mole) and 10 ml of dry ether was added dropwise over a 15 min period. The reaction mixture was stirred for 30 min then quenched with 1.0 g of ammonium chloride. The solvents were allowed to evaporate, water and ether (25 ml each) were added to the residue and the layers were separated. The aqueous layer was saturated with sodium chloride and extracted with three 15-ml portions of ether. The combined ether extracts were washed with saturated brine solution, dried (Na_2SO_4) and the solvent removed in vacuo to leave 0.31 g of an oil which gave the following spectral properties: ir (CCl_4) 1740 cm^{-1} and nmr (CCl_4) δ 1.20 (d, ~3H, 8 α -CH₃) and 3.43 (s, ~3H, 1 α -OCH₃). The spectral properties of the crude reaction mixture indicated that the cyclopropyl ring had been opened. An effort to purify the product by column chromatography proved to be unsuccessful. The crude reaction product was subjected to another lithium-ammonia reduction in an attempt to reductively remove the methoxy group. The residue from the above reaction (0.050 g, 0.00026 mole) was dissolved in 5 ml of dry ether containing one drop of dry t-butyl alcohol. The solution was added

dropwise to a vigorously stirred solution of lithium (0.004 g, 0.0058 mole) dissolved in 30 ml of anhydrous ammonia. The reaction mixture was stirred for an additional 15 min then quenched by adding 1.0 g of ammonium chloride. Workup of the reaction afforded 0.021 g of a dark oil which was shown by glc analysis to contain six major compounds. Nmr and ir analysis of the residue were inconclusive. Separation of the mixture by gas chromatography proved to be unsuccessful.

2-Acetoxy-3-methoxy-10 α -methyltricyclo

[4.4.0.0^{1,5}]dec-3-ene (7)

A 25-ml flask equipped with a magnetic stirrer was charged with lumiproduct 2 (0.500 g, 0.0026 mole) and sodium borohydride (0.11 g, 0.0029 mole). Absolute alcohol (10 ml) was added and the mixture was stirred at room temperature for 48 hr under a nitrogen atmosphere. Acetone (1.0 ml) was added and the mixture was stirred for 2 hr. The solvents were removed in vacuo, water and ether (10 ml) were added, the layers were separated and the aqueous layer was extracted with three 10-ml portions of ether. The combined ether extracts were washed with saturated brine solution, dried (Na₂SO₄) and the solvent removed in vacuo. The residue, 0.501 g of a light yellow oil, was shown to be the expected alcohol (6) by the following properties: ir (CCl₄) 1640 (enol ether), 3445 (-OH, bonded) and 3590 cm⁻¹ (-OH, free); nmr (CCl₄) 1.20 (s, 3H, 10 α -CH₃), 3.56 (s, 3H, 3-OCH₃),

4.33 (s, 1H, 4-CH) and 4.89 (d, J=7Hz, 1H, 2-CH). Glc analysis showed the presence of only one compound. Compound 6 was dissolved in dry pyridine (10 ml) and acetic anhydride (1.5 g). The reaction mixture was allowed to stir at room temperature for 24 hr under a nitrogen atmosphere. After cooling the mixture to 0° with an ice bath, ice cold water (3 ml) was slowly added dropwise and the mixture was stirred for 2 hr at 0°. After warming to room temperature the mixture was poured into 50 ml of ether and washed with two 25-ml portions of cold water. The combined aqueous layers were washed with three 25-ml portions of ether and the combined ether extracts were washed with 25 ml of saturated sodium bicarbonate solution. The ethereal solution was dried (Na₂SO₄) and the solvent removed in vacuo to give 0.512 g (83.4%) of 7 having the following properties: ir (CCl₄) 1734 (ester C=O) and 1640 cm⁻¹ (enol ether); nmr (CCl₄) δ 1.15 (s, 3H, 10α-CH₃), 1.94 (s, 3H, ester-CH₃), 3.55 (s, 3H, 3-OCH₃), 4.46 (s, 1H, 4-CH) and 5.67 (d, J=7Hz, 1H, 2-CH); mass spectrum 80 eV m/e 236 (m+), 176 (m+-HOAc), EMD: 236.139 (calculated 236.141).

2-Acetoxy-3-methoxy-10α-methyltricyclo[4.4.0.0^{1,5}]

dec-3-ene (7) with Lithium in Ethylamine

Ethylamine (40 ml, freshly distilled from lithium) was collected in a 100-ml round bottom flask equipped with a magnetic stirrer, a dropping funnel and a cold trap condenser filled with ice water. Compound 7 (0.40 g, 0.0017

mole) and dry t-butyl alcohol (0.124 g, 0.0017 mole) in 15 ml of dry ether were added and the mixture was cooled by means of a dry ice-acetone bath. Freshly cut lithium wire (0.050 g, 0.007 mole) was added and the reaction mixture was stirred vigorously until the blue color persisted for 5 min. The mixture was then filtered rapidly through glass wool into a flask containing 1 g of ammonium chloride. The solvents were allowed to evaporate, water and ether (25 ml each) were added to the residue and the layers were separated. The aqueous layer was saturated with sodium chloride and extracted with three 15-ml portions of ether. The combined ether extracts were washed with saturated brine solution, dried (Na_2SO_4) and the solvent removed in vacuo to leave 0.29 g of a dark yellow oil which gave the following spectral properties: ir (CCl_4) 2922 cm^{-1} (C-H absorption) and nmr (CCl_4) δ 0.80-1.5 (broad absorption). No conclusive results could be drawn from these spectral properties. Glc analysis of the crude reaction mixture indicated that four major compounds were present. Separation of the reaction mixture by column chromatography proved to be unsuccessful.

2-Acetoxy-3-keto-10 α -methyltricyclo[4.4.0.0^{1,5}]

decane (8)

Compound 7 (0.50 g, 0.002 mole) was dissolved in 10 ml of methanol and added to a solution of oxalic acid (0.1 g) in 3 ml of water. The mixture was stirred at room temperature for 4 hr. The solvents were evaporated in vacuo,

ether and water (5 ml each) were added to the residue, the aqueous layer was separated and thoroughly extracted with four 5-ml portions of ether. The combined ether extracts were washed with saturated brine solution, dried (Na_2SO_4) and the solvent was removed in vacuo. The residue, 0.47 g of a light yellow oil, was shown to be unchanged 7 by nmr analysis.

The same procedure was repeated, except the second time the mixture was heated at reflux for 5 hr. Using the same workup procedure, 0.43 g of a light yellow oil was obtained which consisted of three major compounds, predominantly 8, as shown by glc and nmr analysis. The mixture was subjected to chromatography on 10 g of silica gel. Elution with 1000 ml of one per cent ether in hexane afforded 0.28 g of a light colored oil which was identified as compound 8 by the following properties: ir (CCl_4) 1740 (ester $\text{C}=\text{O}$) and 1763 cm^{-1} (cyclopentanone); nmr (CCl_4) δ 1.03 (s, 3H, $10\alpha\text{-CH}_3$), 1.53 (d, $J=7\text{Hz}$, 1H, 1-CH), 2.03 (s, 3H, ester- CH_3), 2.40 (s, 2H, 4- CH_2) and 5.57 (d, $J=7\text{Hz}$, 1H, 2-CH); mass spectrum 80 eV m/e 198 (m^+) and 138 ($m^+-\text{HOAc}$).

3-Keto- 10α -methyltricyclo[4.4.0.0^{1,5}]decane (9)

Compound 8 (0.200 g, 0.0009 mole) in 5 ml of anhydrous tetrahydrofuran was added dropwise to a solution of lithium (0.014 g, 0.0028 mole) in 20 ml of anhydrous ammonia cooled by means of a dry ice-acetone bath. The reaction mixture was stirred vigorously for 1 hr, then quenched by adding

ammonium chloride (1 g). The solvents were allowed to evaporate, water and ether (10 ml each) were added to the residue and the layers separated. The aqueous layer was saturated with sodium chloride and extracted thoroughly with three 10-ml portions of ether. The combined ether extracts were washed with brine, dried (Na_2SO_4) and the solvent removed in vacuo to leave 0.141 g of a light colored oil. The residue was dissolved in 5 ml of acetone and Jones reagent (21) was added dropwise until the orange color persisted. Several drops of isopropyl alcohol were added followed by 15 ml of water and the mixture was extracted with eight 5-ml portions of ether. The combined ether extracts were washed with brine, dried (Na_2SO_4) and the solvent removed in vacuo leaving 0.101 g of a light colored oil.

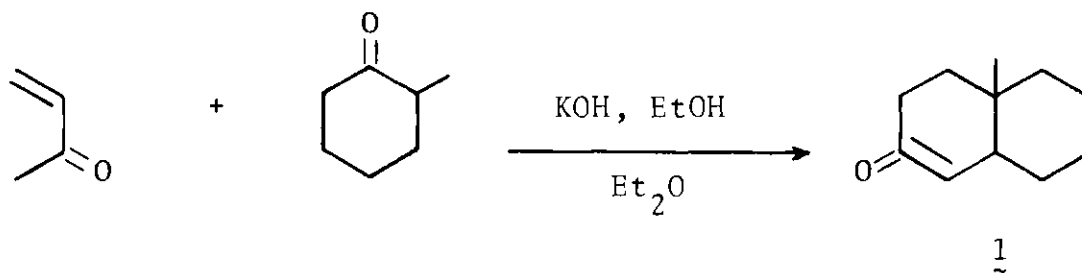
The residue was subjected to chromatography on 2.5 g of silica gel. Elution with 40 ml of 0.5 per cent ether in hexane afforded 0.043 g of a light colored oil which was identified as 9 by the following properties: ir (CCl_4) 1745 cm^{-1} (cyclopentanone); nmr (CCl_4) δ 0.73 (s, 3H, $10\alpha\text{-CH}_3$), 2.22 (s, 2H, 4- CH_2), and 2.43 to 1.03 ppm (broad absorption, 11H); mass spectrum 80 eV 164 (m+) EMD 164.1204 (calculated 164.1201).

CHAPTER IV

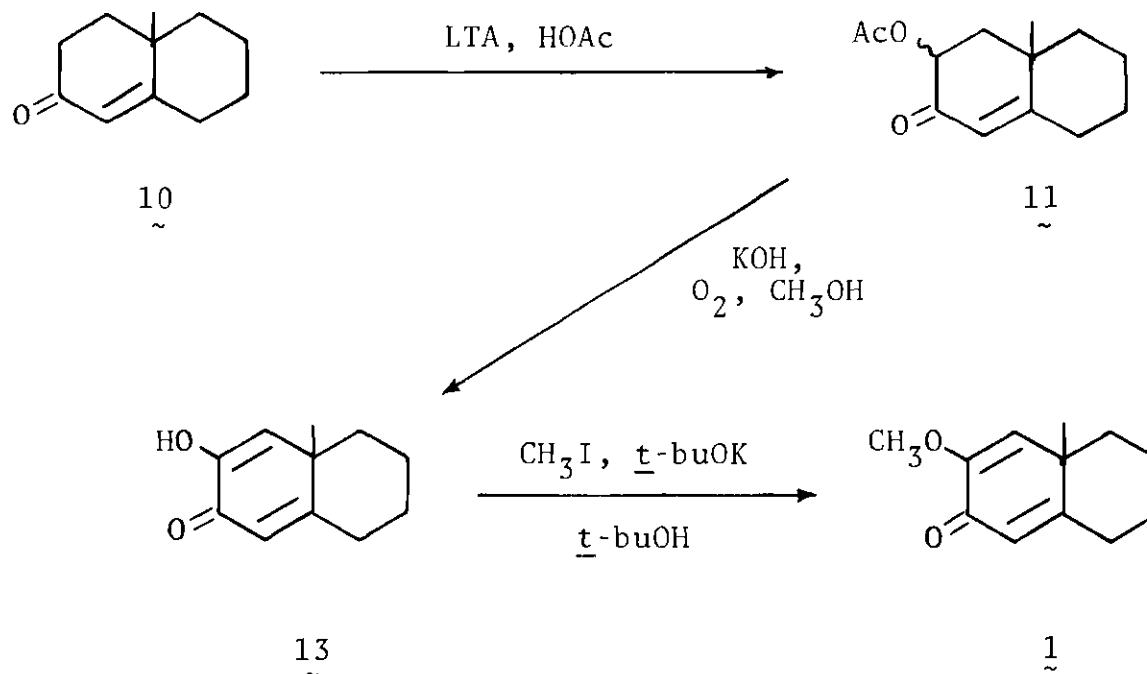
DISCUSSION OF RESULTS

The principal goal of this research, as previously stated, was an investigation of the photochemical behavior of 2-methoxy-3-keto-9-methyl- $\Delta^{1,4}$ -hexahydronaphthalene (1). A major portion of this discussion will be devoted to the evidence for the structural assignments of the photoproducts of 1. The synthetic procedures employed for the preparation of 1 as well as the route used for the conversion of the lumiprodukt 2 into the 2-ketotricyclodecane 9 also warrant discussion.

The starting material for the synthesis of 1 was 3-keto-9-methyl- Δ^4 -octahydronaphthalene (10) prepared according to the method of Ross and Levine (13). By using 2-methylcyclohexanone in excess (1.5 equivalents per equivalent of methyl vinyl ketone), a yield of 49 per cent was obtained. This was slightly better than the yield reported by Ross and Levine (35-40 per cent). In each run to prepare 10 approximately 75 per cent of the 2-methylcyclohexanone was recovered and could be reused in a subsequent preparation.



The methoxy dienone 1 was prepared in three steps from the enone 10. Acetoxylation with lead tetraacetate by the procedure of Seebach (14) gave the α -acetoxy enone 11. Compound 11 was not purified, but used directly in the next step, since distillation of α -acetoxy ketones results in some elimination of acetic acid. Hydrolysis of the acetate and oxidation by air resulted in the formation



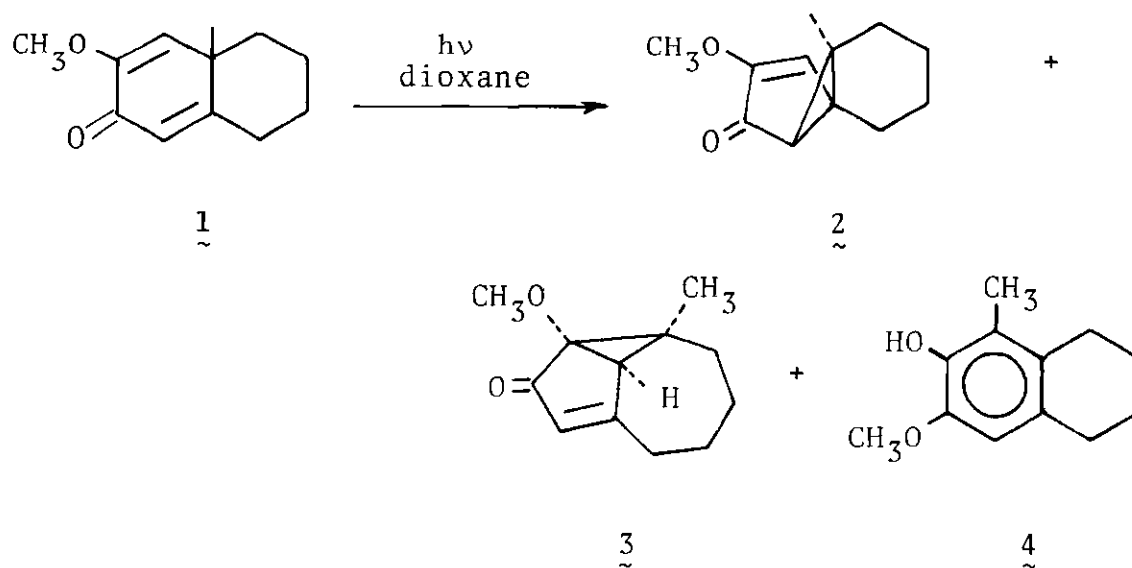
of the hydroxy dienone 13, which was methylated with methyl iodide using potassium t-butoxide as the base to give 1. These steps were straightforward and the dienone, a solid of high purity, was isolated in 16 per cent over all yield from enone 10.

Irradiation of 1 in anhydrous dioxane was performed with a Hanau NK/20 mercury vapor lamp which emits 90 per cent of its radiation at 2537 Å. The irradiations were easily monitored by glc; the disappearance of dienone 1 was noted by the formation of two new major products which were assigned the structures of 2 and 3. It was found that the best results were obtained by irradiating 2.5 g of 1 in 200 ml of dry dioxane for 4 hr. Removal of the solvent in vacuo gave an oil which was shown by glc using acetophenone as an internal standard to contain 31 per cent 2, 27 per cent 3 and approximately 25 per cent starting material (1). A third compound, which was assigned the structure 4 based on its ir and nmr spectra, was formed in less than one per cent yield. It was subsequently found that if the photomixture be allowed to stand undisturbed for 24 hr, crystals of the starting dienone were formed from the oil. These could be separated and used in other irradiations.

Isolation of the photoproducts proved to be a long and tedious operation. Separation of the photomixture was accomplished by successive column chromatography using silica gel (ratio of about 25 g to 1 g of mixture) and eluting

with large amounts of an ether-hexane solvent. TLC analysis of each fraction was performed and this indicated that the best separation was found to be with a 1 per cent mixture of ether in hexane. Chromatography of the mixture afforded about 15 fractions, each consisting of various concentrations of the photoproducts. The fractions were combined in such a manner as to give two mixtures, one enriched in 2 and the other enriched in 3. A second chromatography of each mixture afforded pure 2, pure 3 and pure 4, along with mixtures of the three compounds.

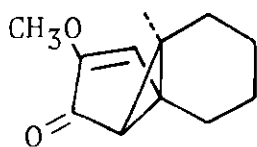
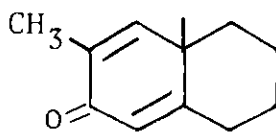
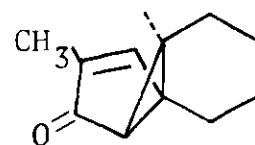
Separation of the photomixture was not a very economic process, 10 g of photomixture provided only 1.5 g of pure 2 and 1.0 g of pure 3. In one case the photomixture was first hydrogenated using a Parr low pressure apparatus



and the mixture of dihydro derivatives was subjected to chromatography, but separation of the isomeric compounds proved even more difficult.

The purified photoproducts were subjected to uv irradiation under the same conditions as were employed for 1. The experiments showed that as expected 2 was converted into 4 on extended irradiation. However, although 3 was slowly converted into several new photoproducts on extended irradiation, glc analysis of the mixture indicated that neither 2 nor 4 was formed from this compound.

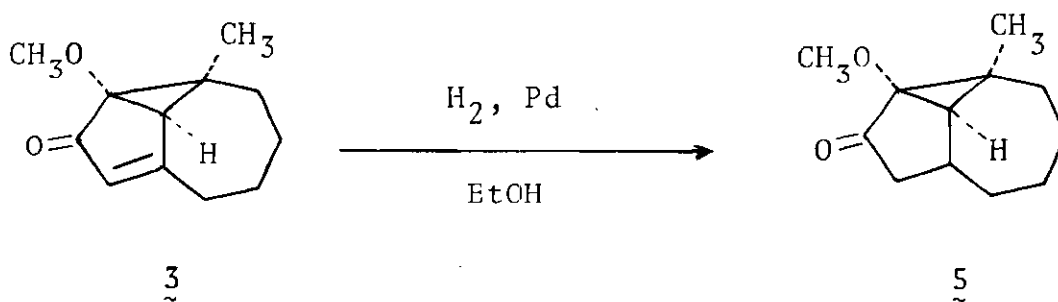
The spectral properties of the tricyclic compounds 2 and 3 and of the phenol 4 were indicative of the assigned structures.

22c2a

Ir absorptions for compound 2 at 1695 and 1618 cm^{-1} indicated the presence of an α,β -unsaturated carbonyl system. An nmr absorption (s, 1H) at 6.07 ppm was consistent with this assignment. The presence of a methoxyl absorption (s, 3H) at 3.61 ppm and a methyl absorption (s, 3H) at 1.13 ppm in

the nmr spectrum was also in agreement with the structure of 2. Assignment of the structure of 2 was based upon the similarity of its spectral properties to those of 2a reported by Kropp (16). Compound 2a exhibited ir absorptions at 1689 and 1629 cm^{-1} . Major nmr absorptions for 2a were: δ 1.12 (s, 3H, 8a- CH_3), 1.69 (d, 3H, $J_{AB}=1.5$ Hz, 3- CH_3) and 6.68 (m, 1H, 4CH). Finally the mass spectral data of 2 was clearly consistent with the assigned structure.

Compound 4 gave an ir absorption at 3535 cm^{-1} which was consistent with the presence of an OH group. Other ir absorptions for compound 4 were 1590 and 1480 cm^{-1} . Principal nmr absorptions for 4 were: δ 2.08 (s, 3H, Ar- CH_3), 3.68 (s, 3H, $-\text{OCH}_3$) and 6.57 (s, 1H, ArH). The structural assignment of 4 was based on these spectral properties.

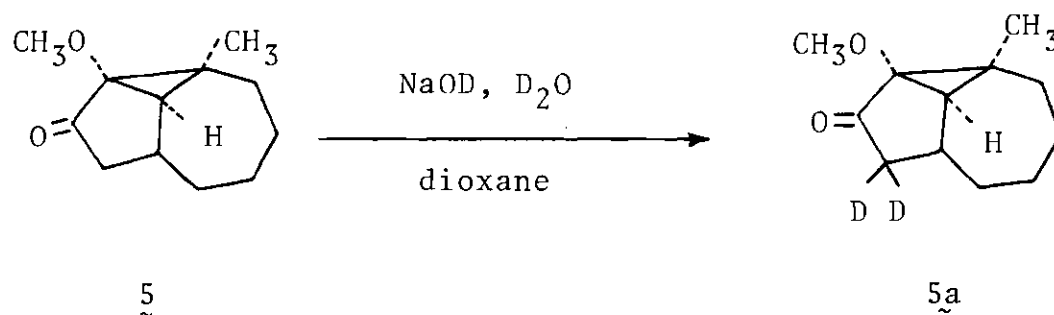


Compound 3 gave ir absorptions at 1695 and 1592 cm^{-1} which indicated the presence of an α,β -unsaturated carbonyl system. The nmr absorption (s, 1H) at 5.50 ppm was consistent with this. The presence of a methyl absorption (s, 3H) at 1.25 ppm and a methoxyl absorption (s, 3H) at 3.43 ppm

in the nmr spectrum only suggested that 3 was isomeric to 2. However, the higher field absorption of the methoxyl group in 3 indicated that it was attached to a saturated carbon atom rather than an unsaturated one as is 2. The mass spectral data confirmed this.

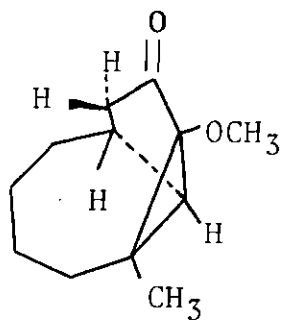
Since the spectral properties of 3 did not allow a conclusive structural assignment, further studies were undertaken to obtain more evidence. The unsaturated ketone 3 was converted into its α,β -dihydro derivative 5 in essentially quantitative yield by hydrogenation in ethanol over a palladium on carbon catalyst. The methyl and methoxy nmr absorptions (s, 3H) were shifted upfield to 1.19 and 3.33 ppm, respectively in compound 5. The absence of a vinyl hydrogen absorption in the nmr spectrum, the presence of an ir absorption in the nmr spectrum, the presence of an ir absorption at 1715 cm^{-1} (in agreement with a conjugated cyclopropyl ketone grouping) and the mass spectral data of the compound were clearly consistent with the structure of 5. However, the nmr absorptions in the 1.7 - 2.2 ppm range did not clearly show the presence of the C-3 methylene protons, which would be expected to appear as an AB system perturbed by the tertiary hydrogen at C-4. Thus 5 was converted into its dideuterio derivative 5a by treatment with deuterium oxide in dioxane containing sodium deuterioxide. Two principal nmr absorptions (s, 3H) for 5a occurred at 1.21 and 3.88 ppm and were assigned to the $\delta\alpha\text{-CH}_3$ and the

1 α -methoxyl, respectively. Two smaller nmr absorptions occurred at 1.77 and 1.67 ppm. The absence of absorptions at 2.17 and 2.02 ppm, which were present in 5, showed that these peaks could be attributed to the C-3 methylene protons. A study of the nmr spectrums of 5 and 5a using an nmr shift reagent confirmed these assignments.

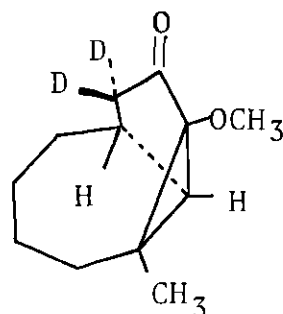


For the nmr shift reagent study a saturated solution of europium (III) tris-1,1,1,2,2,3,3-hepta-fluoro-7,7-dimethyl-4,6-octanedione in carbon tetrachloride was prepared and added dropwise to each compound in an nmr sample tube. TMS was used as an internal standard. Best results were obtained by using 25 drops of the shift reagent solution; absorptions are reported using this concentration of shift reagent. Since the shift reagent complexes with the carbonyl, protons closest to the carbonyl should be shifted farthest. This is precisely what was observed. The C-1 methoxyl in 5 and 5a gave an absorption (s, 3H) at 6.23 and 6.28 ppm, respectively. Four absorptions at 5.63, 5.78, 5.88 and 6.07 ppm were observed for compound 5 and

were assigned to the C-3 methylene protons. The absence of any absorptions in this region for compound 5a confirmed this assignment. Absorptions (m, 1H) at 4.47 and 4.48 ppm were assigned to the C-4 hydrogen in 5 and 5a, respectively. Absorptions (d, $J=7\text{Hz}$, 1H) occurring at 3.78 and 3.82 ppm were assigned to the C-9 hydrogen in 5 and 5a, respectively. Finally the 8a-methyl group gave absorptions (s, 3H) at 2.64 and 2.63 ppm for 5 and 5a, respectively. This interpretation of the nmr shifts further complimented the structure assigned to compound 3.



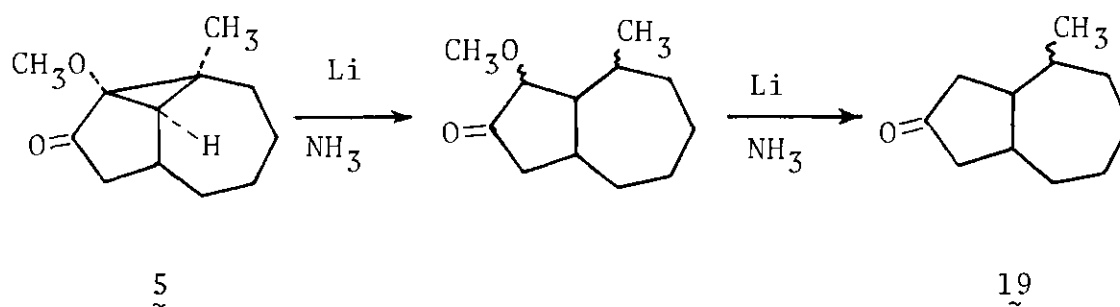
5



5a

While the spectral studies on 3, 5 and 5a were clearly consistent with the structural assignment of 3, they did not positively rule out the alternate structure 3a, which has a trans-fused 3/7-ring system. Thus a goal of this work was to convert 3 into a compound of known structure. The most direct approach would be (after catalytic hydrogenation) to open the cyclopropyl ring and subsequent removal of

the methoxyl group. The resulting compound would be identical, except for the stereochemistry at C-8 to the known azulenone 19 prepared by DeBardeleben.



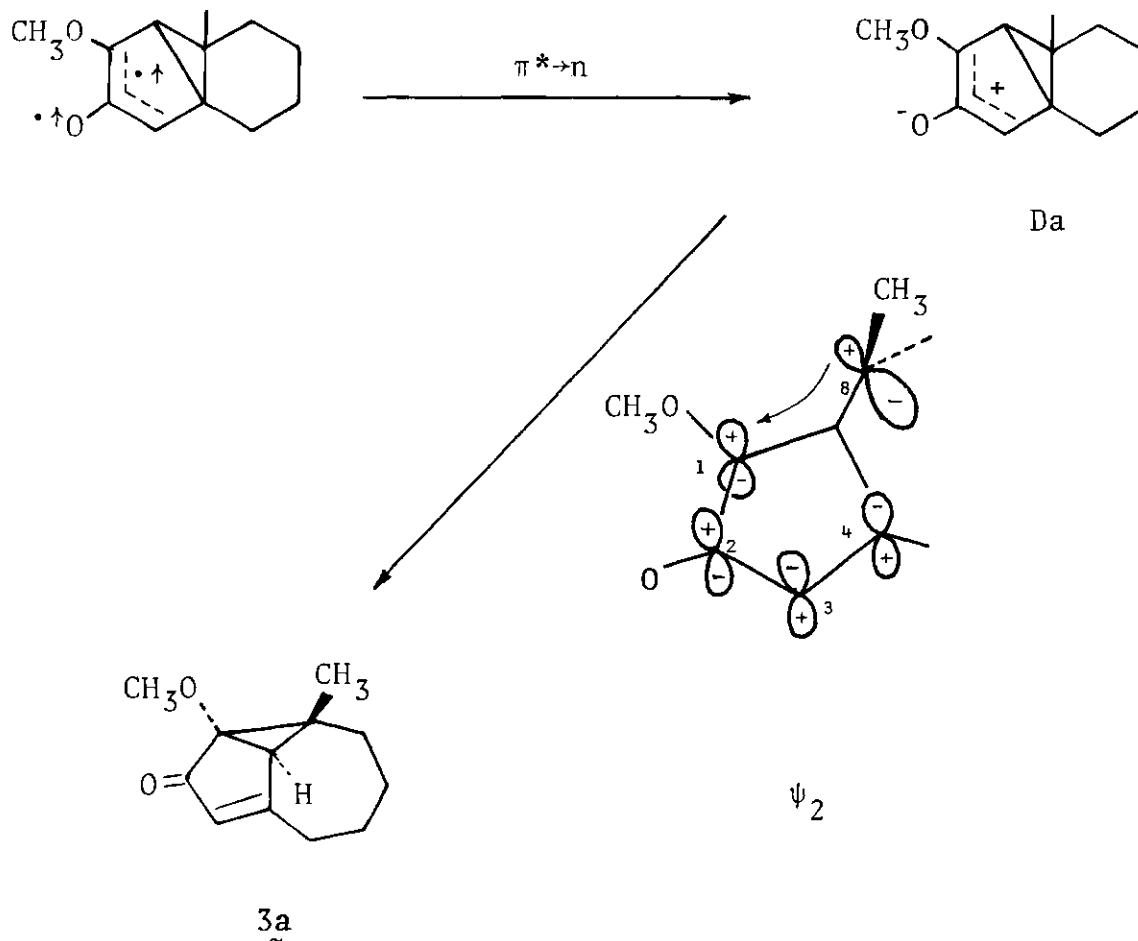
This was precisely the action taken; unfortunately, positive results were not obtained with these transformations. In an effort to obtain the ring opened product, 5 was subjected to lithium-ammonia reduction several times. In each run, the reaction appeared to go with some success; however, pure reaction products could not be isolated. Glc analysis of the crude reduction product indicated that several compounds were formed. It appeared that the cyclopropyl ring had been opened as shown in the nmr spectrum by an ill defined doublet (~3H) at 1.20 ppm and a bathochromic carbonyl shift in the ir spectrum (1715 to 1740 cm^{-1}). An nmr absorption (s, ~3H) at 3.43 ppm indicated that the methoxyl was still present. In an attempt to remove the methoxyl, a second lithium-ammonia reduction in the presence of ethanol was performed on the crude mixture. Glc analysis indicated that as many as six major compounds had been

formed. Ir and nmr spectra on the reaction mixture were inconclusive. Pure products could not be isolated using preparative gas chromatography.

The reduction of 5 was attempted again using an excess of lithium dissolved in ammonia followed by the addition of ethanol. Glc analysis of the crude reaction mixture showed that mostly starting material was present. The crude reaction mixture was subjected to column chromatography, but only starting material could be isolated. It was presumed that the reaction was not allowed to proceed long enough before ethanol was added.

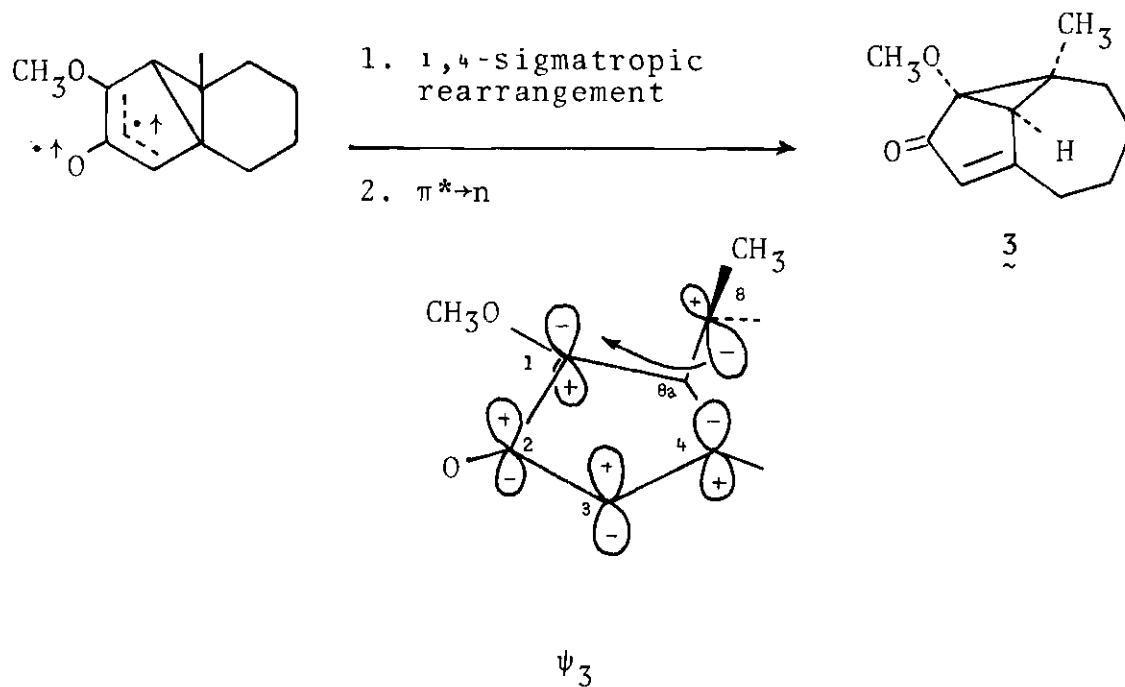
The formation of the lumiprodukt 2 on irradiation of 1 is analogous to the results which have been previously obtained for the 2-methyl cross-conjugated cyclohexadienone 2c. However, the formation of 3 was unexpected and appears to involve a novel pathway of rearrangement of a bicyclic 6/6 fused dienone. Photochemical rearrangements of dienones into products of the type 2 have been considered by Zimmerman and coworkers (17) to involve a 1,4-sigmatropic rearrangement in a ground state zwitterionic species (Da) which can be produced by excitation, 1,5-bonding and electron demotion. Orbital symmetry considerations (6) require that this reaction take place with inversion of configuration at C-8, since ψ_2 of the butadiene system would be the highest occupied MO. Similarly, a 1,4-sigmatropic rearrangement of C-8 from C-5 to C-2 would be symmetry allowed, but would

lead to a highly strained tricyclic system (3a) having a trans-fusion of the three and seven membered rings.

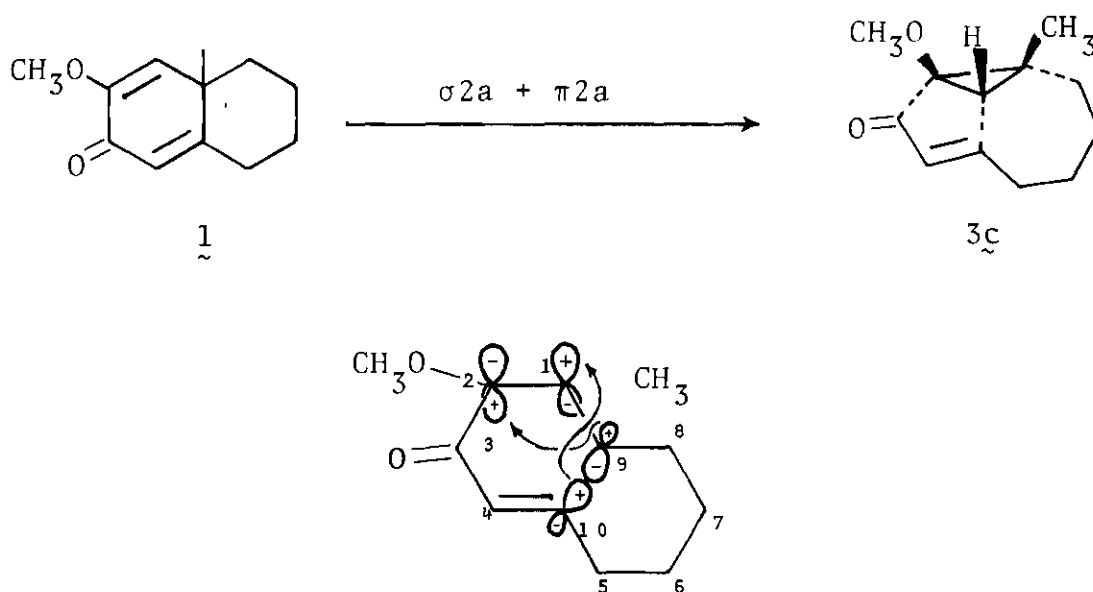


On the other hand, if the rearrangement occurred in the excited state (the precursor to the zwitterion Da), where ψ_3 is the highest occupied MO, 1,4-sigmatropic rearrangement could take place with retention of configuration at C-8. In this case the product, which possesses a cis-fused 3/7-ring system, would be much more thermodynamically

stable.



The same product, although an enantiomer of $\tilde{3}$, can be derived from a Woodward-Hoffmann treatment. As previously stated, Woodward and Hoffmann consider the photochemical rearrangements of cross-conjugated cyclohexadienones to be a concerted $[\sigma 2a + \pi 2a]$ cycloaddition (6). Antara addition of the σ -bond to the 1,2-double bond and inversion at the migrating saturated C-9 atom leads to $\tilde{3}_c$, enantiomeric to $\tilde{3}$.



It is believed that the presence of the methoxy substituent lowers the energy of the triplet species and in some fashion localizes the excitation in the 1,2-bond, since only cyclohexadienones possessing the C-2 methoxyl give rise to significant amounts of tricyclic ketones upon irradiation.

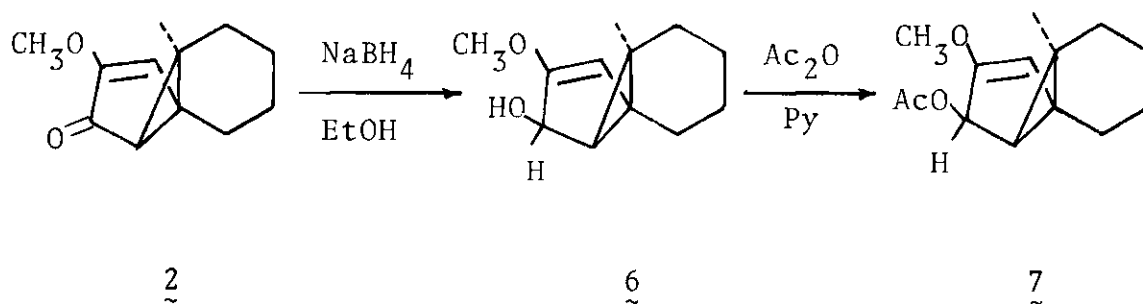
Another goal of this work was to convert 2 into the tricyclic ketone 9. This transformation would not only provide chemical evidence for the structure of 2, but also it appeared that treatment of the dibromo derivative of 9 with zinc would provide a means of chemically generating the zwitterionic species D so that the modes of sigmatropic

rearrangement could be investigated. A study of this type involving 9 would be similar to the work of Zimmerman (18) and Hill (19) on simple bicyclohexanone derivatives.



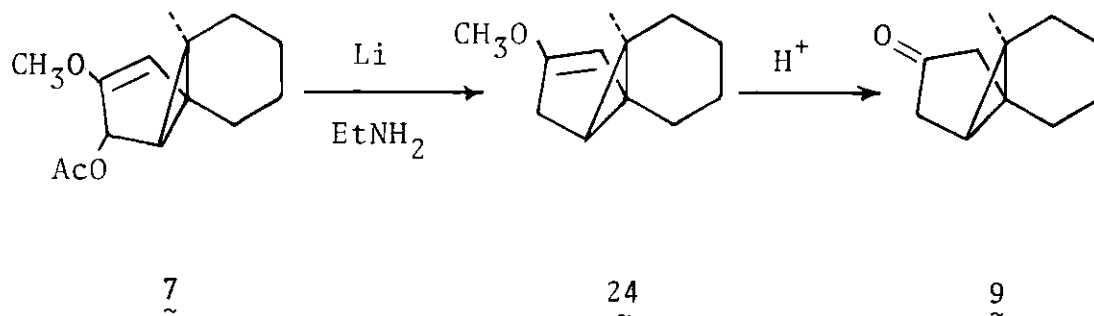
Reduction of 2 with sodium borohydride in ethanol gave the expected alcohol 6 in essentially quantitative yield. Ir absorptions of 6 at 3445 and 3590 cm^{-1} showed that an alcohol had been formed, also the enol ether absorption at 1640 cm^{-1} was very pronounced. The absorption of the carbonyl in 2 had disappeared. The three membered ring was still intact as shown by the presence of a methyl absorption (s, 3H) at 1.20 ppm in the nmr spectrum. Acetylation of 6 with acetic anhydride in pyridine gave the ester 7 in good yield. The ir absorptions at 1734 and 1640 cm^{-1} ; the presence of an acetoxyl absorption (s, 3H) at 2.03 ppm in the nmr spectrum and mass spectral data confirmed the structure of 7. The C-2 hydrogen of 6 showed an absorption at 4.89 ppm (d, $J=7\text{Hz}$) in the nmr spectrum. When the alcohol was esterfied (compound 7) the C-2 hydrogen absorption was shifted downfield to 5.67 ppm (d, $J=7\text{Hz}$). The splitting

of the C-2 hydrogen by the adjacent hydrogen on the cyclopropane ring was shown in both 6 and 7; however, the C-1 hydrogen was buried in the remaining absorptions of the molecule.



Presumably only one stereo isomer was formed during the reduction of 2 and the subsequent esterification of 6, since only one nmr absorption was observed for the C-3 hydrogen. It is also believed that the β -isomer of both 6 and 7 was generated. Although the α -isomer is more thermodynamically stable, attack from the least hindered side would lead to the β -isomer. The size of the nmr coupling constant ($J=7\text{Hz}$) for the C-3 proton (being split by the C-1 proton) is in closer agreement with the β -isomer.

A possible route to 9 would be to reductively remove the acetate group in 7. Hydrolysis of the enol ether function of the resulting compound (24) would give the desired ketone 9.

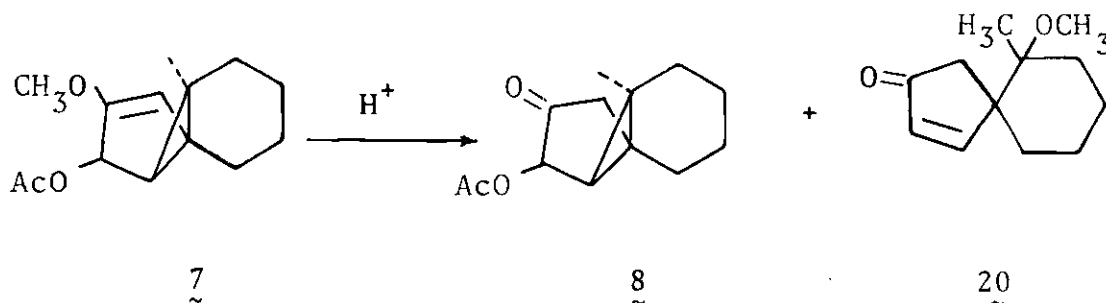


Unfortunately, cleavage of the ester in 7 could not be accomplished without damaging other parts of the molecule. The reduction was attempted using lithium in ethylamine. As shown by glc, nmr and ir, several volatile products were obtained from the reaction, but none of these showed spectral properties bearing any resemblance to those expected for the product 24. There were no methyl, methoxy or vinyl proton absorptions in the nmr spectrum, only high field absorptions were present. The ir spectrum showed only C-H absorptions: no carbonyl or vinyl absorptions were present. Separation of the mixture by chromatography was attempted, but pure products could not be obtained. It was presumed that in addition to cleavage of the ester, the three-membered ring was opened along with reductive removal of the methoxyl group and any double bonds present.

Since reduction conditions using lithium in ethylamine proved to be too vigorous, the reaction was tried using calcium in ammonia and again using lithium in ammonia.

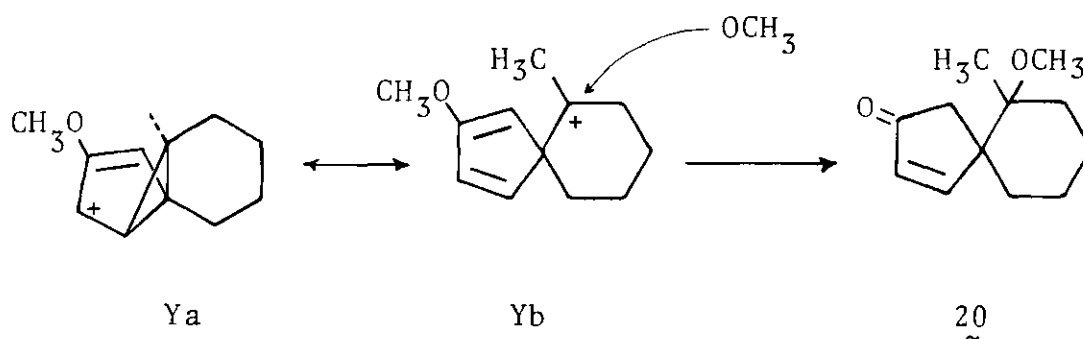
Similar results were obtained from both reactions, a number of products had been formed, none of which could be isolated or identified.

Since the reduction of 7 could not be successfully carried out, an alternate approach was tried. If hydrolysis of the enol ether function could be accomplished without affecting the ester, then reduction of the resulting α -acetoxy ketone might proceed without opening the cyclopropyl ring. Hydrolysis was first attempted by stirring a solution of 7 and 0.1 g of oxalic acid in methanol at room temperature for 4 hr. Workup afforded unchanged starting material. The reaction was repeated except the second time the solution was stirred under reflux for 5 hr. Workup gave three products, the major one being the desired compound 8. Separation of the reaction products was accomplished by chromatography on silica gel and eluting with an ether-hexane solvent.



A second product isolated was assigned the structure

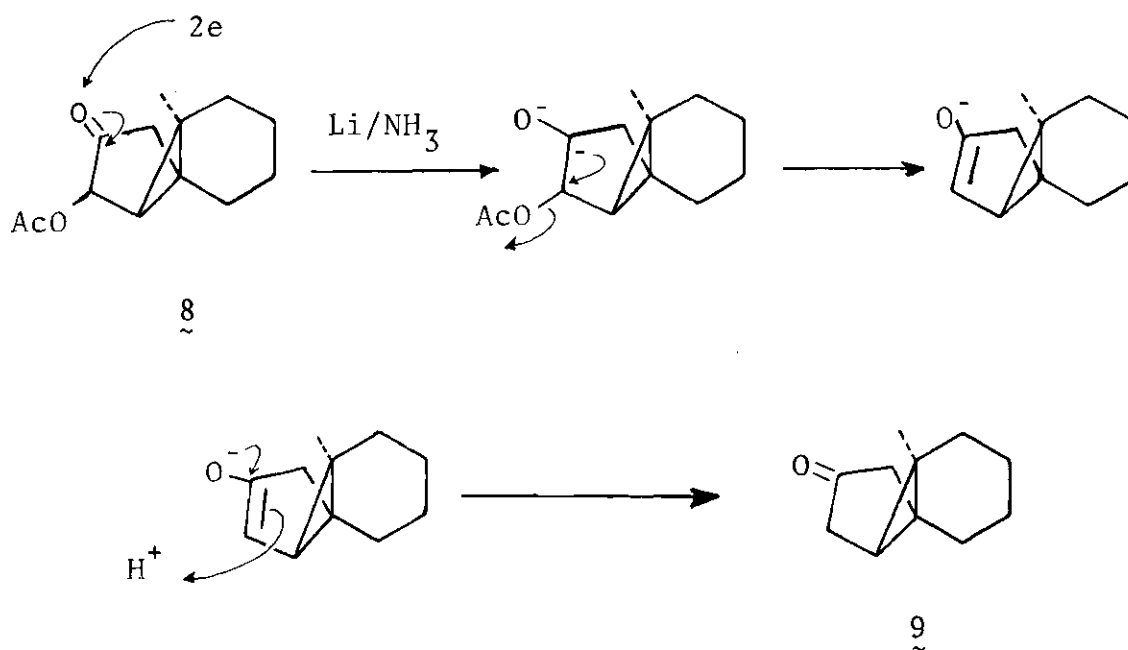
20, based on the ir and nmr spectra. Ir absorptions at 1720 and 1592 cm^{-1} indicated the presence of an α,β -unsaturated cyclopentanone, while the nmr absorptions (s, 3H) at 1.01 and 3.10 ppm indicated the presence of a tertiary methyl and a methoxy group, respectively. Also nmr absorptions (d, $J=6\text{Hz}$, 1H) at 6.02 and 7.55 ppm were consistent with the α,β -unsaturated cyclopentanone. Compound 20 was thought to arise by solvent attack on the species Y generated by solvolysis of the ester:



The structure of **8** was confirmed by the ir, nmr and mass spectral data. Ir absorptions at 1740 and 1763 cm^{-1} indicated that the enol ether had been hydrolyzed to the ketone and that the ester was still intact. Although the absorption at 1763 cm^{-1} was rather high frequency for a cyclopentanone, this is probably due to dipolar interactions with the α -acetoxy group. The cyclopropyl ring was still intact as indicated by the nmr absorptions (s, 3H) at 1.03 ppm. The acetoxy group was also shown to be present by the nmr and mass spectral data. Coupling of both C-1 and

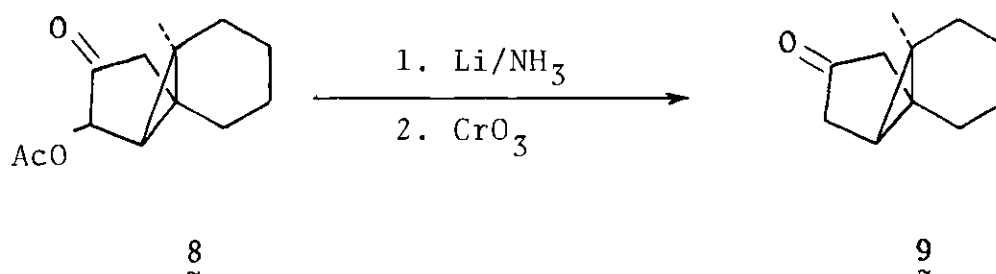
C-2 hydrogens ($J=7\text{Hz}$) of compound **8** were observed in the nmr spectrum. Irradiation at the C-1 hydrogen made the C-2 doublet (5.57 ppm) move into a singlet. Irradiation at the C-2 hydrogen made the C-1 doublet (1.53 ppm) move very close together, almost into a singlet. This double resonance experiment in addition to the coupling constants gave a very strong indication that the two protons were coupled.

In performing the reduction of **8**, it was decided to carry out the reaction at dry ice-acetone temperature to prevent the lithium enolate intermediate from undergoing an intramolecular rearrangement which would lead to opening of the cyclopropyl ring. The mechanism of the dissolving metal reduction is thought to involve a dianion which expels the acetate group to give an enolate intermediate.

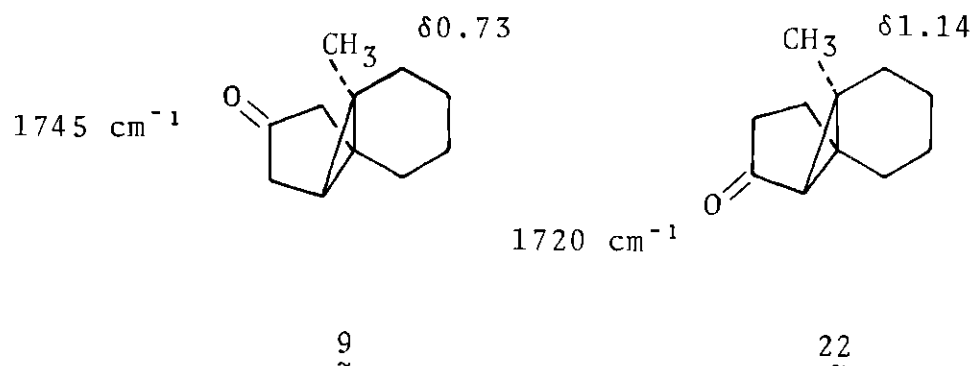


The reaction proceeded smoothly and workup provided an oil that was shown by glc and nmr analysis to be a mixture of three compounds in which 9, the desired compound, predominated.

An ir absorption at 3500 cm^{-1} indicated that some of the ketone had also been reduced. Regeneration of the ketone was easily accomplished using Jones reagent.



The crude reaction mixture was subjected to chromatography on silica gel. A volatile fraction was eluted from the column which was shown to be pure 9 by glc. The product gave an ir absorption at 1745 cm^{-1} , indicating that a cyclopentanone was present. Compound 9 gave an nmr absorption (s, 3H) at 0.73 ppm which demonstrated that the cyclopropyl ring was still intact. An nmr absorption (s, 2H) at 2.22 ppm was assigned to the C-4 methylene protons. Finally the mass spectral data was consistent with the assigned structure.



Compound 22, a similar tricyclic ketone prepared by Chu(20) gave an ir absorption at 1720 cm⁻¹ which demonstrates the effect of a cyclopropyl ring in conjugation with the carbonyl group. The nmr absorption (s, 3H) for the 10 α -methyl at 1.14 ppm also demonstrates this effect. The position of the absorption can also be explained in terms of the anisotropic shielding of the carbonyl.

CHAPTER V

CONCLUSIONS

The 6/6-fused cross-conjugated cyclohexadienone 1 was prepared and irradiated in anhydrous dioxane. The formation of lumipproduct 2 was similar to that reported for the dienone having a methyl instead of an methoxy substituent. However, the formation of 3 was unexpected and an explanation was given for its formation. Efforts were made to confirm the structure assigned to compound 3.

A synthetic route was developed for the conversion of the lumipproduct 2 into the 2-ketotricyclodecane 9.

CHAPTER VI

RECOMMENDATIONS

Compounds 2 and 3 should be isolated again and further investigated, compound 3 in particular. The transformations attempted on 5 should be repeated using a larger quantity of starting material.

The dibromo derivative of the tricyclic ketone 9 should be prepared. Treatment with zinc may provide a means of chemically generating the zwitterionic species proposed by Zimmerman.



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