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Photochemical studies of [alpha], [beta]-unsaturated ketones at low temperatures

Loren Lewis Barber Jr.
Iowa State University

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PHOTOCHEMICAL STUDIES OF α,β-UNSATURATED KETONES AT LOW TEMPERATURES

by

Loren Lewis Barber, Jr.

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

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1969

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VITA

The author was born to Mr. and Mrs. Loren Barber in Albany, New York, on July 7, 1941. He graduated from the Berne-Knox Central High School in June 1960. He enrolled at the Rochester Institute of Technology to begin a five year cooperative program of study with a major in chemistry. In June 1962 he began his cooperative employment with Eastman Kodak Company in Rochester, New York. In 1965, he was granted the Bachelor of Science degree. Graduate work was begun at Iowa State University in July 1965. A National Aeronautics and Space Administration Traineeship provided financial support for this period of study until September 1968. His terminal year of support was obtained from the Petroleum Research Foundation. After receiving the Doctor of Philosophy Degree, the author continued his professional career at the Minnesota Mining and Manufacturing Company in St. Paul, Minnesota.

INTRODUCTION

Stepwise mechanistic photochemical pathways for organic photochemical reactions have evolved from investigations of primary spectroscopic and photochemical processes of organic compounds and also from secondary reactions of reactive intermediates formed from the primary photochemical reaction. The photoreactions of organic compounds are usually considered to follow one of the stepwise pathways delineated in the following scheme. The first case, where

$$K \xrightarrow{h\nu} K^{*} \longrightarrow K_A$$

$$K \xrightarrow{h\nu} K^{*} \longrightarrow K_A^{*} \longrightarrow K_A$$

$$K \xrightarrow{h\nu} K^{*} \longrightarrow K_B \longrightarrow K_A$$

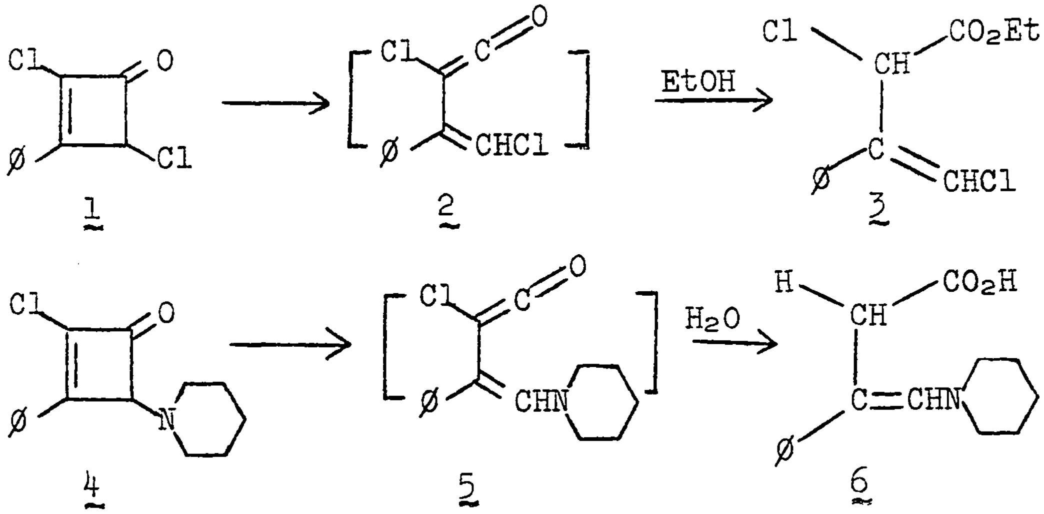
(K^*) goes directly to product (K_A) appears to be the most general mechanism of photochemical rearrangements and cycloaddition reactions. Well documented examples of the second case, where (K^*) transforms to an excited state of the product (K_A^*) are less common but have been observed for processes such as ionization of excited phenols. Some photoinitiated reactions have been further resolved into photo-thermal reaction sequences in which a highly reactive ground state species (K_B) is transformed in a thermal process to the final product (K_A). Photolytic transformations involving free radicals which undergo thermal abstraction reactions occur in this manner.

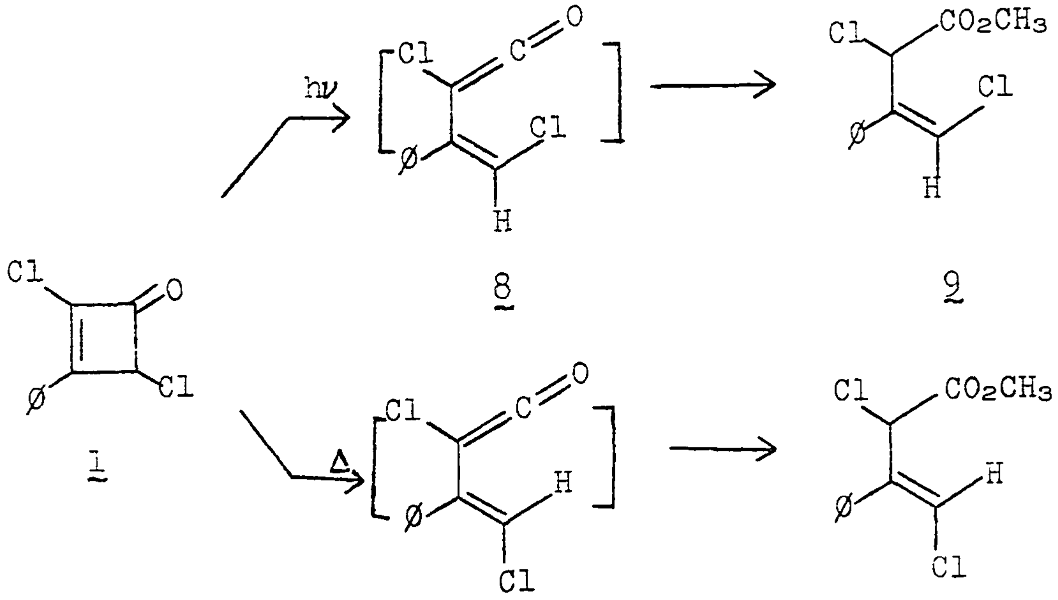
A limited number of indicative examples of photo-thermal processes involving α-cleavage, *cis,trans* isomerization, electrocyclic ring opening and sigmatropic shifts provided information which suggested that the understanding of organic photochemical reactions might be complicated by ensuing thermal reactions of photogenerated intermediates. A distinction between an uncomplicated photoreaction sequence and a photo-thermal reaction sequence could be made if structural and/or spectroscopic information were obtainable about possible photogenerated, thermally labile intermediates. Flash photolysis studies or low temperature photochemical studies could conceivably provide information about intermediates in photoinitiated reactions. Low temperature studies were initiated which included low temperature trapping experiments and spectroscopic studies of trapped thermally labile intermediates formed photochemically in rigid glasses or neat films. The combination of low temperature infrared spectroscopy and low temperature photochemistry provided a remarkably useful method to investigate multistep, photoinitiated transformations of organic compounds by making direct observations of unusually reactive intermediates. This study is concerned with the characterization of reactive intermediates observed in the low temperature photochemistry of cyclic α,β-unsaturated ketones. Primary photochemical processes were established and mechanistic pathways were defined for the photoinitiated transformations of these ketones. An effort was made to relate these pathways to the photochemical transformations of these ketones and similar cyclic ketones at or near room temperature.

REVIEW OF LITERATURE

Electrocyclic Reactions of Cyclobutene Derivatives

Jenney and Roberts (1) reported that thermolysis of 3-phenyl-2,4-dichlorocyclobutenone (1) in ethanol at 100° resulted in formation of ethyl 3-phenyl-2,4-dichloro-3-butenoate (3). Jenney and Druey (2) observed a similar reaction of 2-chloro-3-phenyl-4-(N-piperidinyl) cyclobutenone (4) in the presence of wet ether. The corresponding carboxylic acid, 2-chloro-3-phenyl-4-(N-piperidinyl)-3-butenoic acid (6) was obtained. Presumably both reactions occur by way of vinyl ketene intermediates (2 and 5) which result from thermal electrocyclic opening of the cyclobutenone rings. The stereochemistry of each ring-opened product was not determined in these examples. Baldwin and McDaniels (3) studied the stereochemical course of the thermal and photochemical ring opening processes in the presence of methanol and methanol-O-d. The ring opening





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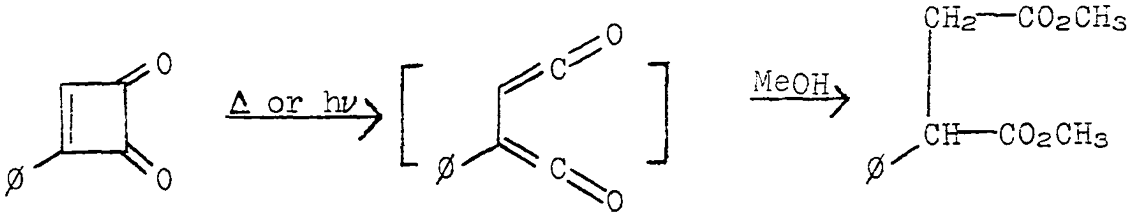
processes were shown to be stereoselective in an opposite sense for the thermal and photochemical processes.

Electrocyclic ring openings of cyclobutenediones should result in the formation of *bis*-ketene derivatives. Such reactions have been indirectly shown to occur when substituted cyclobutenediones are pyrolyzed or photolyzed. Blomquist (4) demonstrated that 3,4-diphenylcyclobutenedione was transformed in ethanol solution to diethyl 1,2-diphenylsuccinate, presumably by way of a *bis*-ketene intermediate. The thermal and photochemical reactions of 3-phenylcyclobutenedione (12) were examined by Roberts (5). Dimethyl phenylsuccinate (14) was obtained from both thermal and photochemical reactions in methanol.



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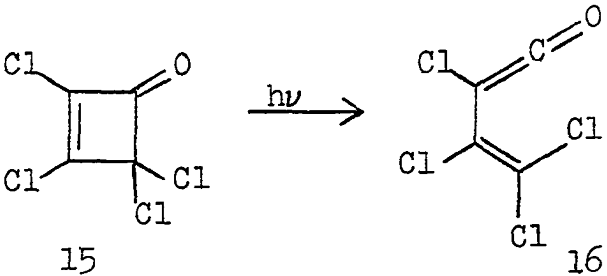
Direct observation of a vinyl-ketene was reported by Chapman and Lassila (6). Irradiation of perchlorocyclobutenone (15) at low temperature resulted in the direct conversion to the corresponding perchlorovinyl-ketene (16) which was observed by low temperature infrared spectroscopy.



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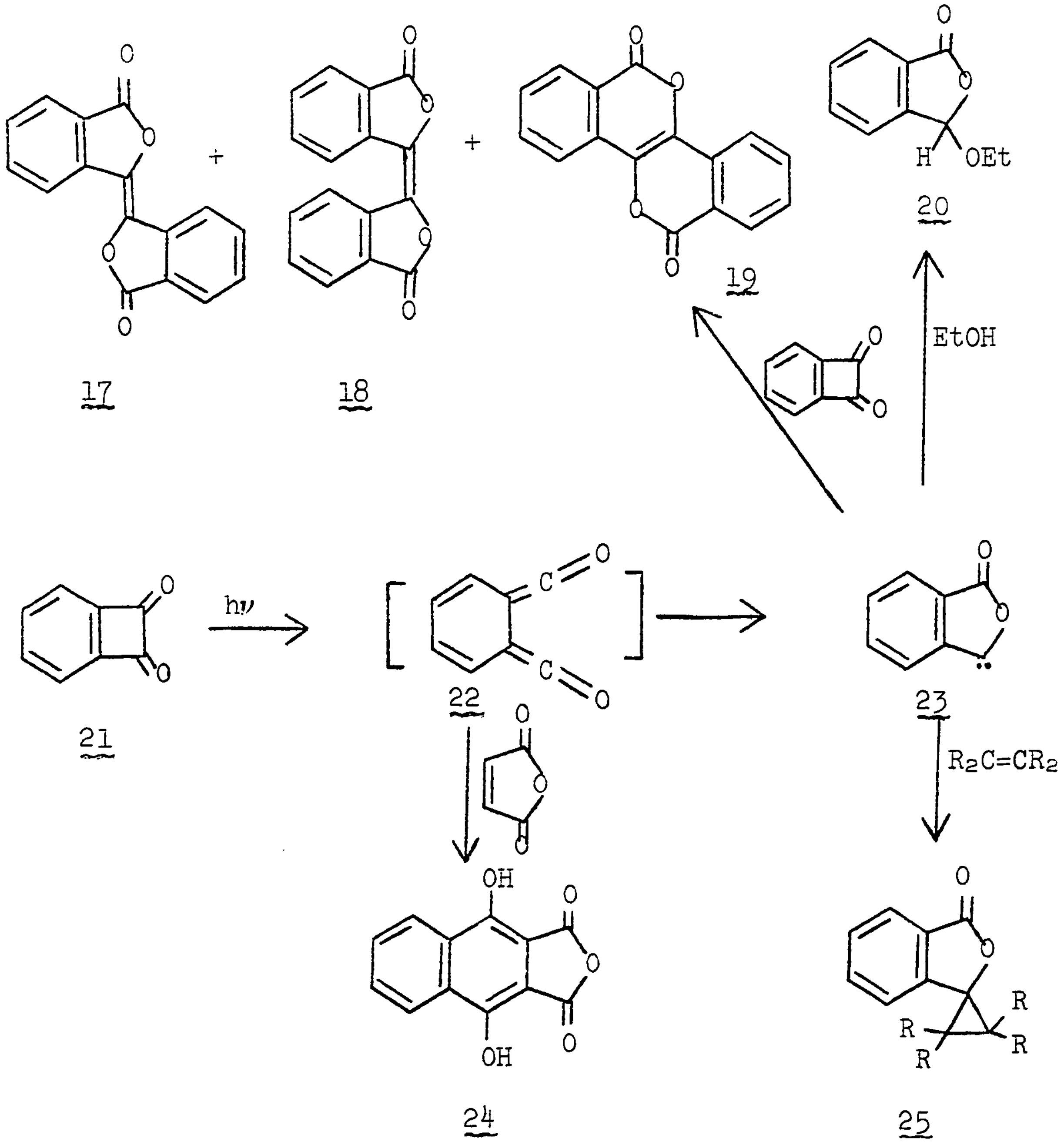
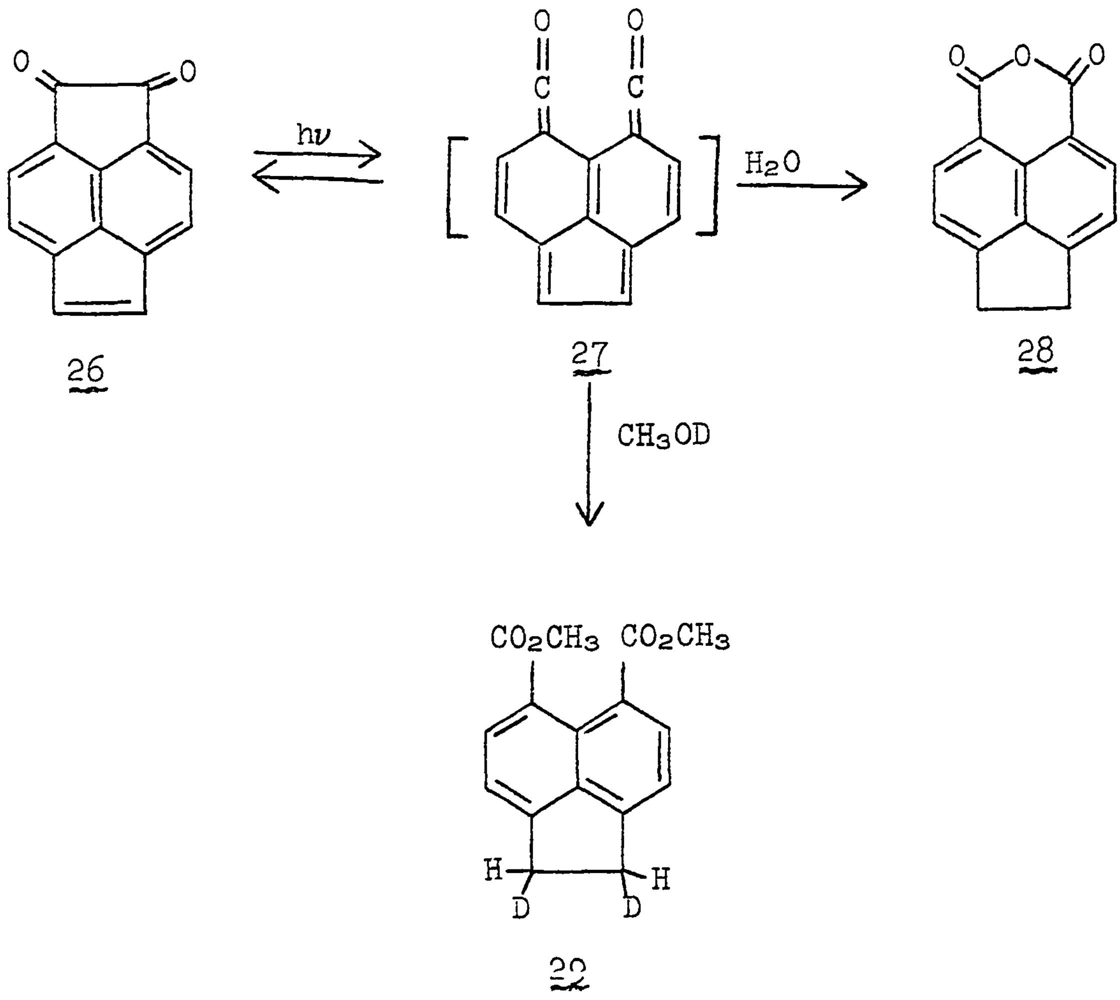
Brown and Solly (7) and Staab and Ipaktschi (8, 9, 10) reported that irradiation of benzocyclobutenedione (21) caused cleavage of the CO-CO bond to produce a bis-ketene (22). Intramolecular cyclization of the bis-ketene gave rise to a carbenoid species (23) which could be trapped with protonic solvents such as ethanol or with olefins which ultimately gave cyclopropane derivatives (25). The bis-ketene was successfully trapped with maleic anhydride before isomerization to the carbenoid species occurred. A naphthalenediol derivative (24) was obtained.



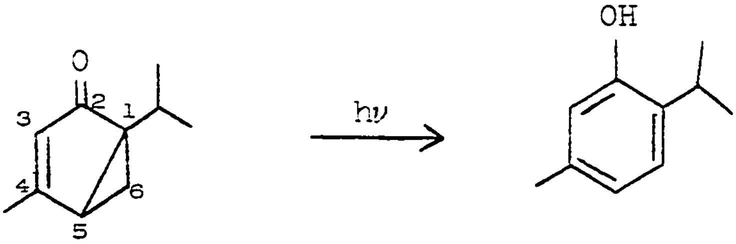
Trost (11) and Beringer (12) reported that irradiation of pyracycloquinone (26) gave rise to a transient red color which was postulated to be a *bis*-ketene (27); however Trost could not detect a ketene by infrared spectroscopy. Hydration of the transient intermediate produced a saturated anhydride (28). Esterification with methanol-O-d gave a diester (29) with incorporation of two deuterium atoms.



Photochemical Rearrangements of Bicyclo[3.1.0]hex-3-en-2-ones

One of the earliest examples of the photochemical conversion of a 2,5-cyclohexadienone derivative to a phenol was reported by Staudinger and Bereza (13) in 1911. This type of conversion has commonly been referred to as the photochemical dienone phenol rearrangement, however, in virtually all documented examples of this type of conversion, it has been demonstrated that intermediates such as bicyclo[3.1.0]hexenone derivatives and 2,4-cyclohexadienone derivatives are directly involved in the overall process. Excellent review articles on cyclohexadienone photochemistry are available (14, 15, 16).

Wheeler and Eastman (17) reported that irradiation of umbellulone (**30**) under a variety of conditions gave a quantitative yield of thymol (**31**). No *sym*-thymol, 3-methyl-5-isopropylphenol, was detected, even though a low yield of *sym*-thymol was obtained upon pyrolysis of umbellulone (**30**) at 280°. Jacquier and Soulier (18) obtained similar results when an isomer of umbellulone, 4-methyl-5-isopropylbicyclo[3.1.0]hex-3-en-one (**32**) was irradiated. Both rearrangements occur with cleavage of the 1,5 bond which is common to both rings.



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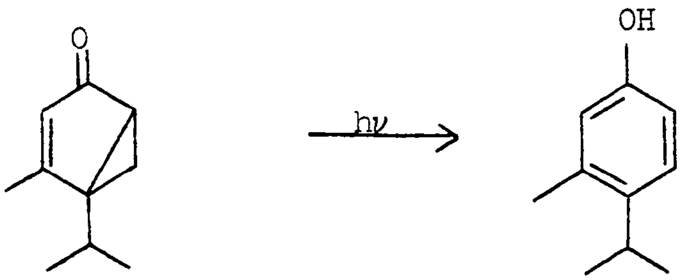

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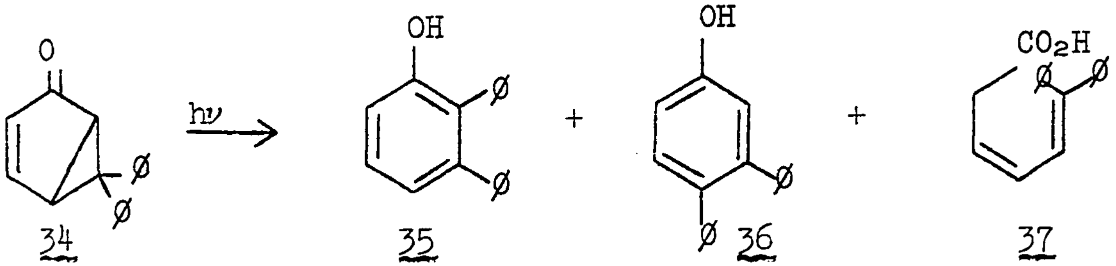
The photochemistry of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (34) was investigated by Zimmerman and Schuster (19, 20). Phenyl migration was found to occur upon



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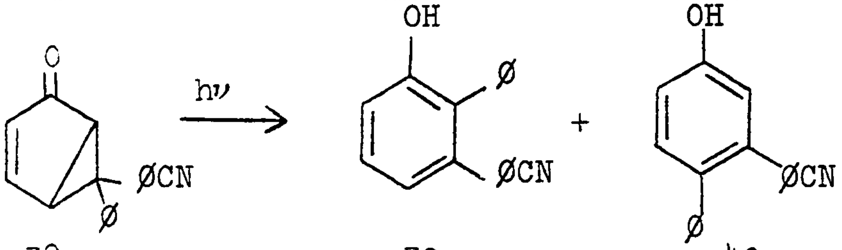
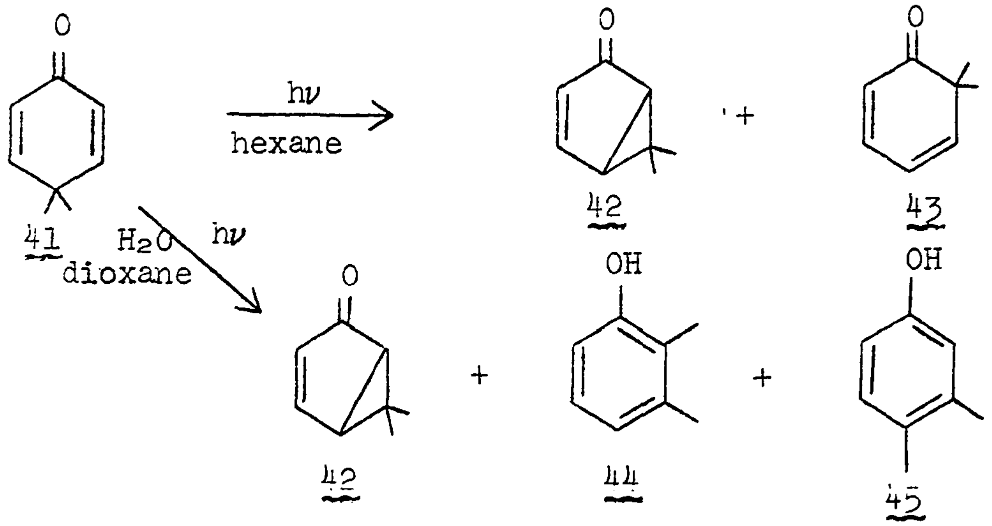
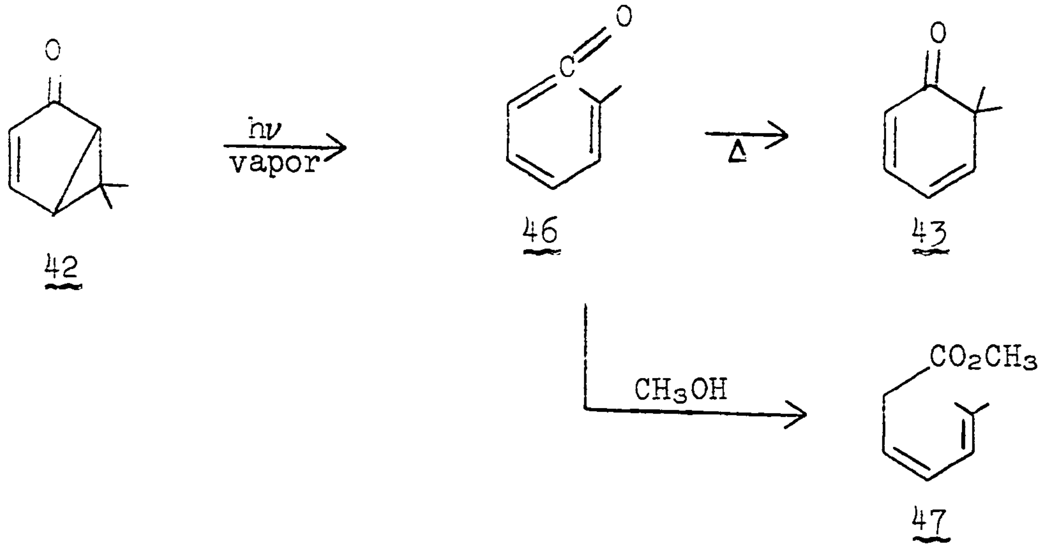


38 39 40

irradiation in aqueous dioxane to give 2,3-diphenylphenol (35) and 3,4-diphenylphenol (36) with a quantum efficiency of 0.066. 6,6-Diphenylhexadienoic acid (37) was obtained with a quantum efficiency of 0.030. Zimmerman and Grunewald (21) studied the migratory aptitudes of phenyl and *p*-cyanophenyl groups in 6-phenyl-6-(*p*-cyanophenyl)-bicyclo[3.1.0]hex-3-en-2-one (38). Exclusive phenyl migration occurred with the 2,3-phenol predominating over the 3,4 isomer. Either stereoisomer of starting material gave the same distribution of phenolic products. *p*-Cyanophenyl migration would have been expected to occur if the migration terminus possessed radical character. Zwitterionic intermediates have been postulated to account for such migrations.

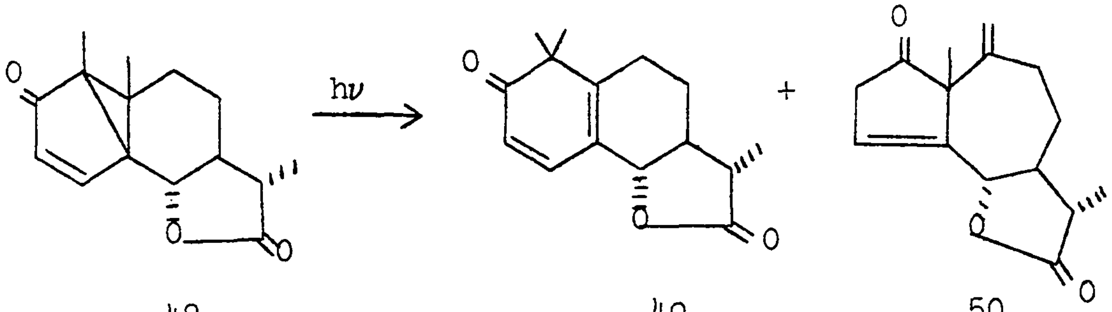
Swenton *et al.* (22) proposed a criterion for zwitterionic intermediates in the photochemistry of 2,5-cyclohexadienones by utilizing 4,4-dimethyl-2,5-cyclohexadienone as a model (41). In hexane solution,





4,4-dimethyl 2,5-cyclohexadienone gave 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (42) and 6,6-dimethylcyclohexa-2,4-dienone (43) when irradiated. In aqueous dioxane, 2,3-dimethylphenol (44) and 3,4-dimethylphenol (45) were obtained with 6,6-dimethylbicyclo[3.1.0] hex-3-en-2-one. Gas phase irradiation of 4,4-dimethyl-2,5-cyclohexadienone gave 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one as the primary product with a quantum efficiency of 0.40. 6,6-Dimethyl-2,4-cyclohexadienone was a secondary photoproduct. Transformation of 6,6-dimethylbicyclo[3.1.0]-hex-3-en-2-one to 6,6-dimethyl-2,4-cyclohexadienone involves a nonionic pathway when it takes place in the vapor phase while formation of phenols most probably involves zwitterionic intermediates since it is only observed in the polar medium.

The photochemistry of α-santonin and α-lumisantonin has been investigated by several independent research groups (23-28). During our low temperature investigations of α-lumisantonin, Fisch and Richards (29, 30) reported their elegant mechanistic and structural studies on the photochemistry of α-lumisantonin. Direct and sensitized irradiation of α-lumisantonin gave mazdasantonin (49) and a cyclopentenone derivative (50) in 80% and 10% yields along with several minor products (10%). The quantum efficiency of the reaction was increased from 0.26 upon direct irradiation to 1.00 when benzophenone was employed as sensitizer. The short lived reactive triplet state of α-lumisantonin ($\tau < 10^{-6}$ sec, $E_T = 64 \pm 1$ kcal/mole) was not quenched by oxygen or azulene. Piperylene and isoprene formed adducts with α-lumisantonin when it was irradiated in the presence of these diene triplet quenches.



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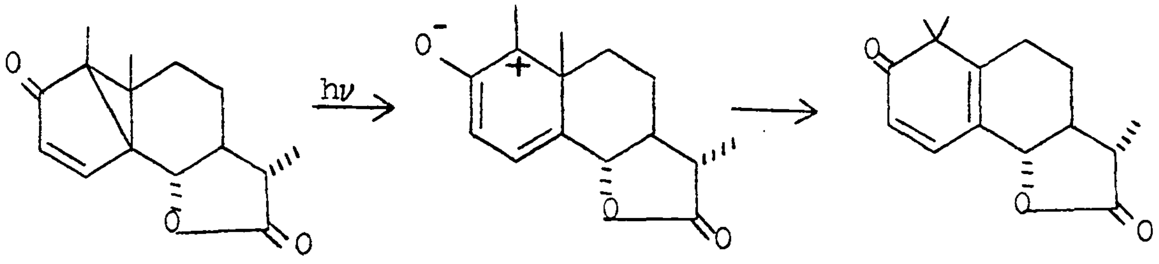
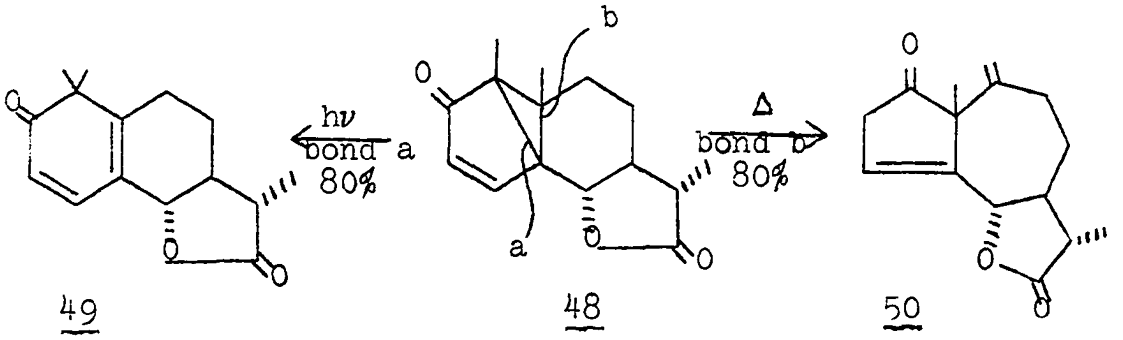
The nature of the skeletal rearrangement between α-lumisantonin and mazdasantonin gives this reaction the characteristics of a triplet derived carbonium ion type of transformation proceeding through a dipolar state such as



48 51 49

(51). In spite of the usefullness of the zwitterionic formalism to predict structural rearrangements, it does not give a priori information about the significant intermediate in the photoreaction of α-lumisantonin.

The possibility that a vibrationally excited ground state (31, 32) might be a significant intermediate in the photoreaction of α-lumisantonin was investigated by studying the pyrolysis products of α-lumisantonin. Pyrolysis



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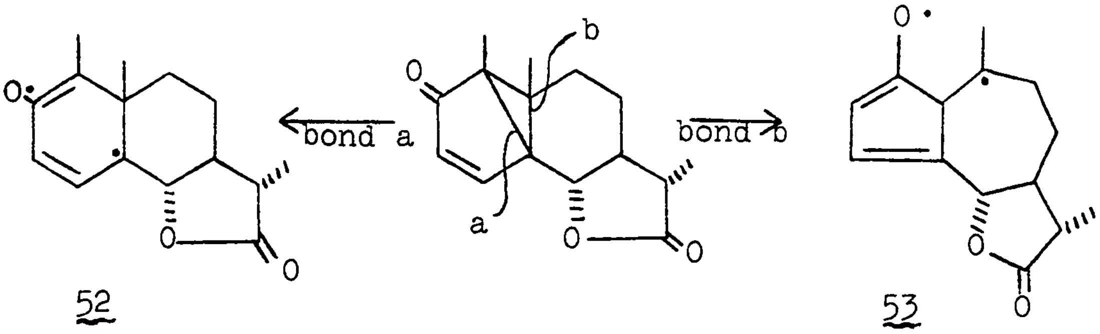
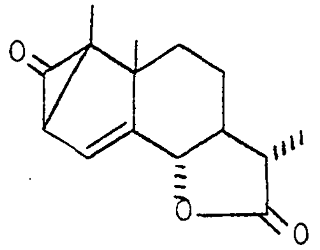
of α-lumisantonin under vacuum at 200° gave in greater than 80% yield the cyclopentenone derivative (50). The population of low-lying levels of the lumisantonin ground state leads to rupture of bond b at least 80% of the time whereas photochemical rupture of bond a occurs at least 80% of the time. It was suggested that bond breaking in the photolytic reaction does not occur in a vibrationally excited level of the ground state, but takes place in an electronically excited state. Alternatively rupture of the bond could occur before deactivation at the moment the molecule crosses from an electronically excited state into the ground state manifold. The evidence which is presently available suggests that deactivation to the first vibrational level is likely to be the fastest process available to a vibrationally highly excited ground-state species. If photolytic rupture were to occur in a high vibrational level of the ground state, it would be expected that collisional deactivation ($k \geq 10^{11}$ sec^{-1}) would occur more rapidly than methyl migration which is relatively slow, at least in the triplet diradical case ($k < 10^{8} sec^{-1}$) obtained by addition of triplet methylene to trans-2-butene (33). The rarity of methyl migration in ground-state diradicals suggests that the process is generally relatively slow (34).

The nature of the triplet involved in the photoconversion of lumisantonin could not be resolved on the basis of spectroscopic evidence presently available. Once bond breaking occurred in the triplet state to form two diradicals, (52) and (53), the manner in which diradical (53) stabilized itself was characteristic of the n,π^* triplet state. This suggests that the triplet of lumisantonin from which (52) and (53) are derived may have n,π^* rather than π,π^* characteristics.



The possibility that a cation radical intermediate was involved in the photoreaction of α-lumisantonin was excluded by electron scavenger studies with nitrous oxide (35) and biphenyl. Irradiation of α-lumisantonin in the presence of nitrous oxide in benzene at room temperature did not produce any nitrogen, and irradiation of lumisantonin in a glass at 77° K in the presence of biphenyl did not give rise to the characteristic spectrum of the biphenyl anion radical.

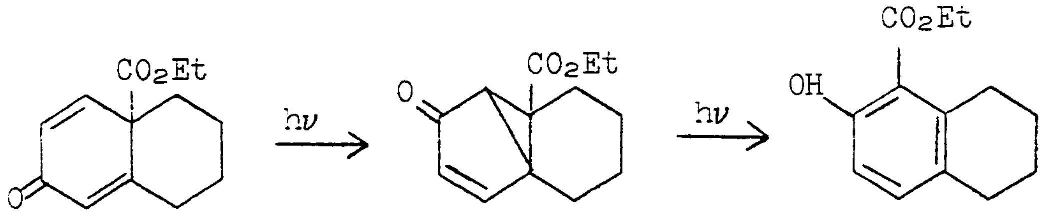
Irradiation of α-lumisantonin at 77° K in ether-pentane-alcohol or in methyltetrahydrofuran-3-methylpentane generated a blue species with an absorption maximum at 6500 Å. At 77° K, the blue species had a very long lifetime but at 100° K it lasted only a few seconds. In a methylcyclohexane-isopentane glass at 77° K, no blue color was observed. At 69° K, the trapped species was not paramagnetic and could not therefore be the diradical (52). It was concluded that the blue species was a zwitterion such as (51) which undergoes ionic rearrangement to mazdasantonin upon warming the rigid glass. The ground state completely bonded isomer (54) was not considered for two reasons. Formation of (54) from (51) or (52) destroys the conjugative stabilization of (51) or (52) and it also requires a significant deviation from planarity in the formation of (54) from (51) or (52). Secondly, the ultraviolet absorption spectra of cyclopropanones (36) occurs in the near ultraviolet (310-350 nm) which is in complete disagreement with the observed spectrum of the trapped



54

species. Attempts to trap the blue species with dimethyl acetylenedicarboxylate at 77° K only gave the usual products in the usual proportions. Trapping of a dipolar intermediate such as (51) following deactivation of a triplet such as (52) has precedence in the photochemistry of diphenyl amine (37, 38). The ionic photochemistry of α-lumisantonin which results in products derived from methyl migration can be resolved into the five discrete steps of the Zimmerman-Schuster mechanism: (a) excitation to a singlet state; (b) intersystem crossing to a very short lived triplet state; (c) bond breaking of the cyclopropane ring to give the triplet diradical (52); (d) electron demotion and redistribution; (e) ionic rearrangement from the dipolar state to mazdasantonin.

Kropp (39, 40) investigated the photochemical transformations of 4a-carbethoxy-5,6,7,8-tetrahydro-2-naphthalenone (55) and 4a,8,8-trimethyl-7-benzoyloxy-5,6,7,8-tetrahydro-2-naphthalenone (58). Both of the lumiketones obtained upon irradiation rearranged to 2-naphthol derivatives in a manner analogous to lumisantonin. There was no indication that a spiro-intermediate was present in these transformations. Further studies by Kropp (41) on 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)-



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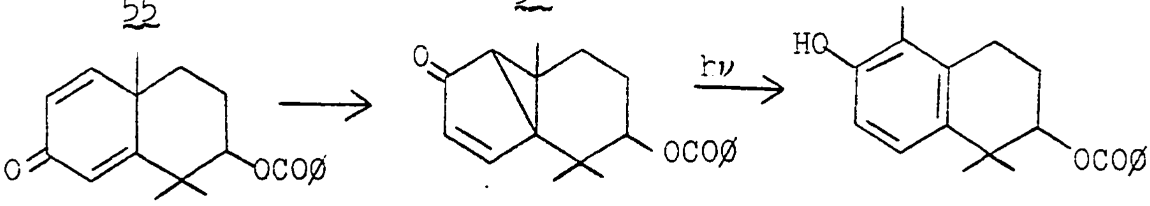
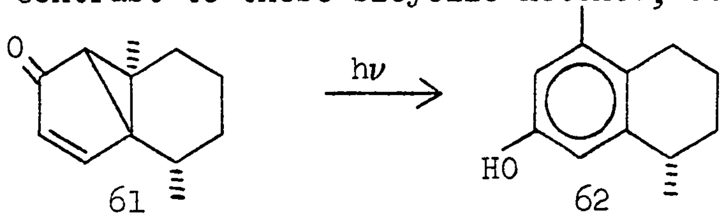


58 59 60

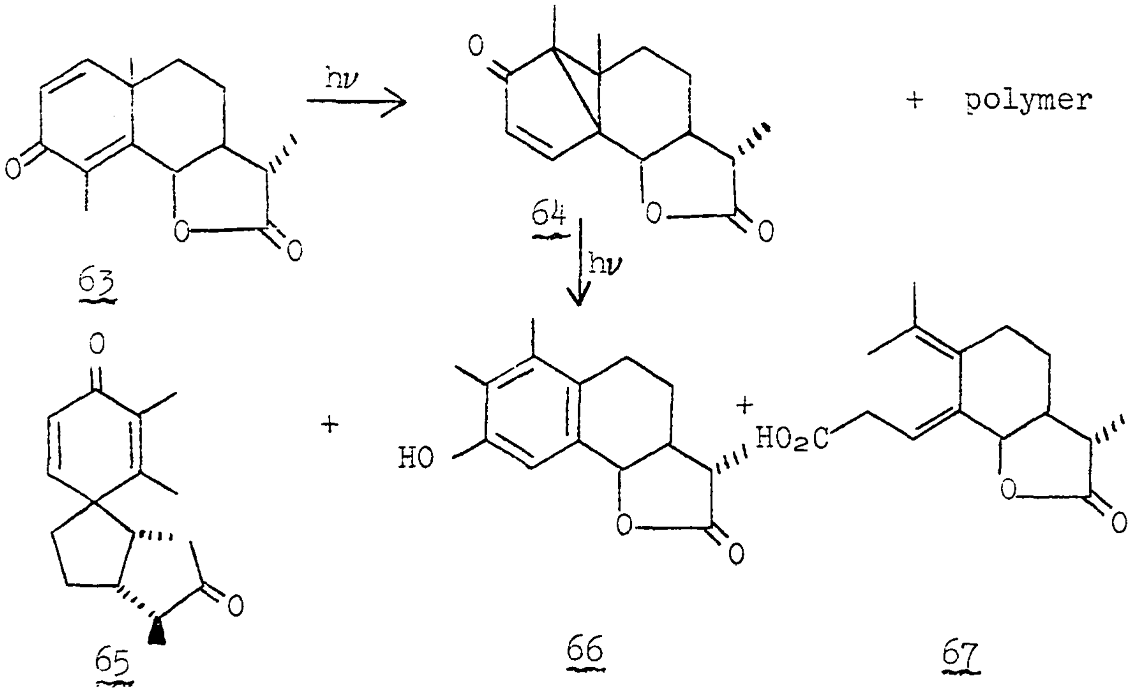
naphthalenone (61) showed that this lumiketone exhibited quite different behavior than lumiketones (56) and (59).

In contrast to these bicyclic ketones, other bicyclo[3.1.0]hexenones in naphthalenone, sequiterpene and steroid ring systems have been observed to undergo ring contraction to spirodienones which subsequently rearrange.



61 62

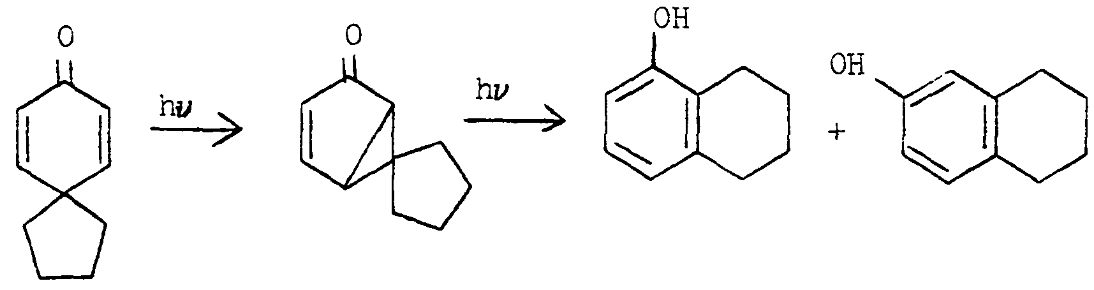
Fabian (42) reported that 6-*epi*-lumisantonin (64) rearranged to 6-*epi*-mazdasantonin in aprotic media. At 0°, 6-*epi*-lumisantonin underwent photochemical rearrangement in aqueous dioxane to a spirodienone, (65) a phenol derivative (66) and 6-*epi*-photosantonic acid (67). α-Lumisantonin gave only the corresponding photosantonic



acid under similar conditions. Such spirodienones are very photochemically labile and can subsequently be converted into bicyclo[3.1.0]hexenones and phenolic products.

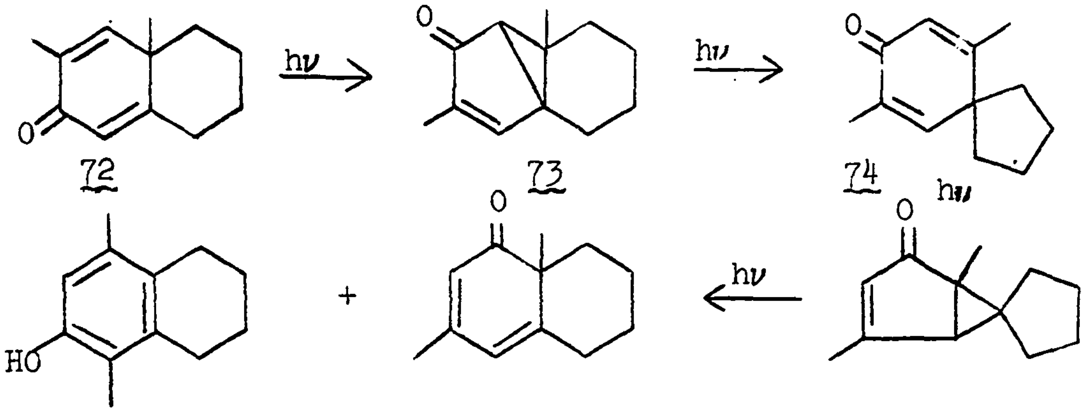
Griswold (43) demonstrated that spiro[4.5]deca-6,9-dien-8-one (68) gave 5,6,7,8-tetrahydro-1-naphthol (70) and 5,6,7,8-tetrahydro-2-naphthol (71) when irradiated. Chapman and Dominiani (44) detected the intermediacy of the corresponding lumiketone (69) in this transformation. A solvent dependence was observed with the 2-naphthol derivative highly favored in more polar media.

Other examples of well documented spirodienone



68 69 70 71

intermediates have been reported by Kropp (45, 46). 3,4a-Dimethyl-5,6,7,8-tetrahydro-2-naphthalenone (72) rearranged through a sequence requiring four photoinitiated steps. One intermediate, 6,9-dimethylspiro[4.5]deca-6,9-



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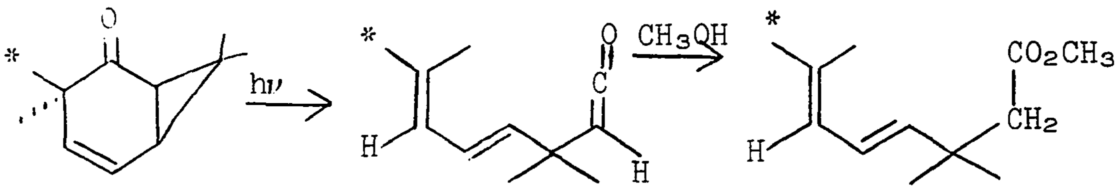
dien-8-one (74) was synthesized independently and was shown to give rise to the lumiketone (77) which underwent further rearrangement to the dienone (76) and phenol (75). However, it could not be detected in the rearrangement sequence which started with 3,4a-dimethyl-5,6,7,8-tetrahydro-2-naphthalenone.

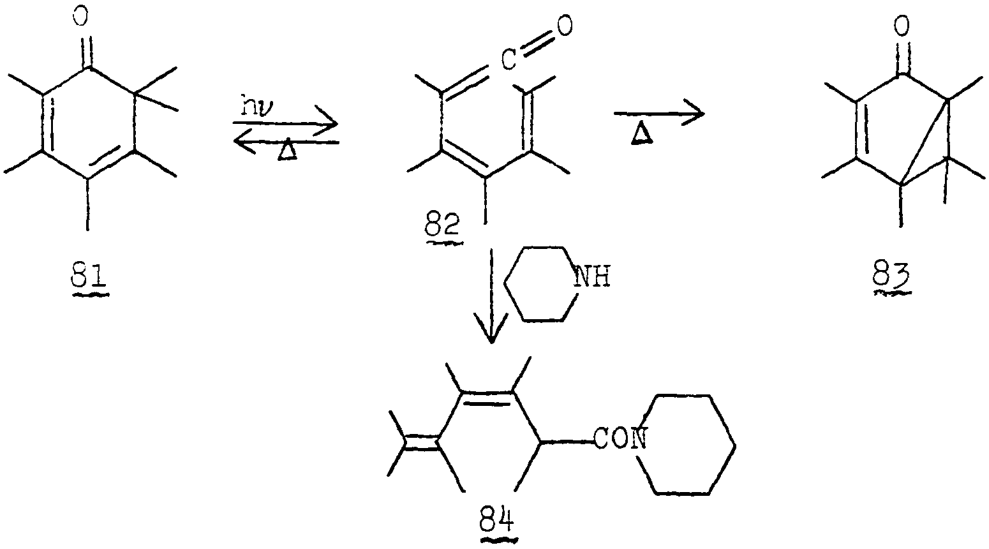
The photochemistry of 0-acetyl-1-dehydrotestosteron, a dienone type steroid, and three of its monosubstituted methyl derivatives and the C-10 epimer of 0-acetyl-1-dehydrotestosteron has been reported by Jeger et al. (47). Structural and mechanistic schemes describing the photochemistry of these compounds are presented. The transformations are analogous to the transformations of less complex compounds already described in this section.

Baldwin and Druger (48) have investigated the stereoselective valence isomerization of 3-methylcar-4-en-2-one (78). A ketene derivative (79) was detected at -190° with a strong infrared absorption at 2110 cm^{-1}. Even at room temperature in ether the ketene could be generated and observed.



78 79 80

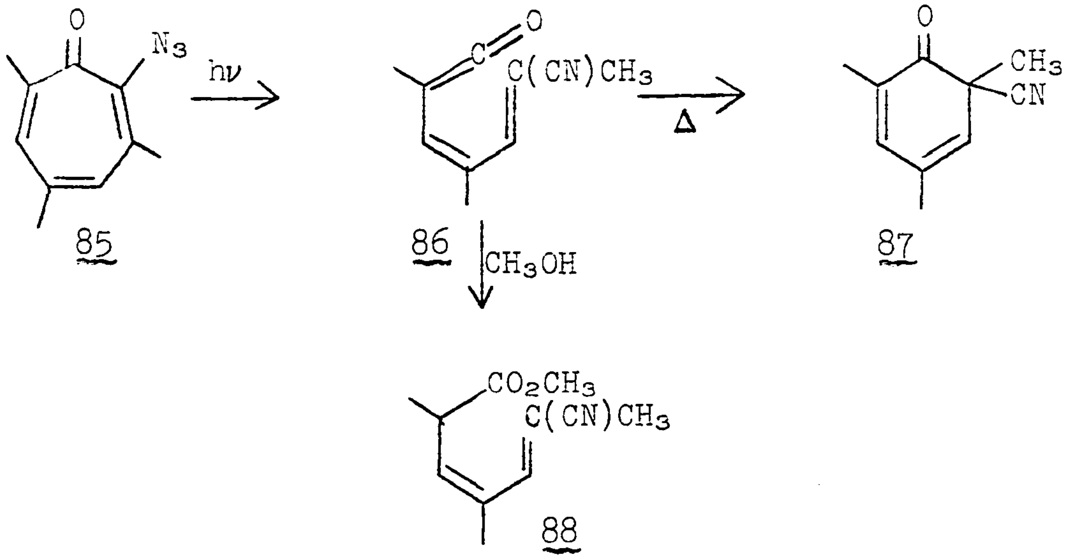
Griffiths and Hart (49) reported that hexamethyl-2,4-cyclohexadienone (81) underwent photolytic ring cleavage at -100° to give a stable diene-ketene derivative (82) with an absorption at 2050 cm^{-1}. When the sample was allowed to warm, cyclization of the ketene occurred to produce the starting material in addition to hexamethyl-bicyclo-[3.1.0]hexenone (83). Isomerization to the bicyclic ketone was catalyzed by ethanol which did not add to the ketene. The ketene could be trapped with amines. In the absence of amines, the ketene derivative cyclized with virtually 100% efficiency in ethanol. It was suggested from attempted sensitization studies that the ketene is formed from an excited singlet state.



Photochemical Reactions of Some Unsaturated Cycloheptane and Cyclooctane Derivatives

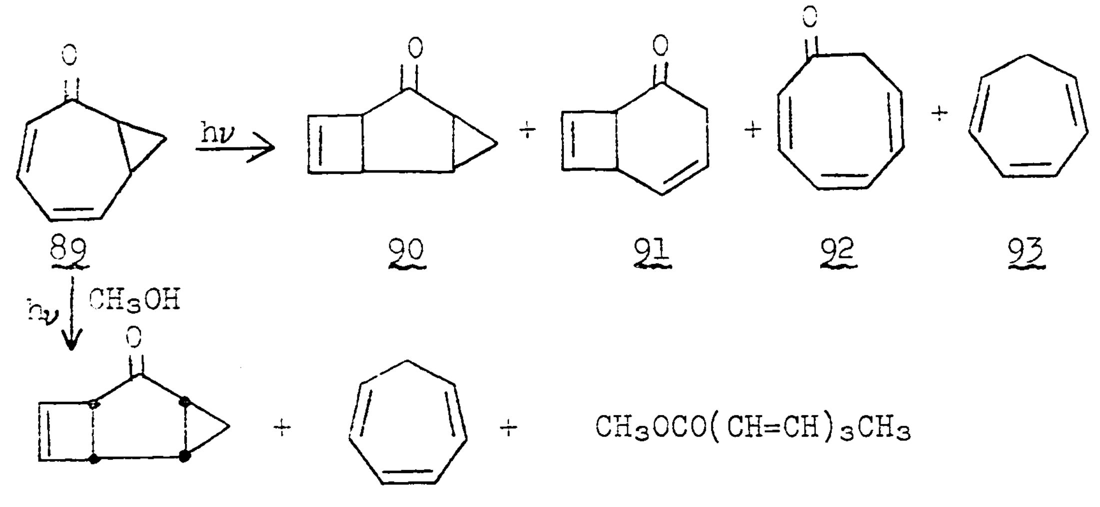
Hobson *et al.* (50) investigated the low temperature photochemistry of 1-azido-2,4,6-trimethyltropone (85). Upon irradiation loss of nitrogen occurred with ring fission to give a diene-ketene derivative (86) which underwent thermal cyclization to 2,4,6-trimethyl-6-cyanocyclohexadienone (87) with $\Delta H^{\ddagger} = 13.9$ kcal/mole and $\Delta S^{\ddagger} = -3.5$ e.u.

The cyclization was shown to compete effectively with solvent addition to the intermediate ketene at -50°.



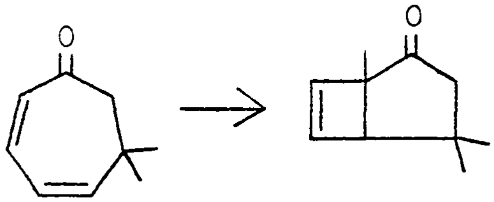
Paquette and Cox (51, 52) investigated the photochemistry of 2,3-homotropone in aprotic and protic solvents. Cycloheptatriene (93), bicyclo[4.2.0]octa-4,7-dien-2-one (91), 1α,2α,4α,6α-tricyclo[4.2.0.$0^{2,4}$]oct-7-en-5-one (90) and 2,4,6-cyclooctatrienone (92) were obtained when the irradiation was performed in ether. Irradiation in methanol enhanced the amount of tricyclic ketone (90) with a concomitant decrease in the yield of cycloheptatriene. 2,4,6-cyclooctatrienone was completely converted to methyl 2,4,6-octatrienoate (94) under these conditions.

Hurst (53) and Buchi (54) reported that irradiation of eucarvone (95) resulted in the formation of three

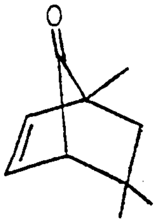


90 93 94

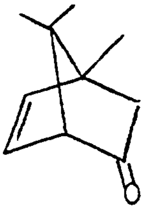
bicyclic ketones, 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one (96), 1,5,5-trimethyl-7-keto-norborn-2-ene (97) and 1,7,7-trimethyl-5-keto-norborn-2-ene (98). Photodecarbonylation was not mentioned in either of these two reports.



95 96



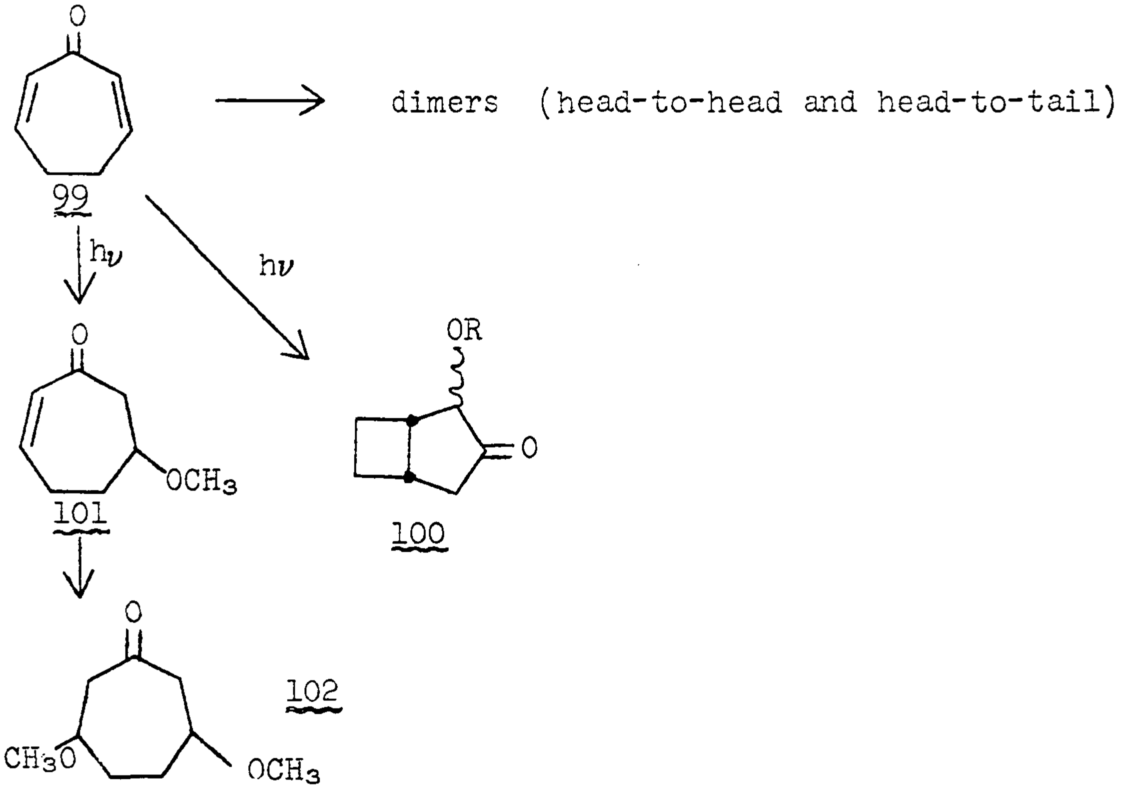
97



98

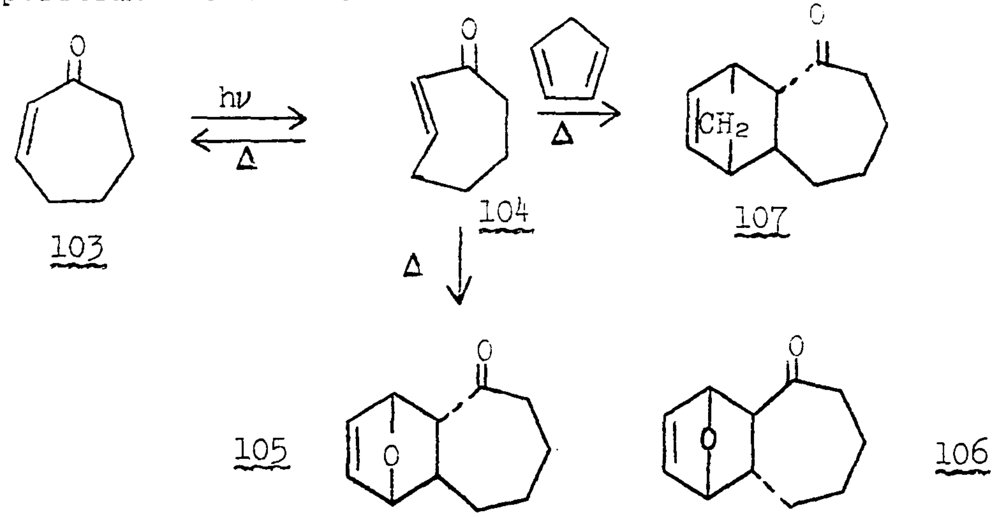
Nozaki (55) reported that cross conjugated cycloheptadienones behave much differently than do their linearly conjugated isomers. Irradiation of 2,6-cycloheptadienone (99) in hexane gave a 40-50% yield of head-to-head and head-to-tail dimers. Stepwise addition of solvent was observed when the irradiation was carried out in methanol leading to 6-methoxy-2-cycloheptenone (101) and 3,6-dimethoxycycloheptanone (cis and trans). No bicyclic

[3.2.0] adducts were observed. In more acidic media, e.g., acetic acid or *t*-butyl alcohol and sulfuric acid this was the only mode of addition. A mixture of *endo* and *exo*-2-acetoxy-*cis*-bicyclo[3.2.0]heptan-3-one (100) was obtained by irradiation in acetic acid. An intermediate, highly strained *trans, cis* isomer may actually be involved in these transformations.



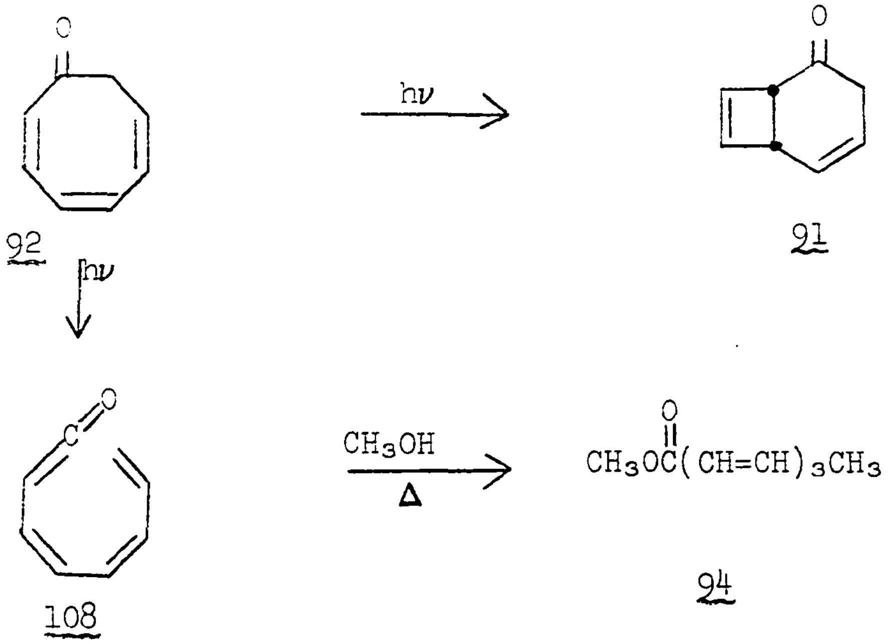
Corey (56) and Eaton (57) made direct observations of *trans*-2-cycloheptenone (103) at -190° by low temperature infrared spectroscopy. The highly strained *trans*-2-cycloheptenone (104), which was stable below -120°, isomerized back to the *cis* isomer and dimerized upon warming. The photoisomer, *trans*-2-cycloheptenone was trapped at -50°

and -190° with cyclopentadiene. A single 1:1 adduct (107) was obtained. Two Diels Alder adducts (105, 106), derivatives of 7-oxa-norbornene with *trans* ring fusion were obtained in excellent yield when the irradiation was performed in furan.

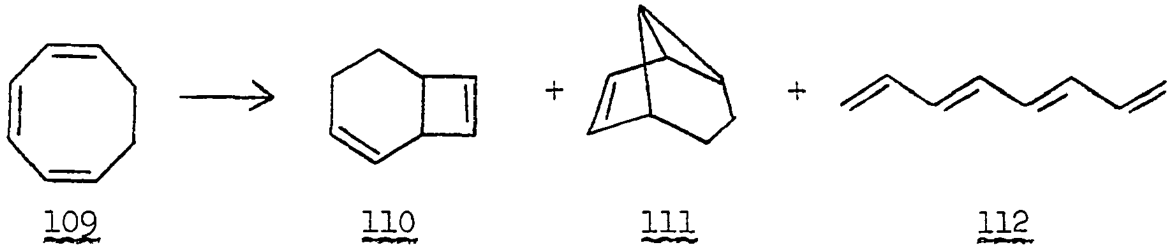


Buchi and Burgess (58) investigated the room temperature photochemistry of 2,4,6-cyclooctatrienone (92) in aprotic and protic solvents. When the irradiation was performed in pentane, an isomer of 2,4,6-cyclooctatrienone, bicyclo[4.2.0]octa-4,7-dien-2-one (91) was obtained. Methyl 2,4,6-octatrienoate (94) was obtained when the irradiation was performed in methanol. A triene-ketene (108) was proposed as an intermediate to account for the ester formation.

Roth (59), Winstein (60) and Chapman (61) reported the formation of bicyclo[4.2.0]octa-2,7-diene, (110)

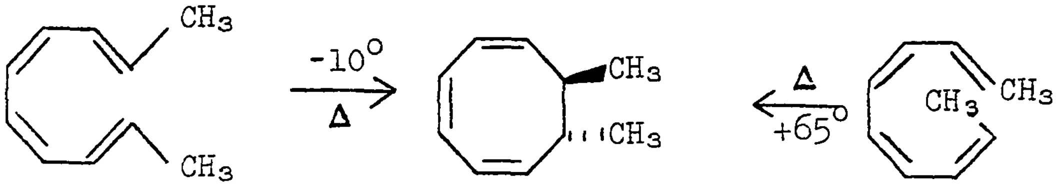


tricyclo[3.2.1.0^{2,8}]oct-6-ene (111) and 1,3,5,7-octatetraene (112) upon irradiation of 1,3,5-cyclooctatriene (109).

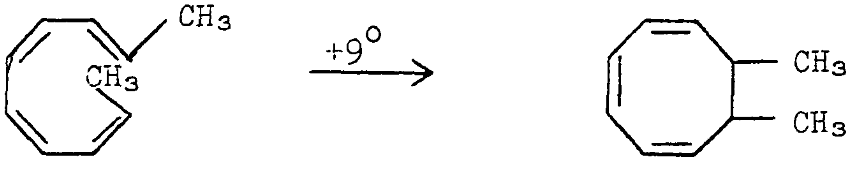


Chapman and Shim (62) were not able to detect any new modes of reaction for 1,3,5-cyclooctatriene at low temperatures. Trapping experiments with furan failed to detect any transients such as *trans*, *cis*, *cis* or *cis*, *trans*, *cis*-1,3,5-cyclooctatriene. Goldfarb and Lindquist (63) detected two intermediates with lifetimes of 91 and 23 msec during flash photolysis of 1,3,5-cyclooctatriene. The long lived species was identified as *cis*,*cis*-1,3,5,7-

octatetraene which recyclized readily at room temperature to 1,3,5-cyclooctatriene. The Arrhenius activation energy for this cyclization is seventeen kcal/mole. The short lived transient was believed to be a strained cyclic stereoisomer of 1,3,5-cyclooctatriene which underwent ring opening with an activation energy of sixteen kcal/mole. Ziegenbein (64) and Marvel (65) demonstrated that the cyclization of 1,3,5,7-octatetraenes at room temperature occurred provided cis stereochemistry was maintained at the 3,5-double bonds. Neither all trans or mono-cis-octatetraene gave 1,3,5-cyclooctatriene. Meister (66) and Huisgen (67) demonstrated that the stereochemistry of the products obtained by these electrocyclic cyclizations could be predicted by the Woodward-Hoffman orbital symmetry rules.



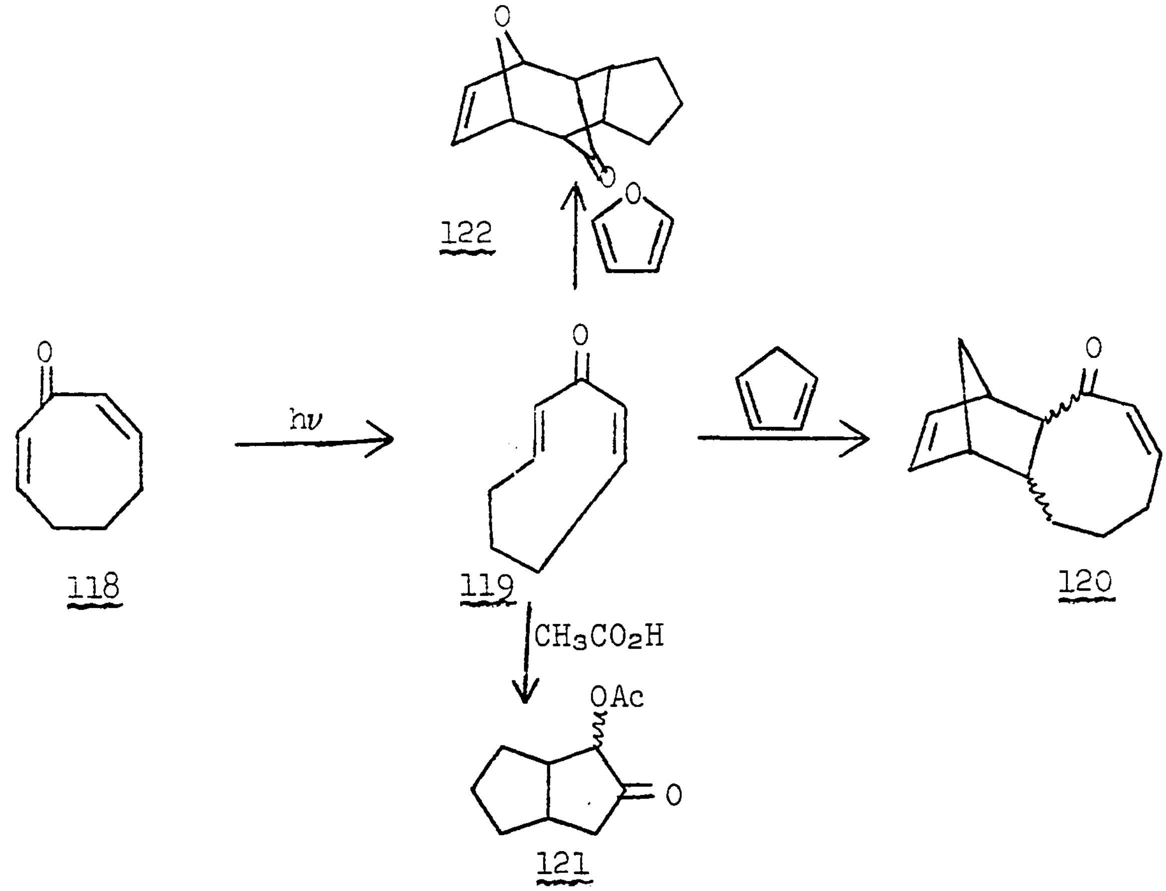
113 114 115



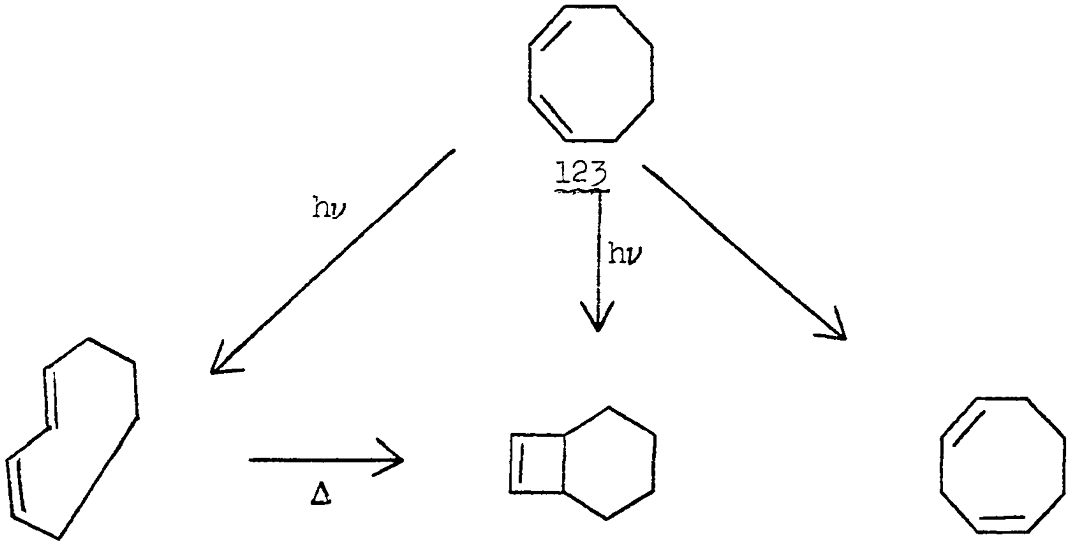
116 117

Crandall (68) and Noyori (69) investigated the effects of solvents upon the photochemistry of 2,7-cyclooctadienone (118). When the irradiation was performed in acetic acid, a 1:4 mixture of endo and exo-2-acetoxy-cis-bicyclo[3.3.0]octan-3-one (121) was obtained. A small amount of cis-bicyclo[3.3.0]octan-3-one was obtained as a secondary product. Irradiation in methanol gave a more complex mixture in which exo-2-methoxy-cis-bicyclo[3.3.0]octan-3-one was the major component. Minor components were cis-bicyclo[3.3.0]octan-3-one, 7-methoxy-2-cyclooctenone and 3,7-dimethoxycyclooctanone. Irradiation of 2,7-cyclooctadienone in the presence of cyclopentadiene yielded a mixture of stereoisomeric adducts (120) which presumably arose by way of trans,cis-2,7-cyclooctadienone. When furan was employed as a trapping agent, a different type of adduct (122) was obtained which was shown to be a 1,3-dipolar adduct to furan.

A reactive ground state intermediate was shown to be involved in each of these reactions. Irradiation of 2,7-cyclooctadienone at -78° in an inert solvent followed by addition of acetic acid, methanol, cyclopentadiene or furan and warming to room temperature showed the respective products to be present. cis,trans-2,7-Cyclooctadienone seems to be the most exact representation for this intermediate.



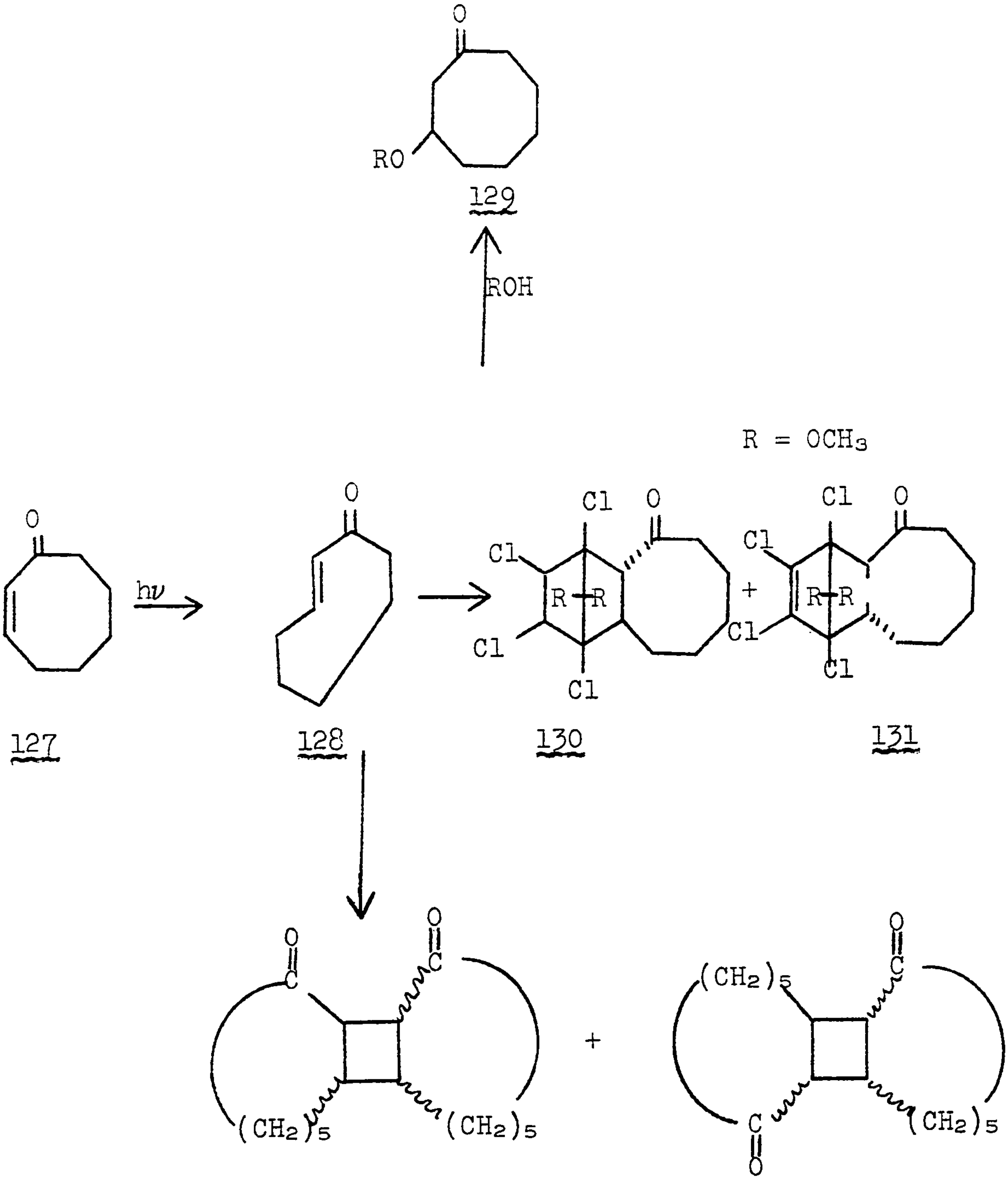
Srinivasan (70), Clark (71) and Dauben (72) reported that bicyclo[4.2.0]oct-7-ene (**125**) was obtained by direct irradiation of *cis,cis*-1,3-cyclooctadiene (**123**). Liu (73) reported that sensitized irradiation of *cis,cis*-1,3-cyclooctadiene resulted in *cis,trans* isomerization to give *cis,trans*-1,3-cyclooctadiene (**124**) which underwent electrocyclic ring closure at 80° to give bicyclo[4.2.0]oct-7-ene. Fonken (74) demonstrated that *cis,trans* isomerization also occurred upon direct irradiation with a quantum efficiency of 0.28 while bicyclo[4.2.0]oct-7-ene formed with a quantum efficiency of 0.01. A photostationary state with a *cis,trans*/*cis,cis* ratio of 0.60 was obtained upon prolonged irradiation.



123

124 **125** **126**

Cis,trans isomerization was demonstrated by Eaton (75) to be the primary photo-pathway when 2-cyclooctenone was irradiated in aprotic solvents. A mixture (4:1) of *trans* and *cis* isomers was obtained at room temperature which could be converted to the all *cis* isomer with a trace of mineral acid. Two *trans*-fused Diels-Alder adducts (**130**, **131**) were obtained at room temperature when *trans*-2-cyclooctenone was treated with 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopentadiene. Similar *trans*-fused adducts were readily obtained with furan and cyclopentadiene. In the dark, *trans*-2-cyclooctenone dimerized to give head-to-head and head-to-tail cyclobutane dimers (**132**, **133**).



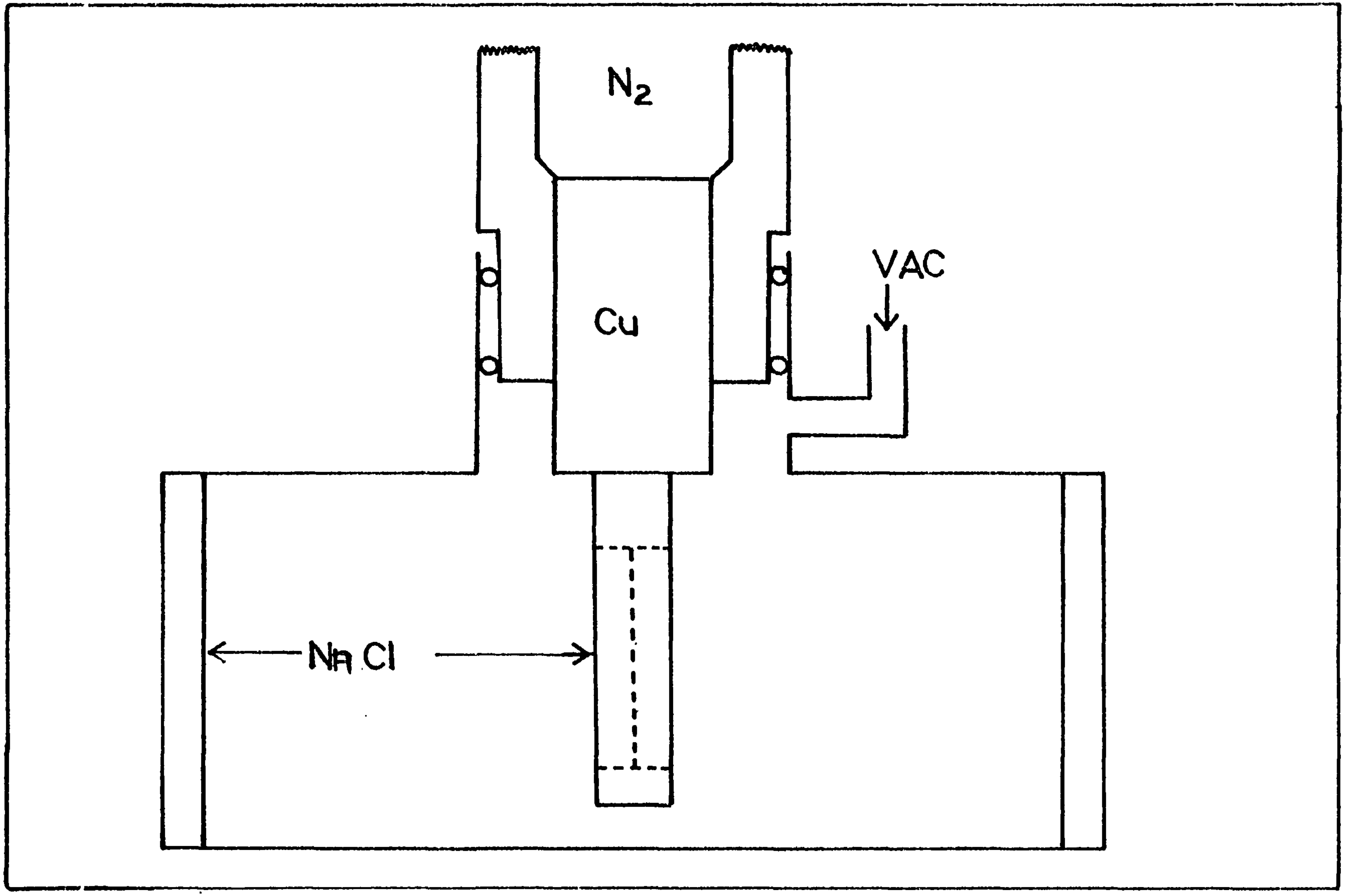
127 128 129 130 131 132 133

RESULTS AND DISCUSSION

The low temperature investigations presented in this thesis are part of an extensive study designed to detect and investigate in detail photo-thermal reaction sequences. 2,3-Dimethylcyclobutenedione, umbellulone, α-lumisantonin, 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone, 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone and 2,4,6-cyclooctatrienone were selected for investigation by low temperature infrared spectroscopy and low temperature trapping experiments. These cyclic α,β-unsaturated ketones and closely related derivatives undergo a variety of rearrangements and isomerizations at room temperature. The structures of the products obtained from room temperature photochemical studies on these compounds have been characterized prior to this investigation.

The low temperature infrared experiments were performed in cells based upon a design of a low temperature cell employed by Hornig (Figure 1) (76). The samples were usually studied as neat glassy or crystalline films at liquid nitrogen temperatures. The irradiations could be easily followed by plotting the absorbances of selected bands in the starting material and product(s) versus the irradiation time. These plots helped distinguish primary photoproducts from secondary photoproducts. Similar plots

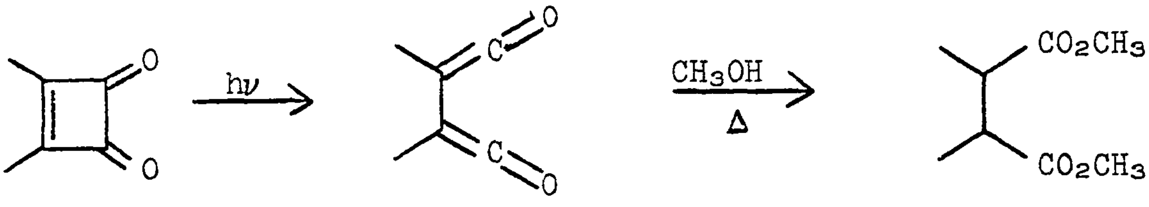
Figure 1. Schematic diagram of the Air Products low temperature unit.


N_2
VAC
Cu
Na Cl

of the absorbances of selected bands versus temperature may be obtained from the spectra of the postirradiation warmup. Such plots are useful for interpreting the thermal behavior of the intermediates formed upon warming.

2,3-Dimethylcyclobutenedione

Irradiation of 2,3-dimethylcyclobutenedione (**134**) as a neat liquid film at -190° produced a *bis*-ketene derivative (**135**) with carbonyl absorptions at 2070, 2090, 2120 and 2138 cm^{-1}. Continued irradiation resulted in coalescence of these four absorptions so that only two absorption bands at 2120 and 2090 cm^{-1} could be resolved under these conditions. The irradiation was discontinued after the ketene absorption bands reached approximately 75% of full scale transmission (Figure 4). During the irradiation, an absorption band at 1280 cm^{-1} increased steadily. An assignment of this absorption was not made. Plotting the absorbances of the two ketene absorption bands at 2090 and 2120 cm^{-1} and the absorption band at 1280 cm^{-1} as a function of time showed that they formed at a comparable rate (Figure 2). At -190°, the *bis*-ketene derivative (**135**) was stable in the



134 **135** **136**

dark within the limits of detection by low temperature infrared spectroscopy.

It was not clear from the spectrum of the cold, irradiated 2,3-dimethylcyclobutenedione whether an alternate reaction, i.e., elimination of carbon monoxide might have competed with electrocyclic opening to the bis-ketene derivative (135). The absorption at 2138 cm^{-1} could conceivably be carbon monoxide which could result from loss of one or two molecules of carbon monoxide from the starting material. Extrusion of one molecule of carbon monoxide would leave dimethylcyclopropenone or an isomer. A careful examination of the low temperature infrared spectra in the regions of 1850 and 1640 cm^{-1} did not reveal any absorptions which could be assigned to a cyclopropenone derivative. If loss of two molecules of carbon monoxide occurred from a molecule of starting material, dimethyl acetylene would be formed which, due to its symmetry would not be easily detected by infrared spectroscopy.

As the sample was allowed to warm, a smooth diminution of both absorptions at 2120 and 2090 cm^{-1} began to occur at -120°. A greater than 50% loss of intensity had occurred when the cell reached -60°. The simultaneous disappearance of both absorptions with nearly identical responses to temperature indicate that they belong to the same species (Figure 3). Poorly resolved absorption bands appeared at 1638, 1285, 1265, 1140-25 and 978 cm^{-1} during the warm-up. The probable disappearance of the 1280 cm^{-1} band is masked by the appearance of the 1285 cm^{-1} band. The product or products obtained by warming the bis-ketene (135) could not be directly identified by interpretation of the warm infrared spectra. Observation of the bis-ketene derivative (135) and its reaction with methanol clearly provided evidence for its intervention in the photoreaction of 2,3-dimethylcyclobutenedione.

Irradiation ($\lambda > 360$ nm) of 2,3-dimethylcyclobutenedione in a methanol solution at room temperature resulted in rapid disappearance of starting material. After complete destruction of starting material was achieved, the crude photomixture was analyzed by gas liquid partition chromatography (glpc) and was shown to consist of a mixture of meso and racemic dimethyl 2,3-dimethylsuccinates (136). Preparative glpc of this crude photomixture gave a mixture of the two esters. The structures of these esters were assigned on the basis of the following data. The infrared spectrum (Figure 4) of this mixture showed a strong carbonyl absorption at 1740 cm^{-1}. Strong absorptions at 1200 and 1160 cm^{-1} were observed and assigned to the asymmetric and symmetric stretching modes of the C-O-C ester bond. The nuclear magnetic resonance (nmr) spectrum revealed two methoxyl groups as singlets at δ 3.65. A two proton

Figure 2. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of 2,3-dimethylcyclobutenedione

▮ – 2120 cm^{-1}

▲ – 2090 cm^{-1}

● – 1280 cm^{-1}

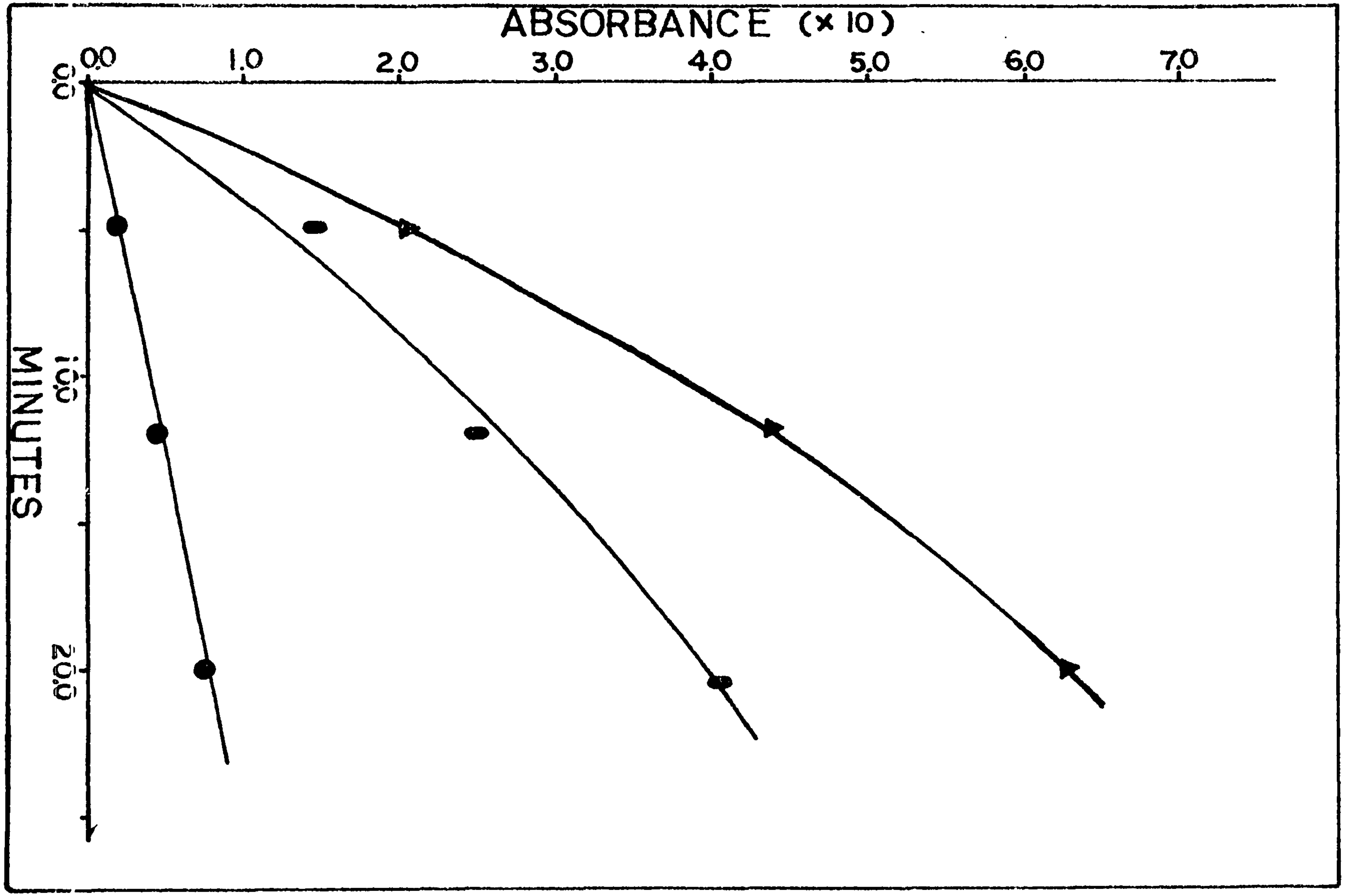

ABSORBANCE (× 10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
MINUTES
0.0
10.0
20.0

Figure 3. A plot of absorbances of selected absorption bands versus temperature which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 2,3-dimethylcyclobutenedione

● - 2120 cm^{-1}

▲ - 2090 cm^{-1}

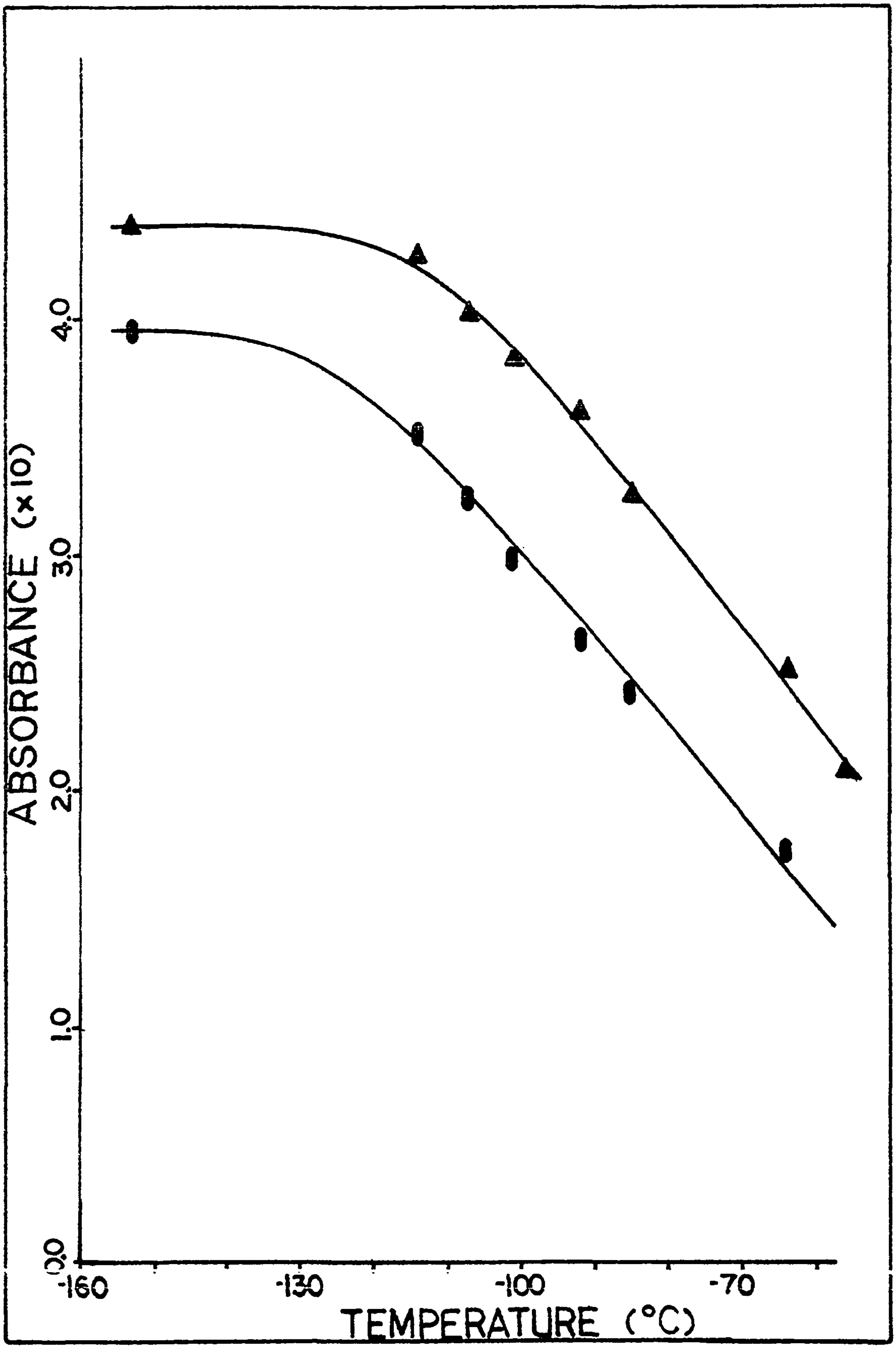

ABSORBANCE (×10)
4.0
3.0
2.0
1.0
0.0
-160
-130
-100
-70
TEMPERATURE (°C)

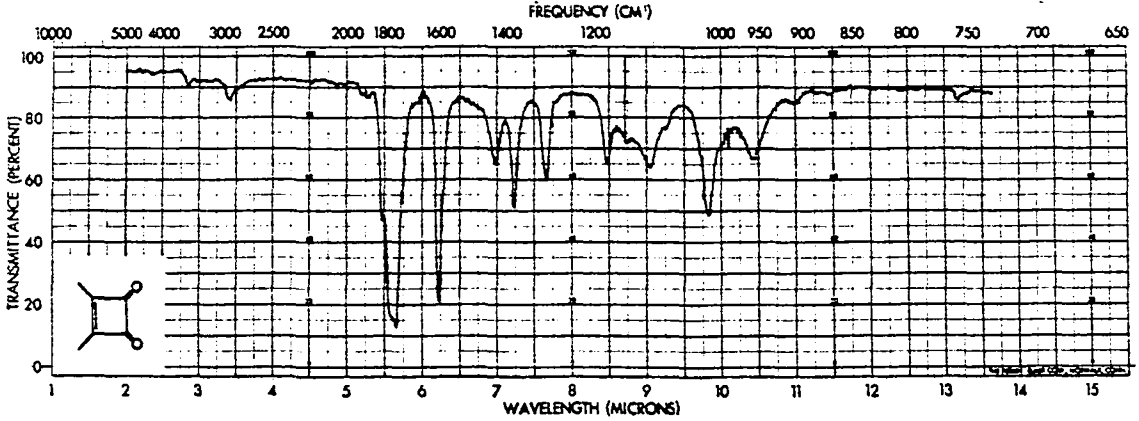
Figure 4. Infrared spectra (neat)

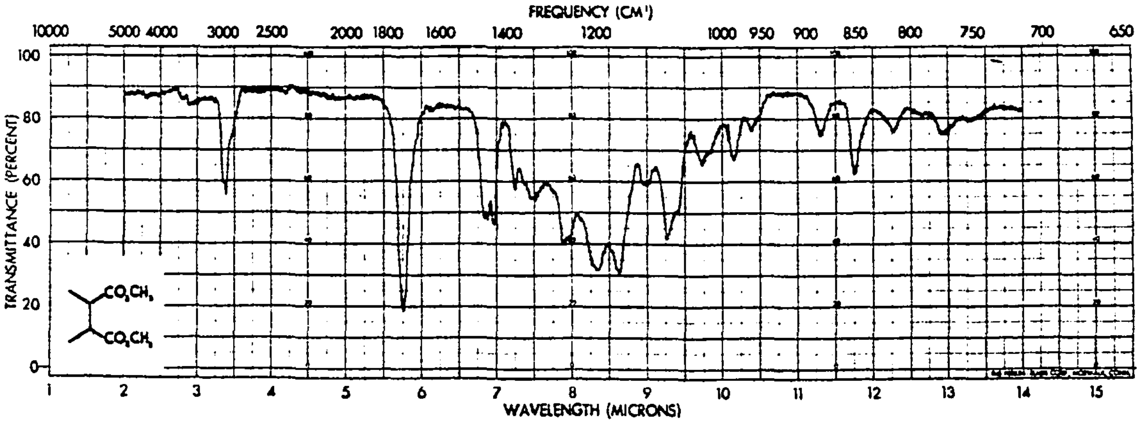
Top--2,3-dimethylcyclobutenedione

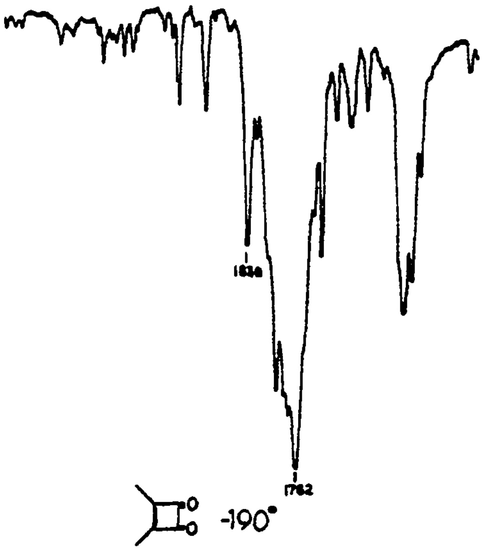
Middle--*meso* and racemic dimethyl 2,3-dimethylsuccinate

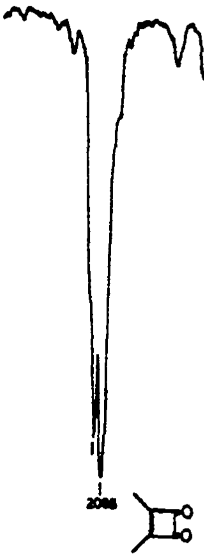
Bottom left--2,3-dimethylcyclobutenedione (-190°)

Bottom right--irradiated 2,3-dimethylcyclobutenedione (-190°)







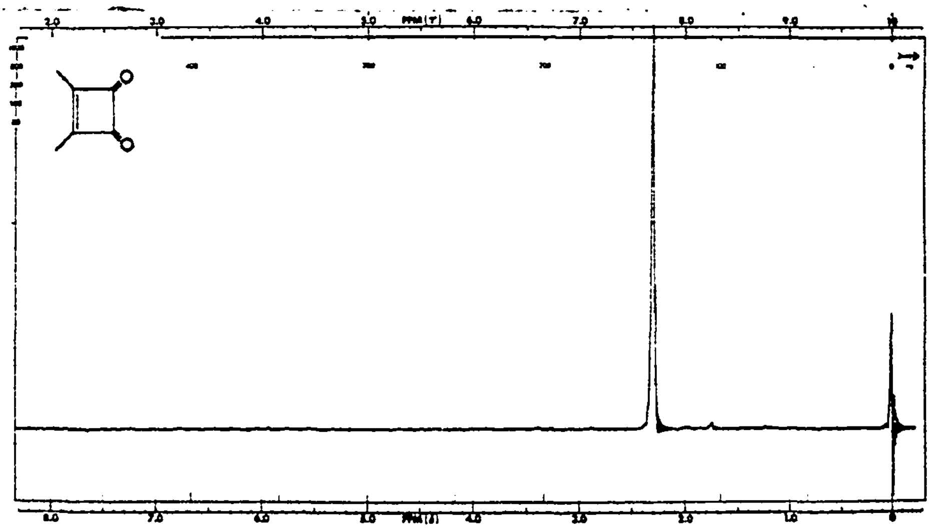


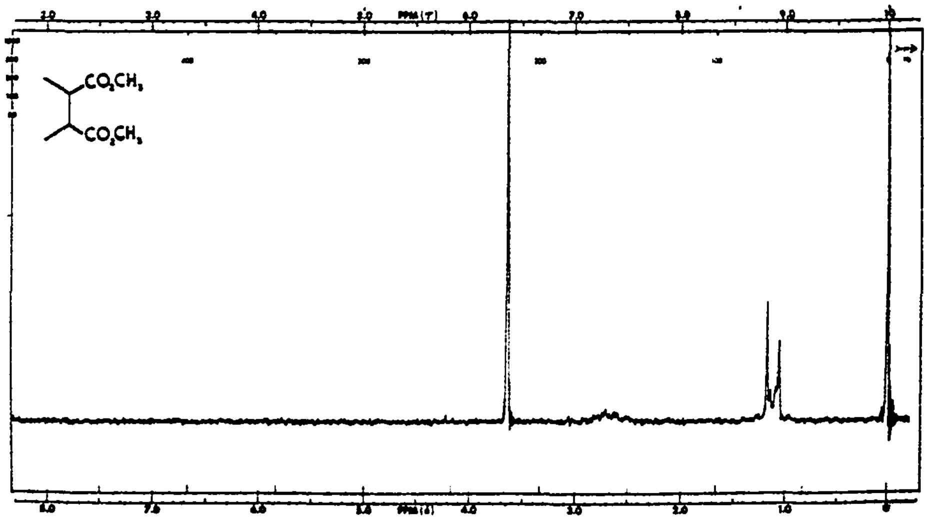
30 MIN IRRADIATION
PYREX FILTER
-190°

Figure 5. Nuclear magnetic resonance spectra (CCl_4)

Top--2,3-dimethylcyclobutenedione

Bottom--*meso* and racemic dimethyl
2,3-dimethylsuccinate


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


CO₂CH₃
CO₂CH₃
2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

multiplet assigned to the two methine protons appeared between δ 2.85 and δ 2.35 and two methyl groups appeared as superimposed doublets at δ 1.11.

A sample of meso and racemic dimethyl 2,3-dimethylsuccinate was synthesized by esterification of meso and racemic 2,3-dimethylsuccinic acid with diazomethane. The infrared and nmr spectra of the mixture of esters obtained from the photomixture were superimposable with those spectra of dimethyl 2,3-dimethylsuccinate obtained by esterification of the acid.

Umbellulone

The room temperature photochemistry of umbellulone (30) has been reported by Wheeler and Eastman (17). Thymol (31) was obtained in quantitative yield. The low temperature photochemistry of umbellulone has revealed two distinctly different photo-thermal pathways which lead to the formation of thymol.

Irradiation ($\lambda > 290$ nm) of a neat film of umbellulone at -190° produced two primary photoproducts, a diene-ketene derivative (137) with a carbonyl absorption at 2113 cm^{-1} and a transient (138) with absorptions at 1670 and 1630 cm^{-1} (Figure 6). Under these conditions, thymol was not obtained as a primary photoproduct. Both the diene-ketene derivative and the 1670 cm^{-1} transient appeared to be primary photoproducts (Figure 7). If formation of the diene-ketene derivative was the result of a biphotonic process which involved the 1670 cm^{-1} transient, an induction period would have been observed. Formation of the diene-ketene derivative occurred immediately upon irradiation of the cold umbellulone sample. Both the diene-ketene derivative and the 1670 cm^{-1} transient were stable in the dark at -190°.

As the glassy film of irradiated umbellulone was allowed to warm, the 1670 cm^{-1} transient went rapidly to thymol at about -90°. Virtually no changes in the diene-ketene absorptions occurred during this transformation (Figure 8). As the temperature increased above -70°, the diene-ketene derivative underwent cyclization and tautomerization to thymol. The stepwise process could not be observed, since the expected intermediate dienone was not stable above -90°. The disappearance of the diene-ketene absorptions correlated well with increases in the intensities of the thymol absorption bands. Ketene dimers were not detected in the infrared spectrum of the crude photomixture. At the end of the warmup, the photomixture within the cell was analyzed by thin layer chromatography (tlc) and glpc. Both methods of analysis showed that umbellulone and thymol were the only constituents of the mixture.

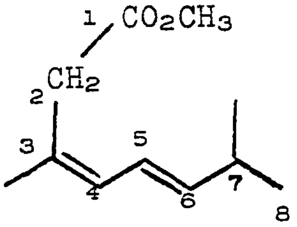
The structures of the diene-ketene derivative and the 1670 cm^{-1} transient were inferred from their behavior upon warming, from spectroscopic evidence and from trapping experiments in a methanol-ether glass at -190°. The absorption bands at 1670 and 1630 cm^{-1} of nearly equal intensity are characteristic of 2,4-cyclohexadienone derivatives. The behavior of both of these absorption bands during warmup provided evidence that they belong to the same intermediate. The thermal conversion of the 1670 cm^{-1} transient to thymol upon warming permitted identification of this transient as 3-methyl-6-isopropyl-2,4-cyclohexadienone (138). The observed cyclization of the ketene derivative followed by tautomerization to thymol implied that it is a diene-ketene derivative.

In order to characterize this diene-ketene derivative in greater detail, trapping experiments at low temperatures in a protonic medium were performed. The diene-ketene derivative could not be trapped at room temperature and only a trace of an ester could be detected when the irradiation was performed in methanol at -80°.

A direct observation that the diene-ketene derivative could be trapped was made by irradiating a thin film of umbellulone which contained about 25% methanol by volume in the low temperature infrared cell at -190°. The diene-ketene derivative and the cyclohexadienone derivative were clearly observed and behaved similarly during irradiation to the previously studied sample of umbellulone which did not contain any methanol. Upon warming this irradiated methanol-umbellulone sample, the dienone derivative isomerized to thymol at -90°. Continued warming to -65° resulted in disappearance of the diene-ketene, but it did not cyclize to the dienone. Instead 1,2-addition of methanol to the diene-ketene derivative occurred to form an ester with an absorption at 1739 cm^{-1}. The failure of the room temperature irradiation of umbellulone in methanol to trap the diene-ketene derivative may be rationalized if it is assumed that the rate of intramolecular cyclization of the diene-ketene derivative is much faster at room temperature than methanol addition and that at lower temperatures the rate of methanol addition competes effectively with intramolecular cyclization.

The methyl ester (139) was obtained in sufficient quantity for characterization by irradiating a sample of umbellulone in an ether-methanol glass at -190° followed by warming the frozen glass to room temperature. During the warmup, a light yellow color which formed upon irradiation disappeared. This could be due to the disappearance of the cyclohexadienone derivative since cyclohexadienone derivatives normally possess a faint yellow color. The ester was isolated by preparative glpc. The only other product that was detected was thymol which was obtained in a yield nearly equal to that of the ester (139).

An element analysis in good agreement with the value calculated for $C_{11}H_{18}O_2$ was obtained. A molecular ion at m/e 182 was observed in the mass spectrum and the ultraviolet spectrum possessed a maximum at 238 nm ($\log \epsilon$ = 4.42). The nmr spectrum of this methyl ester showed three vinyl protons between δ 6.30 and δ 4.9. A three proton singlet assigned to the methoxyl group was observed at δ 3.63. The two methylene protons at position two appeared as a singlet at δ 3.06. A calculated value of 3.10 was obtained for the chemical shift of a methylene group flanked by a vinyl group and a carbomethoxy group from nmr shielding constants (77). The isopropyl methine appeared as a broad multiplet between δ 2.2 and δ 3.0. The remainder of the spectrum consisted of three methyl groups. A three proton singlet at δ 1.85 was assigned to the methyl group at position three. The remaining two methyl groups at position seven appeared as a doublet (J = 6.5 Hz) centered at δ 1.0.



139

The mass spectrum (Figure 11) gave a molecular ion at m/e 182 which was 32% of the base peak at 110. Loss of methyl was not a highly favored process, but was detected by a low intensity peak at m/e 167. Loss of methoxyl and carbomethoxyl occurred readily to give major fragments at m/e 151 and 123. Cleavage between atoms two and three with intramolecular transfer of hydrogen resulted in loss of mass 74 to give a strong peak at m/e 109. The base peak at m/e 110 most probably occurred by cleavage between positions two and three without intramolecular transfer of hydrogen.

The stereochemistry of the $C_{3,4}$ double bond must be *cis* in the diene-ketene derivative that is initially formed because cyclization to the dienone would be prohibited if *trans* stereochemistry existed at this double bond. If it is assumed that this *cis* stereochemistry was preserved when the diene-ketene was trapped, the carbomethoxy group would be *cis* to the vinyl substituent at position four in the resulting ester. The stereochemistry at the $C_{5,6}$ double bond was not determined, however it was assumed to be *trans*. This conclusion seemed reasonable based upon the ease of cyclization of the diene-ketene derivative to the dienone.

The carbon skeleton of methyl 3,7-dimethylocta-3,5-dienoate was rigorously established by catalytic hydrogenation

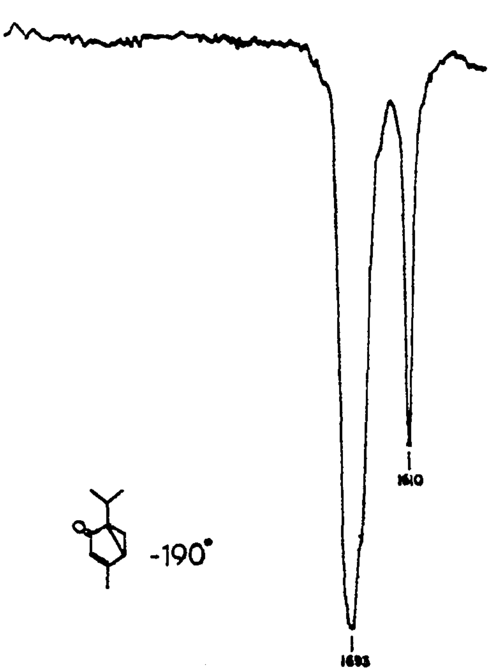
Figure 6. Low temperature infrared spectra (neat)

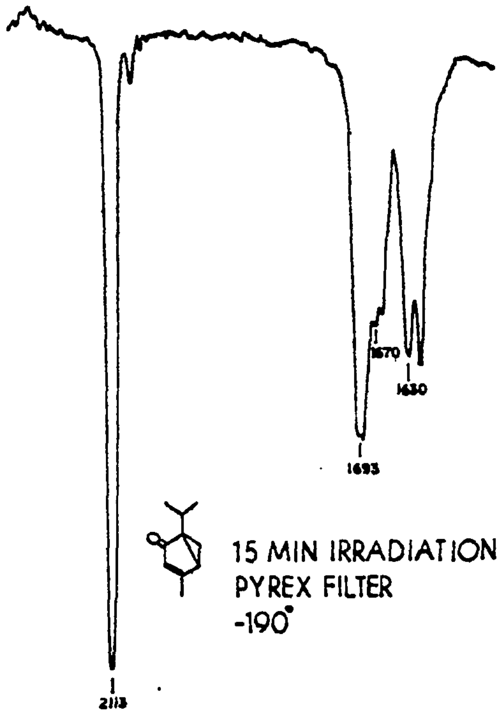
Top left--umbellulone (-190°)

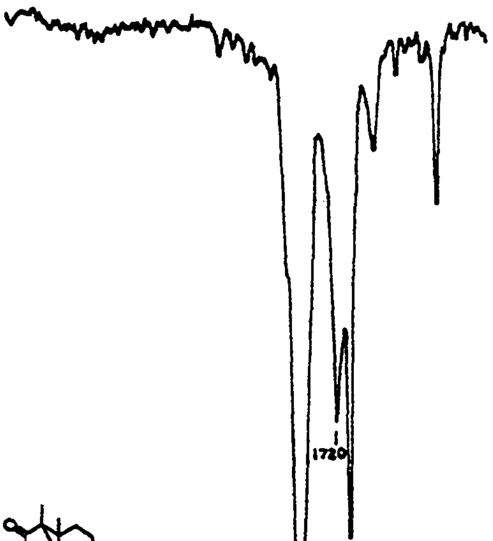
Top right--umbellulone (-190°) irradiated through a Pyrex filter

Bottom left--lumisantonin (-190°)

Bottom right--lumisantonin (-190°) irradiated through a Pyrex filter


1610
1693
-190°


2113
1693
1670
1630
15 MIN IRRADIATION
PYREX FILTER
-190°


1720
1700
-190°

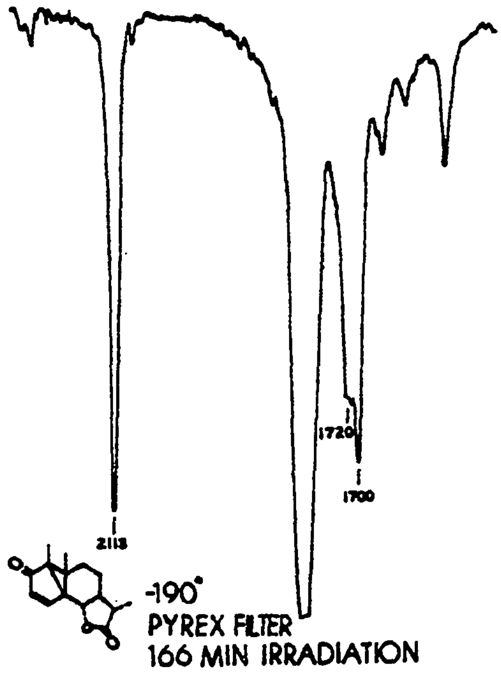

2113
1720
1700
-190°
PYREX FILTER
166 MIN IRRADIATION

Figure 7. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of umbellulone

x - 2113 cm^{-1}

▲ - 1695 cm^{-1}

| - 1670 cm^{-1}

● - 1630 cm^{-1}

⬬ - 1610 cm^{-1}

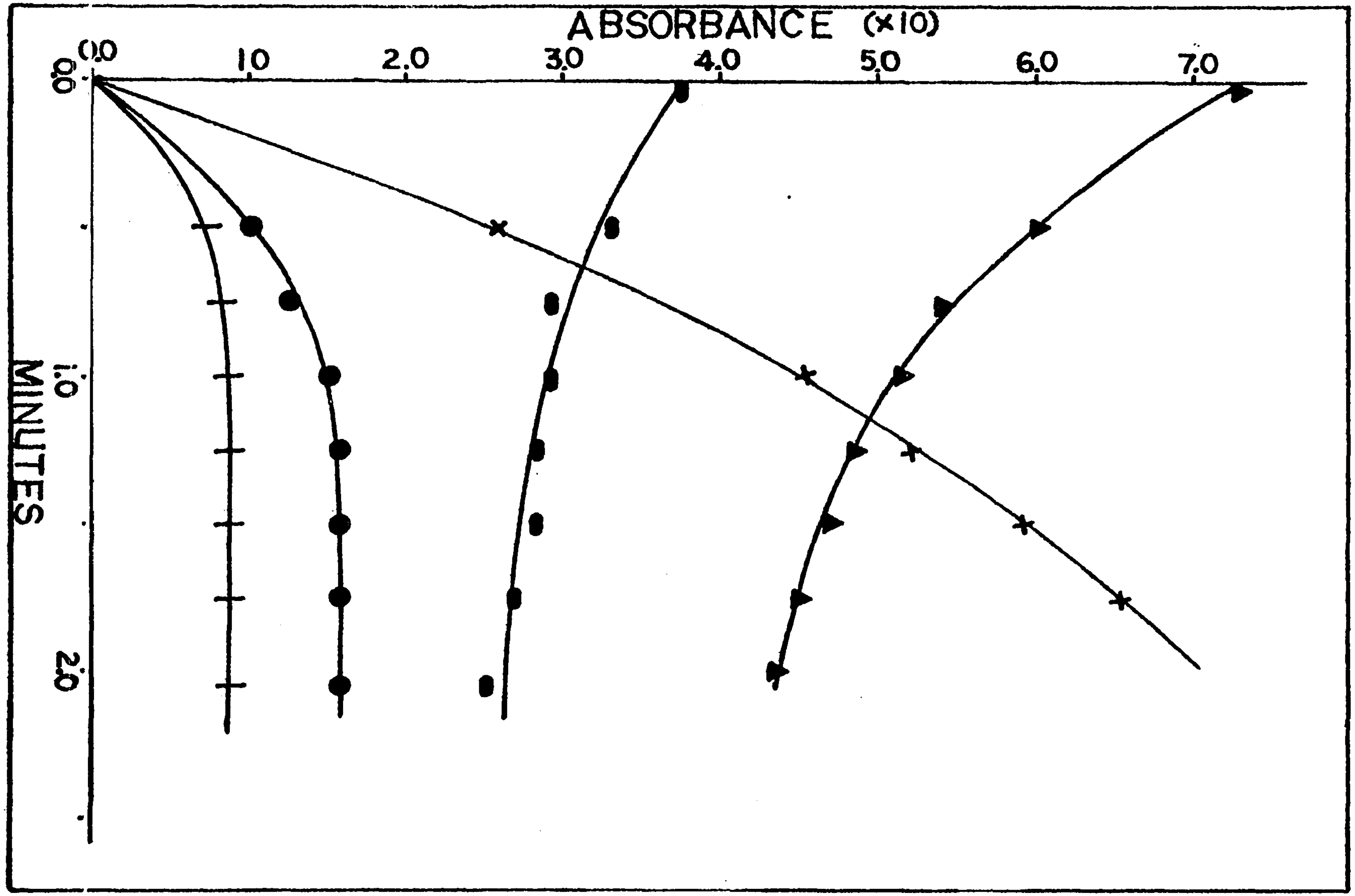

ABSORBANCE (×10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
0.0
1.0
2.0
MINUTES

Figure 8. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of umbellulone

x - 2113 cm^{-1}

▲ - 1695 cm^{-1}

● - 1630 cm^{-1}

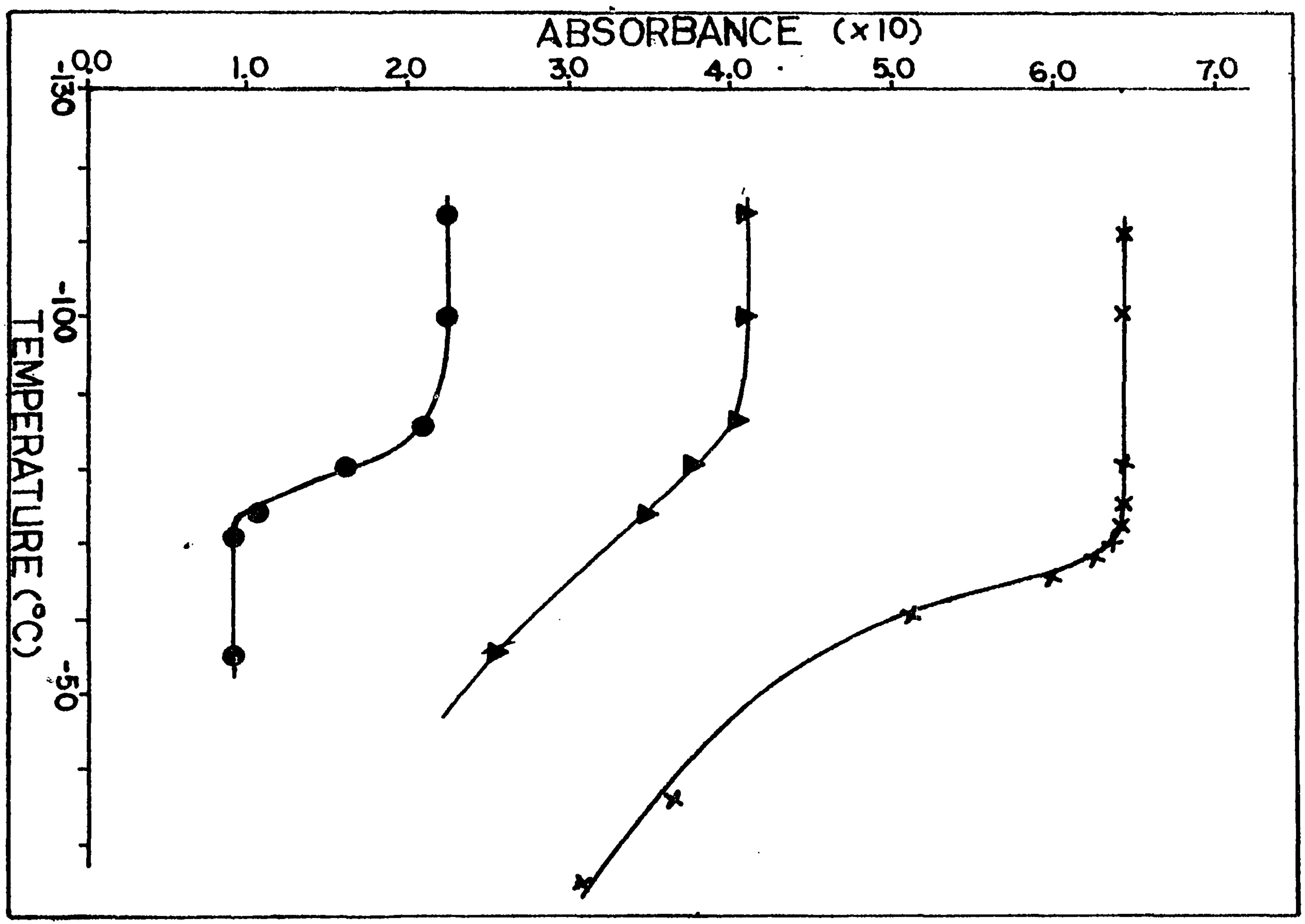
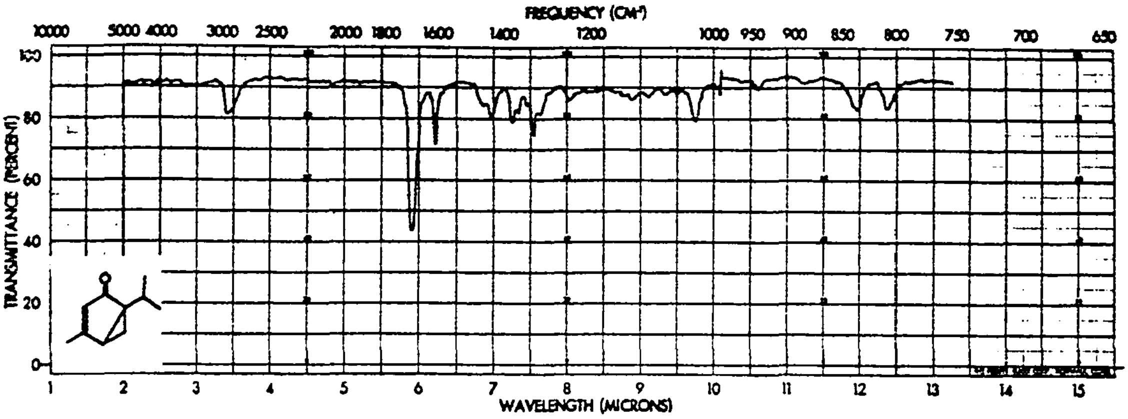

ABSORBANCE (x10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
-130
-100
-50
TEMPERATURE (°C)

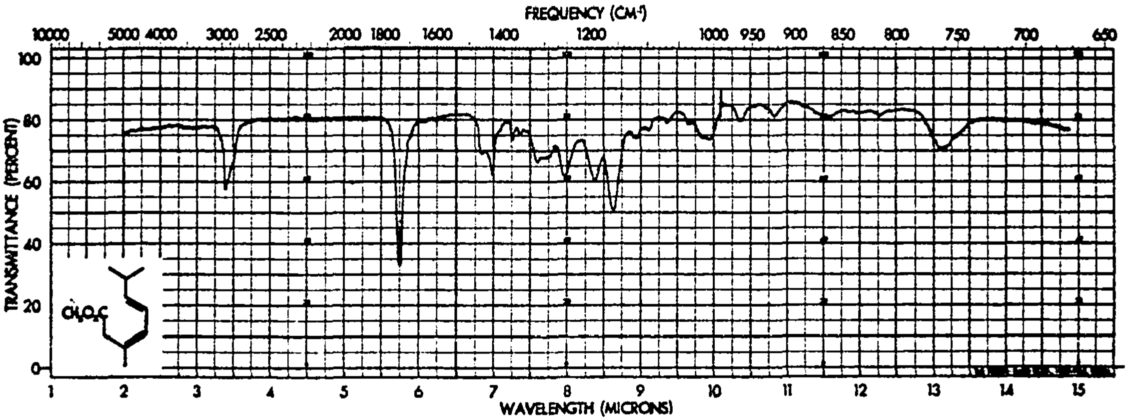
Figure 9. Infrared spectra (neat)

Top--umbellulone

Middle--methyl *cis,trans*-3,7-dimethylocta-3,5-dienoate

Bottom--methyl 3,7-dimethyloctanoate


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


FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
CH₃O₂C
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

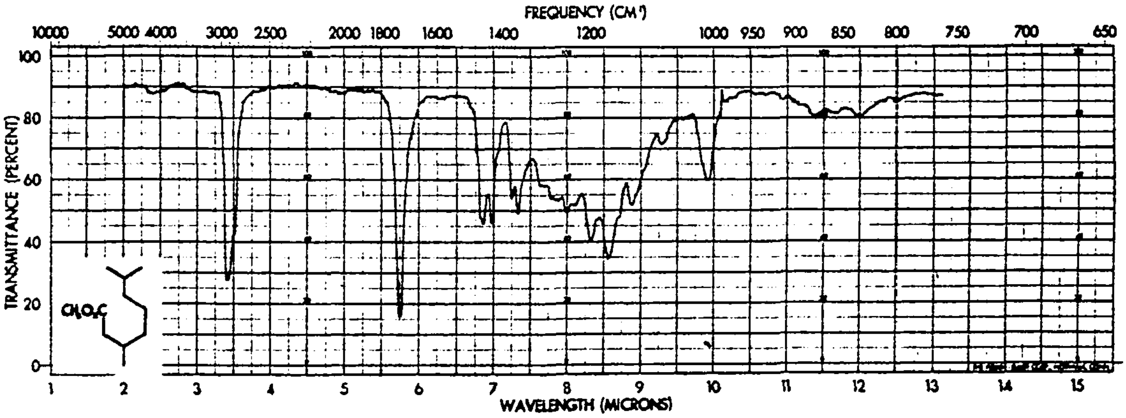
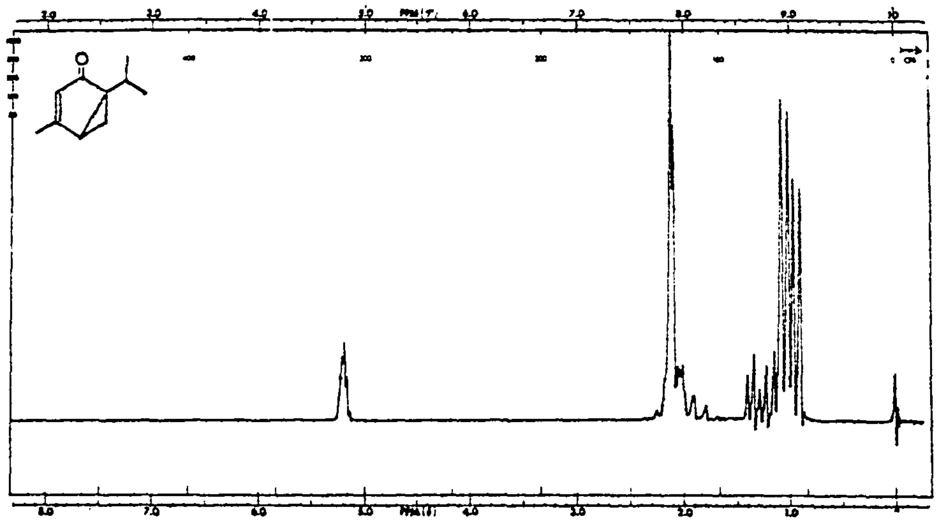

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
CH₃O₂C
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

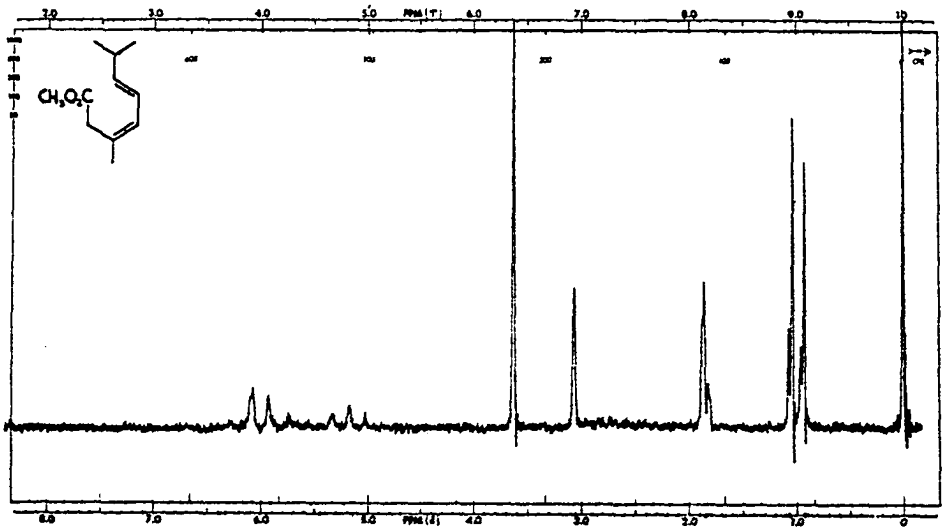
Figure 10. Nuclear magnetic resonance spectra (CCl_4)

Top--umbellulone

Middle--methyl *cis*,*trans*-3,7-dimethylocta-3,5-dienoate

Bottom--methyl 3,7-dimethyloctanoate


PPM (τ)
PPM (δ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1.0
0
O


PPM (τ)
PPM (δ)
CH₃O₂C

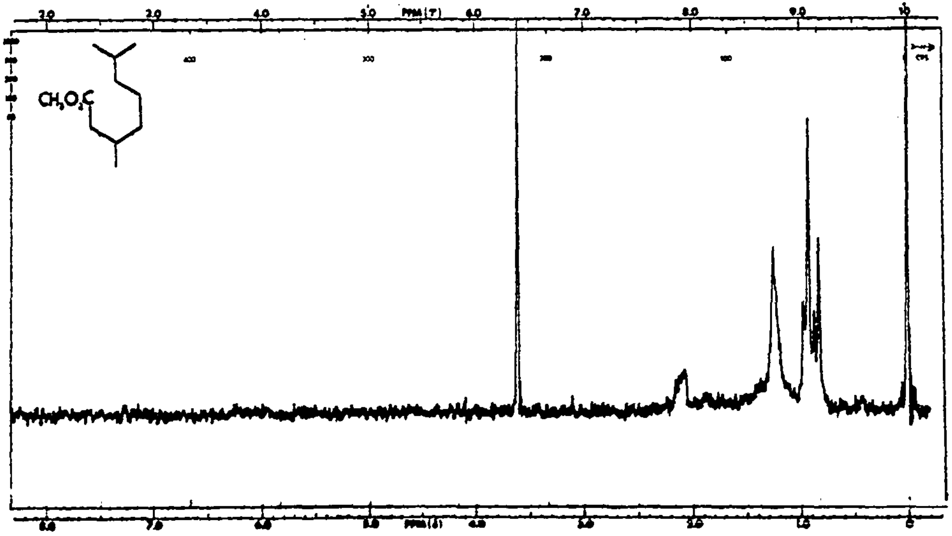

PPM (τ)
PPM (δ)
CH₃O₂C

Figure 11. Mass Spectrum (70 ev)

Methyl *cis,trans*-3,7-dimethylocta-3,5-dienoate

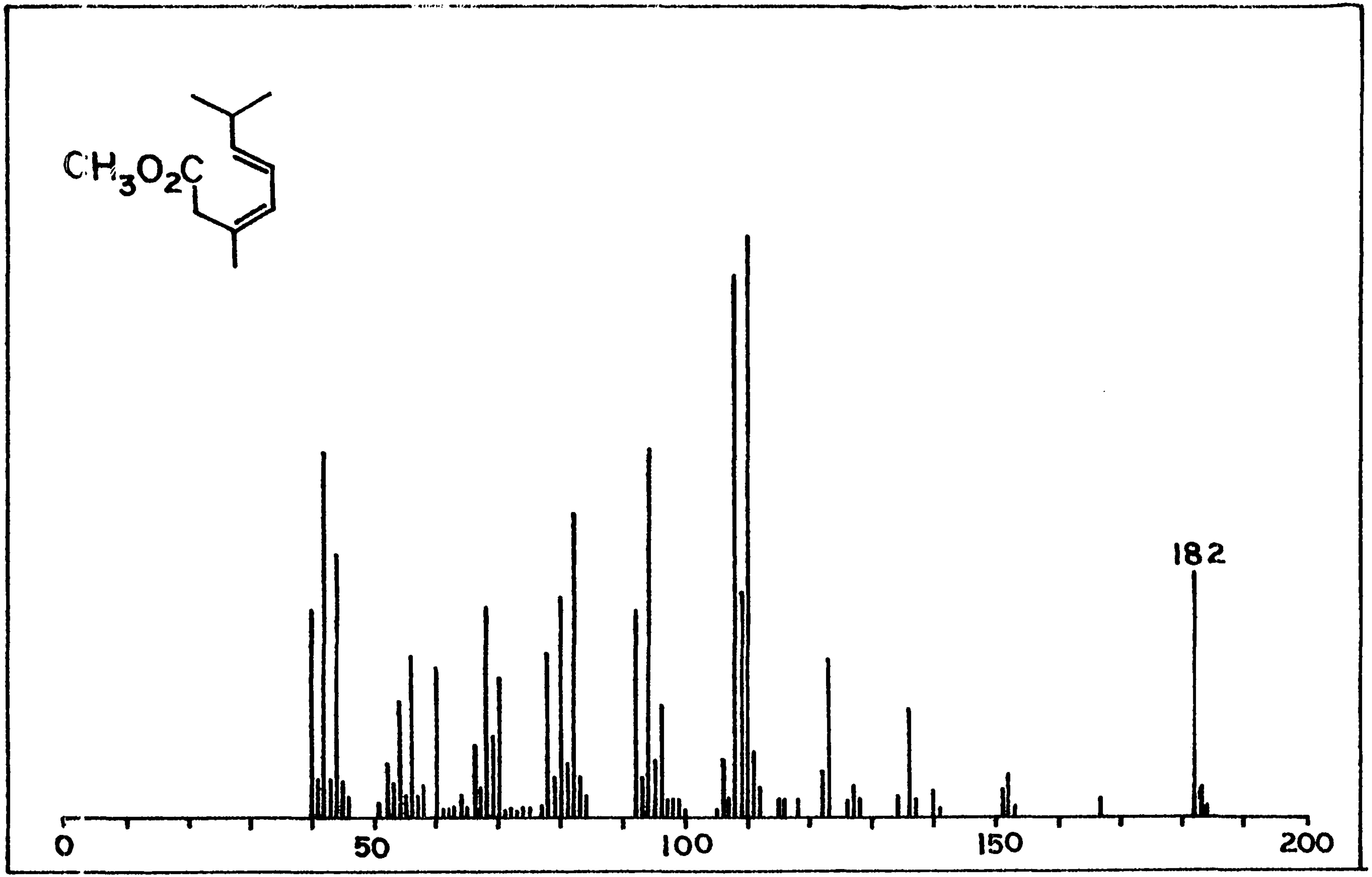

CH₃O₂C
182
0
50
100
150
200

Figure 12. Mass spectrum (70 ev)

Methyl 3,7-dimethyloctanoate

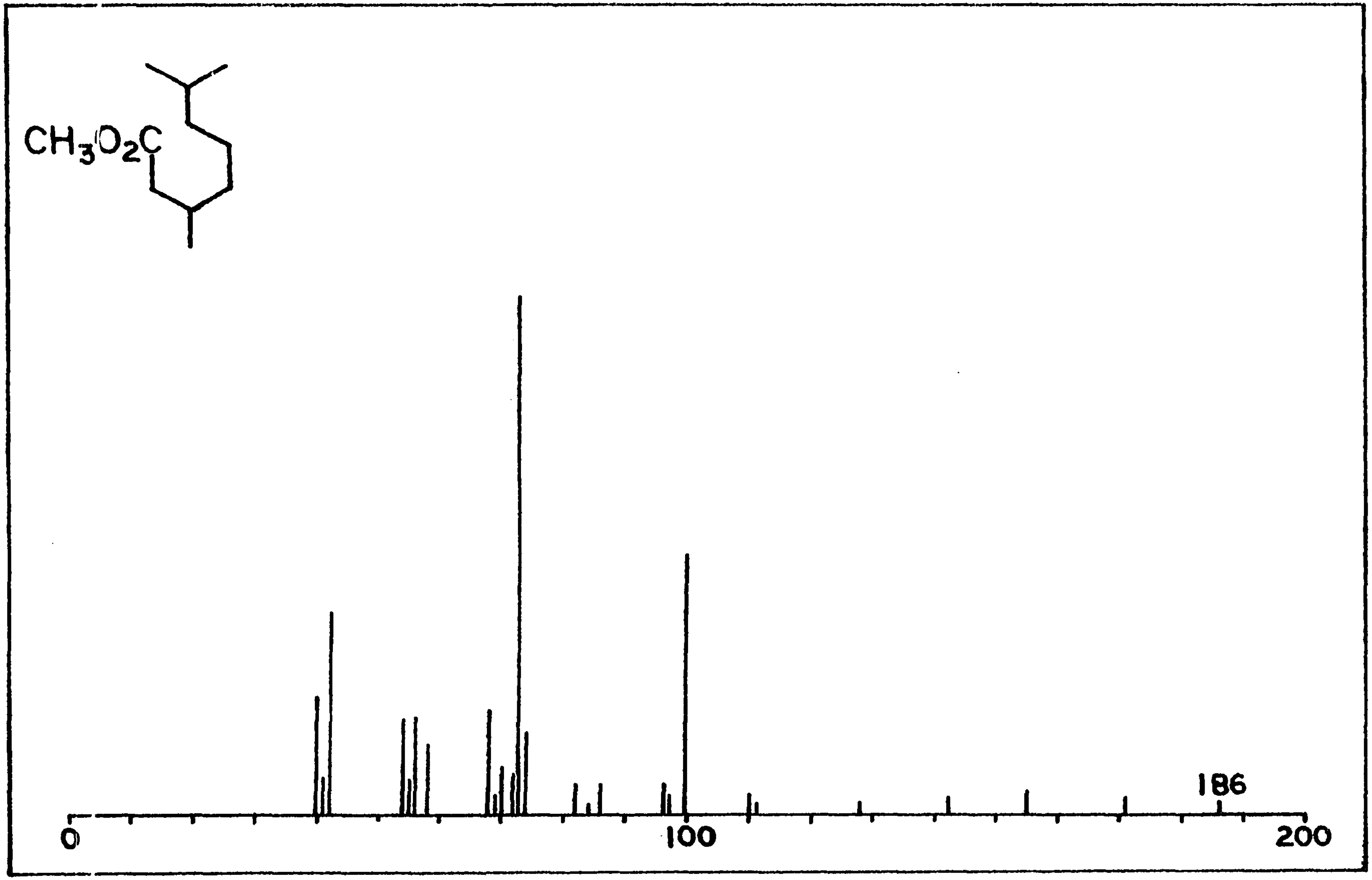
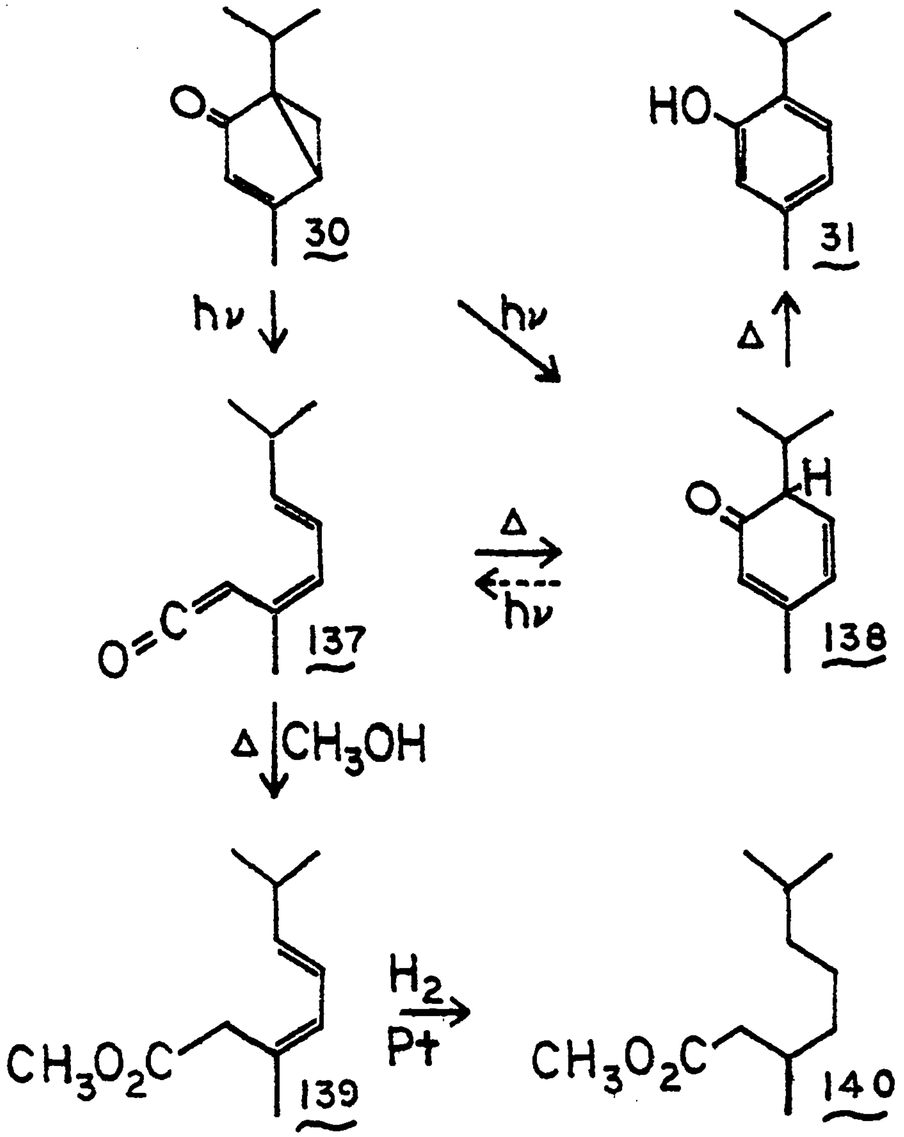

CH3O2C
186
0
100
200

Figure 13. A summary of the photochemistry of umbellulone


30
31
137
138
139
140
hν
hν
Δ
Δ
hν
Δ
CH₃OH
H₂
Pt
HO
O
O=C
H
CH₃O₂C
CH₃O₂C

of the diene-ester with reduced platnium oxide which gave the tetrahydro derivative methyl 3,7-dimethyloctanoate. The mass spectrum of this derivative (Figure 12) showed a molecular ion at m/e 186, and the infrared spectrum (Figure 9) showed a strong carbonyl absorption at 1740 cm^{-1}. The nmr spectrum (Figure 10) showed a three proton singlet at δ 3.60 and three proton and six proton overlapping doublets between δ 1.05 and δ 0.74. Ten unresolved protons appeared between δ 2.40 and δ 1.05.

An authentic sample of methyl 3,7-dimethyloctanoate was independently synthesized from 3,7-dimethylocta-2,6-dien-1-ol by catalytic hydrogenation to the saturated alcohol, 3,7-dimethyl-1-octanol, by oxidation to 3,7-dimethyloctanoic acid with cold potassium permanganate and by esterification of this acid with an ethereal solution of diazomethane. The infrared spectra and glpc retention times of the tetrahydroester were identical to the infrared spectrum and glpc retention times of the ester synthesized from 3,7-dimethylocta-2,6-dien-1-ol.

Lumisantonin

A detailed investigation of the photochemistry of α-lumisantonin was recently reported by Fisch and Richards (28, 29). Low temperature irradiation of α-lumisantonin revealed remarkably different behavior from that observed at room temperature.

Irradiation of α-lumisantonin as a neat crystalline film or in an ether-pentane-alcohol (EPA) glass at -190° gave a diene-ketene derivative (**144**) with an absorption at 2113 cm^{-1} (Figure 6) and a species with an intense blue color (**51**). Under both types of conditions the blue species exhibited thermal properties similar to the blue species reported by Fisch and Richards. The diene-ketene derivative and the blue species were both stable at -190°, however the blue species disappeared when the sample was warmed above -170° without significant change in the infrared spectrum of the sample. The absorption bands of mazdasantonin (**49**) could not be detected in the cold irradiated sample of α-lumisantonin, however, as the cell temperature was allowed to increase above -90°, the diene-ketene derivative disappeared with concurrent appearance of the absorption bands of mazdasantonin. Low temperature irradiation of mazdasantonin also gave this diene-ketene derivative (**144**) which upon warming recyclized to mazdasantonin. The blue species was not obtained when mazdasantonin was irradiated at low temperatures. The identity of the two ketenes (**144**) was confirmed by low temperature trapping experiments. A sample of the ester (**145**) obtained by the room temperature irradiation of α-lumisantonin in ethanol was compared to the ester that

Figure 14. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of α-lumisantonin

| - 2113 cm^{-1}

⬮ - 1720 cm^{-1}

▲ - 1700 cm^{-1}

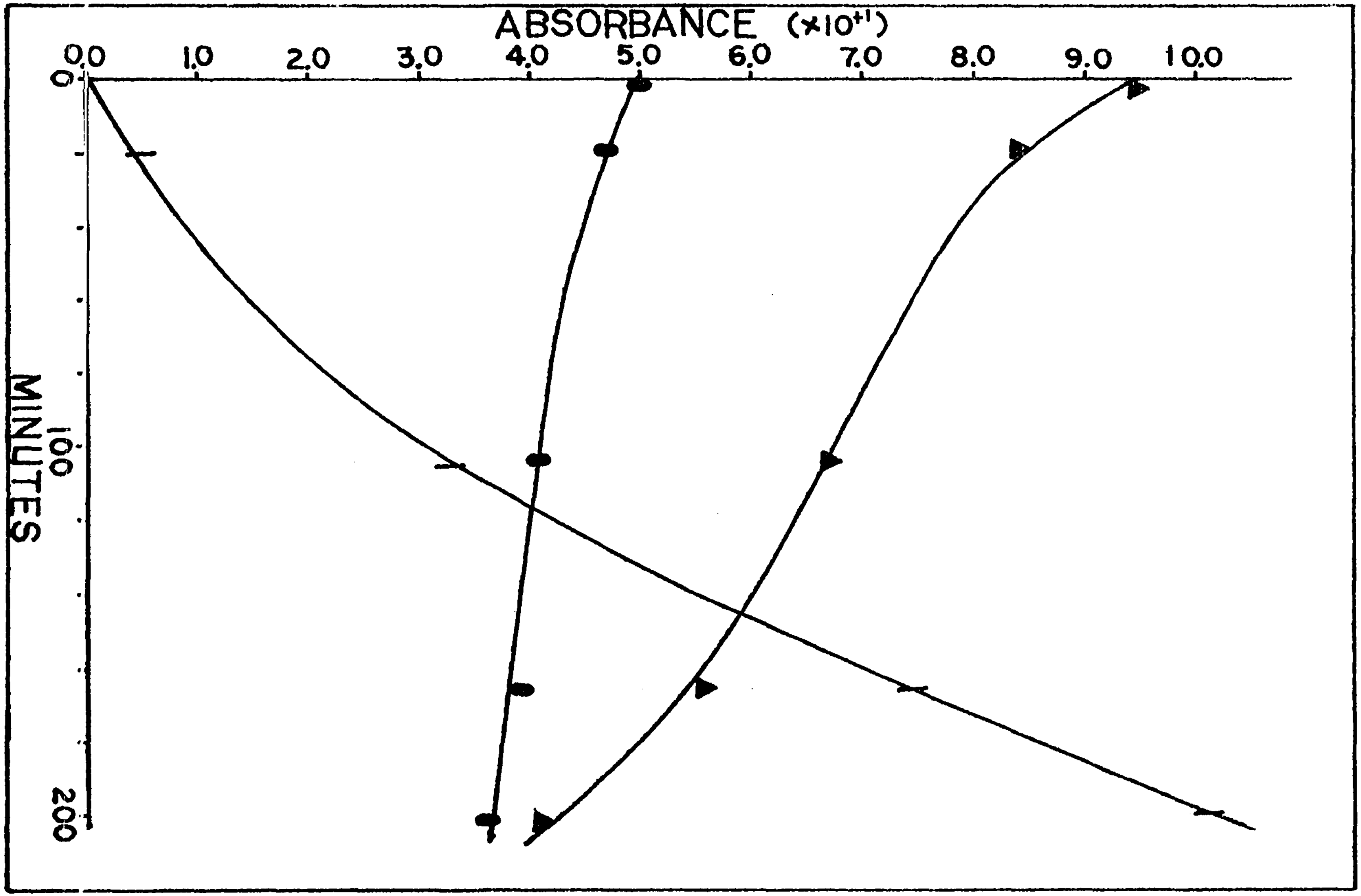

ABSORBANCE (×10+1)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
MINUTES
0
100
200

Figure 15. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of α-lumisantonin

| - 2113 cm^{-1}

▲ - 1700 cm^{-1}

● - 1670 cm^{-1}

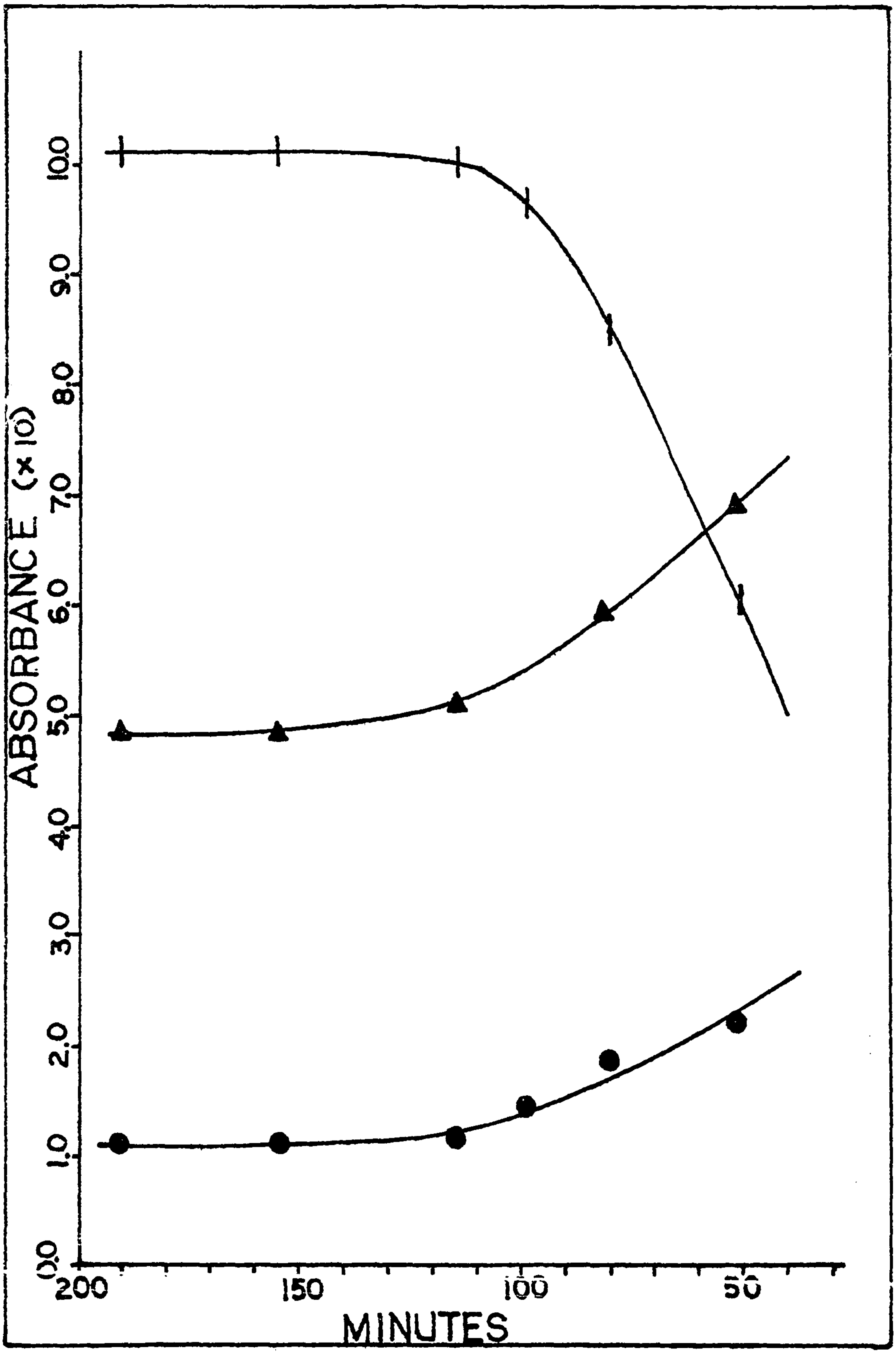

ABSORBANCE (×10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
200
150
100
50
MINUTES

Figure 16. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of mazdasantonin

▲ - 2111 cm^{-1}

▮ - 1661 cm^{-1}

● - 1630 cm^{-1}

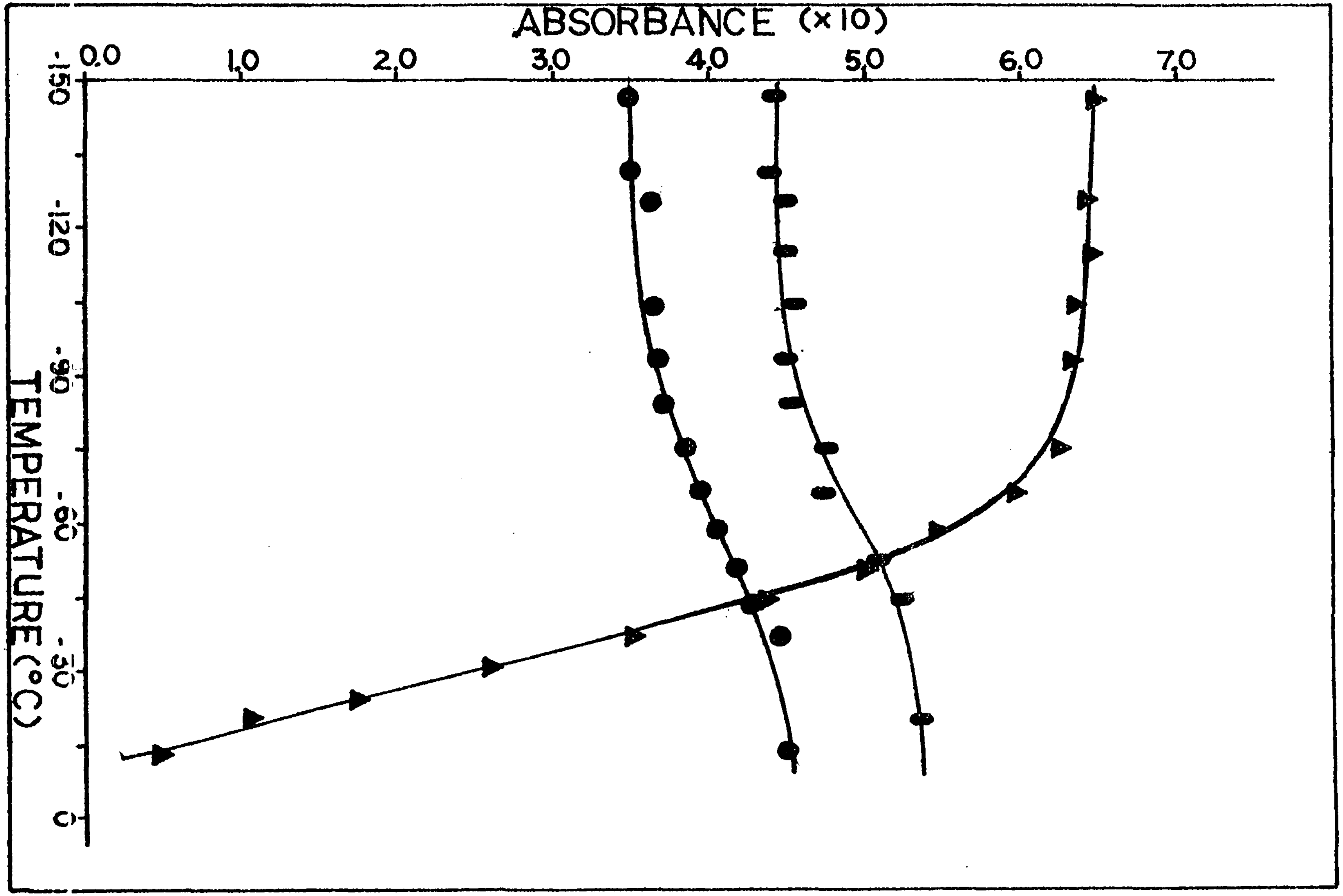
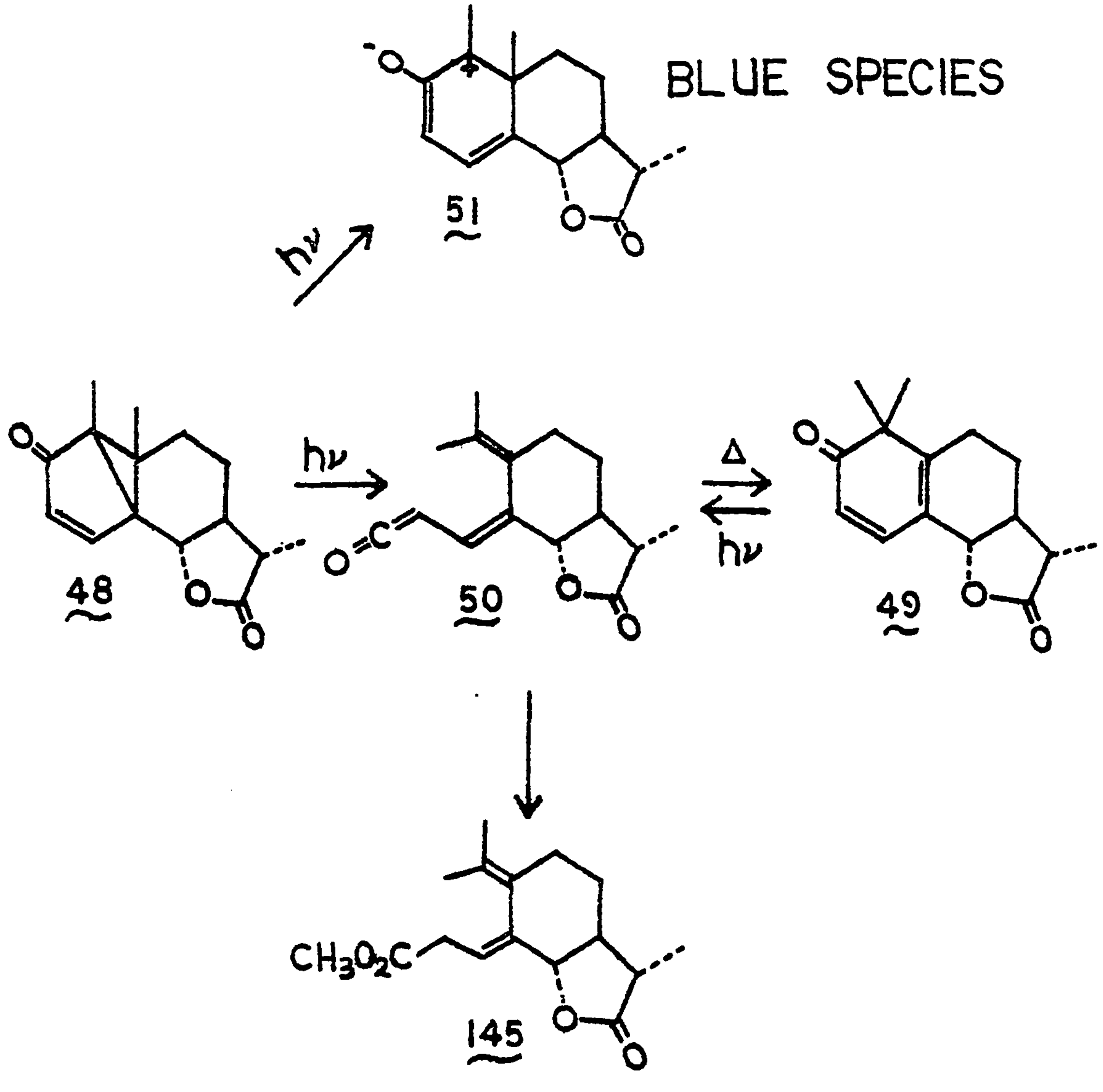

ABSORBANCE (x10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
TEMPERATURE (°C)
-150
-120
-90
-60
-30
0

Figure 17. A summary of the photochemistry of α-lumisantonin


BLUE SPECIES
51
hν
48
hν
50
Δ
hν
49
CH₃O₂C
145

was trapped by low temperature irradiation of α-lumisantonin in EPA. The two esters were identical as judged by their glpc retention times.

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)-naphthalenone (61)

Kropp (41) reported that 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone gave a 60% yield of 4,8-dimethyl-5,6,7,8-tetrahydro-2-naphthol (62) upon irradiation in aqueous acetic acid. No other products were reported under these conditions.

Irradiation of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone at -190° produced a new species with strong carbonyl absorptions at 1812 and 1840 cm^{-1}. A very small amount of a ketene derivative with an absorption at 2106 cm^{-1} and carbon monoxide were also formed (Figure 29). The 2-naphthol derivative obtained by Kropp was not observed under these conditions. The relative amount of carbon monoxide obtained during an irradiation was highly dependent upon the wavelength of the light used during the irradiation. The least amount of carbon monoxide and the maximum amount of the species with absorptions at 1812 and 1840 cm^{-1} could be obtained if light with wavelength equal to 253.7 nm or greater than 360 nm was employed throughout the irradiation. This selective control over the relative amounts of products formed was further demonstrated. A significant quantity of the species with absorptions at 1812 and 1840 cm^{-1} was formed using light with wavelength greater than 360 nm. This species was then destroyed by irradiating the sample with light of shorter wavelength between 360-300 nm. The structure of the photodecarbonylated product will be discussed later. Formation of carbon monoxide must occur by way of a secondary photochemical process (Figure 18). The rate of formation of the 1812 and 1840 cm^{-1} species and the ketene derivative decreased significantly after the sample had been irradiated for twenty minutes at 253.7 nm but formation of carbon monoxide increased steadily. At -190^{0}, all the species were stable upon standing in the dark. Loss of carbon monoxide from the cold sample could not be detected.

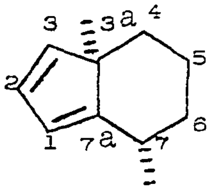
When the sample was allowed to warm, these species displayed independent thermal behavior (Figure 19). As the sample temperature increased, loss of carbon monoxide began to occur at -160^{0} and behaved independently of the other changes that occurred. At -120^{0}, the species with absorptions at 1812 and 1840 cm^{-1} began to disappear. Simultaneously, a species with an absorption at 1670 cm^{-1} appeared. 2,4-Cyclohexadienones and 2,5-cyclohexadienones display carbonyl absorptions at 1670 cm^{-1}. This new species with an absorption at 1670 cm^{-1} has not been identified, but its formation did not involve thermal loss of carbon monoxide. The disappearance of the ketene derivative occurred almost simultaneously with the disappearance of the 1812 cm^{-1} species. During the irradiation photochemical destruction of the 1812 cm^{-1} species produced no change in the ketene derivative. This suggests that they are two different compounds. It is conceivable that loss of carbon monoxide could occur from a species which also possessed a ketene functional group. No products derived from such a species with this type of dual functionality have been isolated from the room temperature or low temperature investigations.

The behavior of the 1812 cm^{-1} species during irradiation and its thermal lability above -120° suggested that a cyclopropanone derivative had been formed initially as the major product when the starting material was irradiated. The structure of the cyclopropanone derivative (146) was determined from information obtained about the photodecarbonylated product (148) and a furan adduct (150) obtained by trapping the cyclopropanone at low temperatures and at room temperature.

Photodecarbonylation of the cyclopropanone derivative (146) seemed to be an efficient process which occurred in high yield when the irradiation was performed with a broad spectrum of light with wavelength greater than 300 nm. Preparative scale irradiation of starting material (61) in a rigid glass at -190° gave in high yield the photodecarbonylated product (148) which was isolated by column chromatography on silica gel and purified by preparative glpc.

The mass spectrum (Figure 24) of this secondary photoproduct showed a molecular ion at m/e 148, which is consistent with loss of carbon monoxide from an isomer of the starting material. The element analysis calculated for $C_{11}H_{16}$ agreed well with the value obtained for this sample. The neat infrared spectrum (Figure 20) of this $C_{11}H_{16}$ hydrocarbon showed 1,3-diene absorptions at 1640 and 1600 cm^{-1}, a trisubstituted double bond absorption at 851 and 796 cm^{-1} and a strong absorption at 728 cm^{-1} assigned to the double bond. The ultraviolet spectrum showed a π,π^* absorption at 256 nm (ϵ = 3,850).

The nmr spectrum of this hydrocarbon (Figure 21) in carbon tetrachloride provided a rather deceptively simple example of an ABX system. A two proton two line pattern was observed at δ 6.09 and a one proton closely spaced three line pattern was centered at δ 5.79. A symmetrical one proton multiplet between δ 3.30 and δ 2.70 was assigned to the allylic methine proton at position seven. A three



148

proton doublet (J = 7.2 Hz) at δ 1.18 and a three proton singlet at δ 1.15 were assigned to the two methyl groups at positions 7 and 3a, respectively. Six methylene protons were observed as unresolved multiplets between δ 2.2 and δ 0.8 and were assigned to those protons at positions four, five and six. In spite of the compelling desire to believe that the photodecarbonylated product was indeed compound (148) it seemed less than obvious that the three vinyl proton system could give rise to a pattern which appeared to exhibit such a high degree of simplicity. Since fortuitous overlap of several lines was required in this system, it seemed reasonable to assume that they might separate into a more recognizable pattern if a different solvent, e.g., hexadeuteriobenzene was employed while recording the spectrum. In hexadeuteriobenzene the high field region of the nmr spectrum (Figure 22) remained nearly unchanged as compared to the spectrum obtained in carbon tetrachloride. The two line pattern observed in carbon tetrachloride at δ 6.02 was clearly separated into several lines. A complete analysis of this pattern was not possible from this spectrum, but expansion and decoupling at 100 Mc provided the necessary information to analyze the spectrum as an ABX system (Figures 22, 23, and 24) (77).

The AB part of this spectrum appeared as a twelve line pattern from which the two respective AB quartets could readily be obtained. The presence of twelve lines in this pattern instead of the expected eight lines for a normal AB pattern resulted from a small allylic coupling ($J =$ 0.5 Hz) of one of the AB protons to the allylic methine proton at position seven. J_{AB} was readily obtained from this twelve line pattern and was found to be ± 5.3 Hz. To carry out this analysis, the two respective quartets of the AB pattern were chosen so that the absorptions at 615.9, 610.6, 609.6 and 604.3 Hz composed one quartet and the absorptions at 614.4, 608.9, 608.0 and 602.7 Hz composed the second quartet. The value of $\frac{1}{2}(\nu_A + \nu_B)$ was then determined to be 609.3 Hz and $J_{AX} + J_{BX}$ equal to 3.20 Hz. Two sets of data were then obtained which led to two sets of values for J_{AX} and J_{BX}. The first set with $\delta_{AB} = 3.41$ and $J_{AX} - J_{BX} = 0$ gave $\frac{1}{2}(J_{AX} + J_{BX})$ 1.60 Hz. The second set with $\delta_{AB} = 0$ and $J_{AX} - J_{BX}$ 6.82 gave $J_{AX} = \pm 5.01$ and $J_{BX} = \pm 1.81$ Hz. A choice was made between these two sets of data by calculating the positions and intensities of the lines in the X part of spectrum. It was easily shown that the first set of data gave the correct line positions and intensities for the X part of the spectrum.

Further evidence for the structure of 3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane (148) was obtained by degradation of the diene with ozone. During workup of the crude ozonolysis mixture, oxidative decarboxylation occured to give a mixture of cis and trans 2,6-dimethylcyclohexanones (151). Comparison of the infrared and nmr spectra and glpc retention times of this mixture to the spectra and retention times of a sample which consisted of 90% cis, 10% trans-2,6-dimethylcyclohexanone showed that they contained nearly equal amounts of cis and trans isomers.

The intermediacy of the cyclopropanone derivative was proven by performing trapping experiments at room temperature and at low temperatures. Furan was chosen as a trapping agent because of its propensity to form 1,3-dipolar addition products with cyclopropanones (36). A single adduct (150) was obtained when the intermediate cyclopropanone derivative was generated at -190° in a furan-ether glass followed by warming. The adduct could also be obtained in high yield when the experiment was performed in an ether-furan solution at -80° and at room temperature. The pure adduct, (mp 131-2°), was isolated by column chromatography on silica gel followed by recrystallization from an ether-hexane solution. The mass spectrum (Figure 27) of this adduct gave a molecular ion at m/e 244. An element analysis was obtained which agreed well with that calculated for $C_{16}H_{20}O_2$. The infrared spectrum (Figure 20) possessed a strong carbonyl absorption at 1729 cm^{-1}. The nmr spectra (Figures 21 and 26) of this adduct along with double resonance experiments were particularly valuable in establishing the overall structure. The following scheme summarizes the results of the double resonance experiments. The cleanly resolved doublet at

$$\begin{tikzcd}
6.20 & 5.00 \arrow[l] & 1.99 \arrow[l] \arrow[d, shift right] & \\
6.30 & 4.62 \arrow[l] \arrow[r, shift right] & 2.75 \arrow[l, shift right] \arrow[u, shift right] \arrow[r, shift right] & 5.42 \arrow[l, shift right]
\end{tikzcd}$$

δ 5.42 ($J_{2,3}$ = 6.0 Hz) was used as a reference in performing the double resonance experiments and in assigning the remaining protons to their respective positions. The

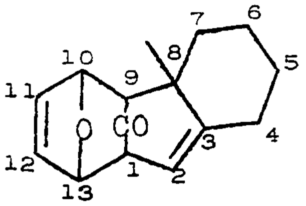


Figure 18. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

○ -2130 cm^{-1}

x -2106 cm^{-1}

⬬ -1840 cm^{-1}

● -1812 cm^{-1}

▲ -1700 cm^{-1}

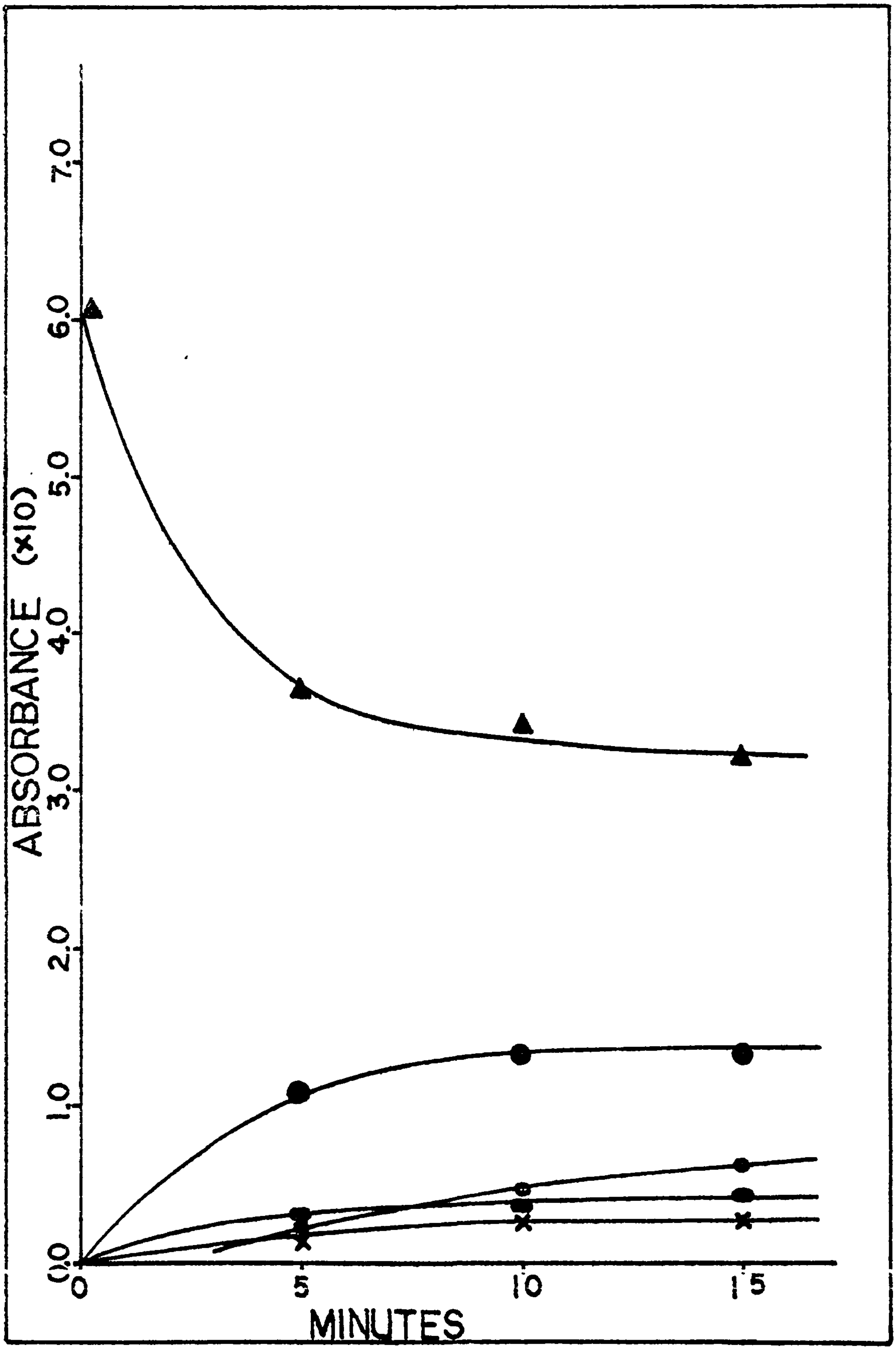

ABSORBANCE (×10)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
MINUTES

Figure 19. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

○ - 2130 cm^{-1}

x - 2106 cm^{-1}

⬬ - 1840 cm^{-1}

● - 1812 cm^{-1}

▲ - 1670 cm^{-1}

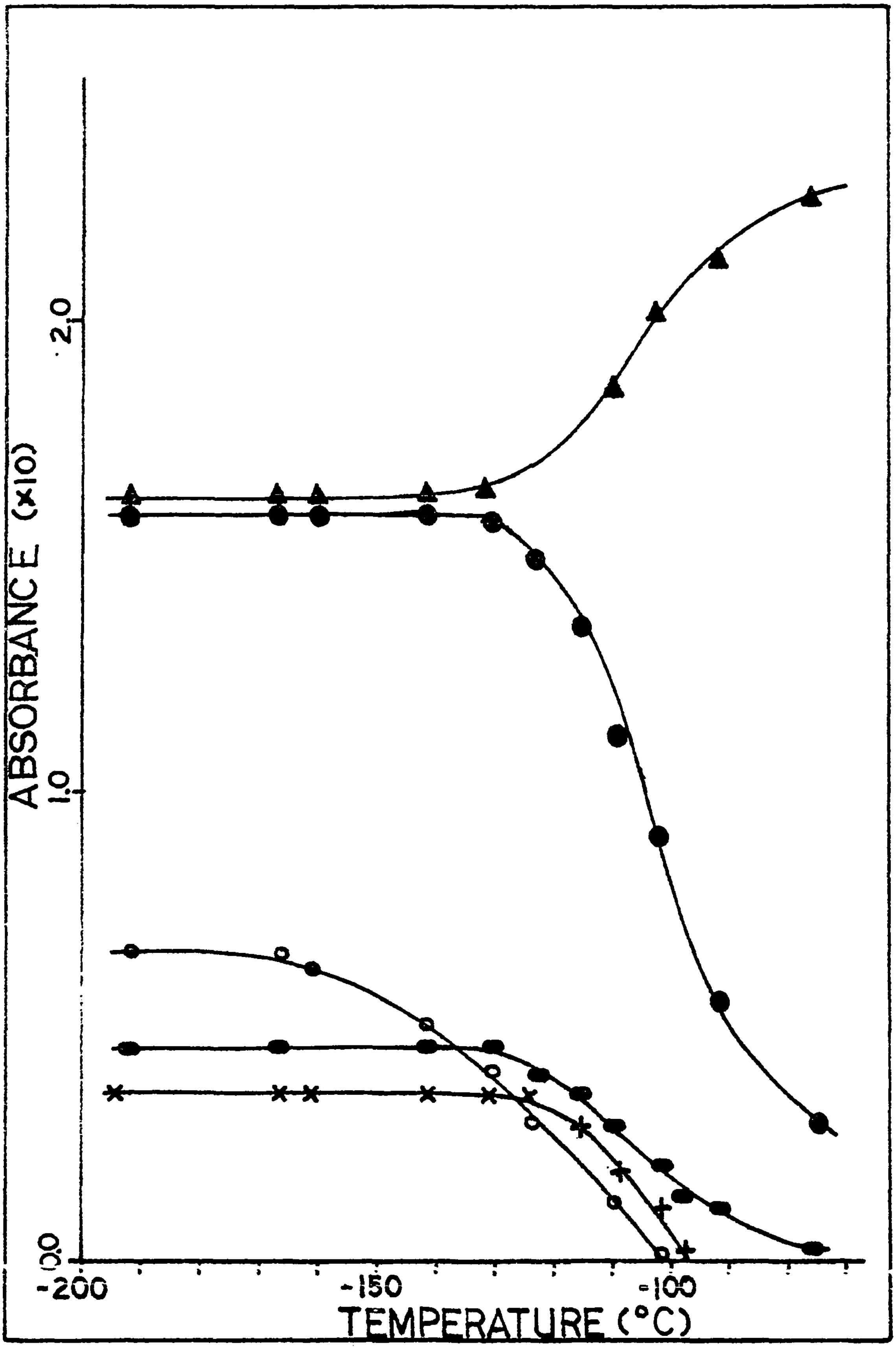
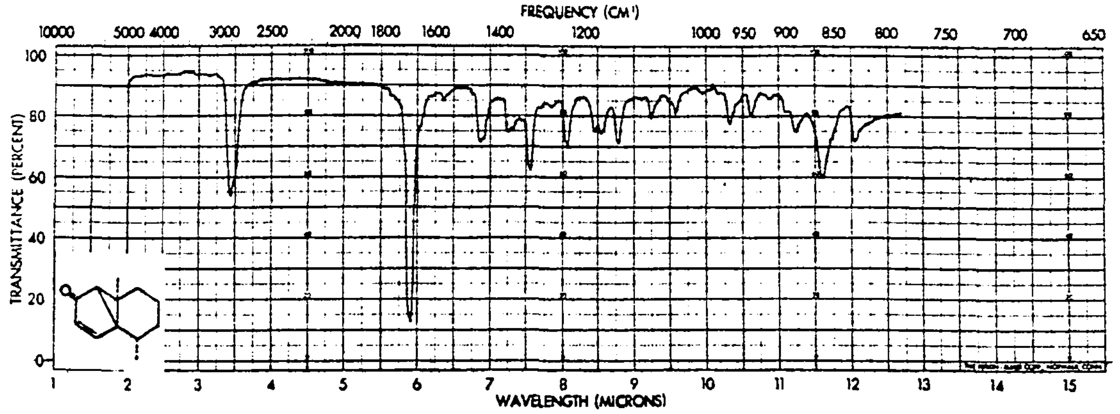

ABSORBANCE (x10)
0.0
1.0
2.0
-200
-150
-100
TEMPERATURE (°C)

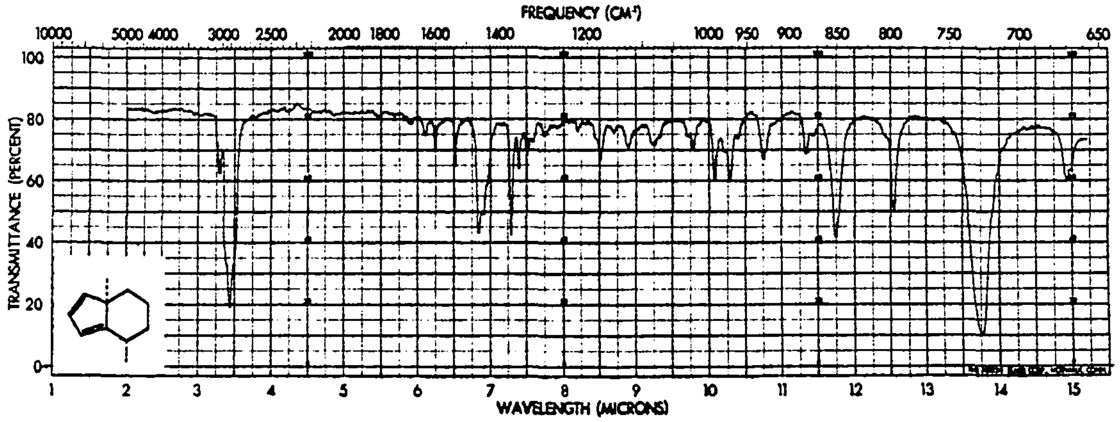
Figure 20. Infrared spectra (CCl_4)

Top--5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

Middle--3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane

Bottom--4,8-dimethyl-15-oxa-tetracyclo [7.4.1.1.^{10,13}0^{3,8}]pentadeca-2,11-dien-14-one


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


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

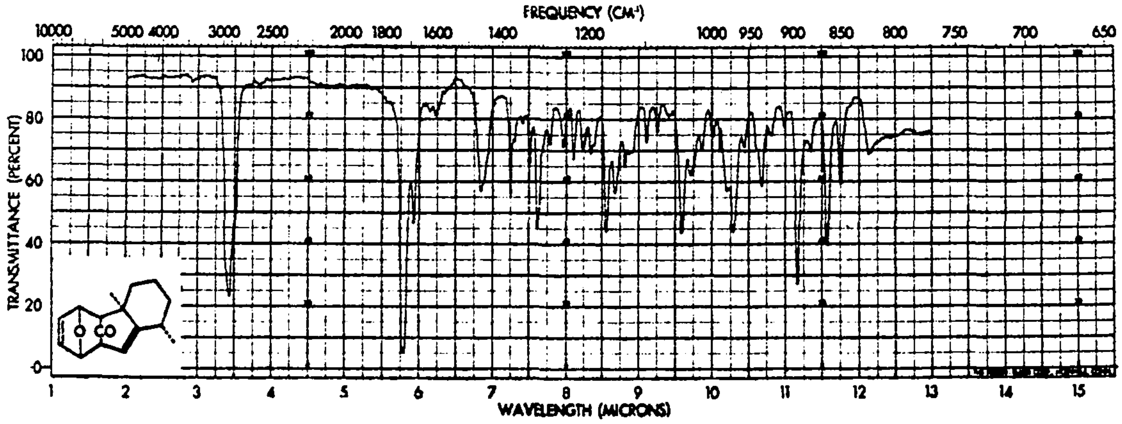
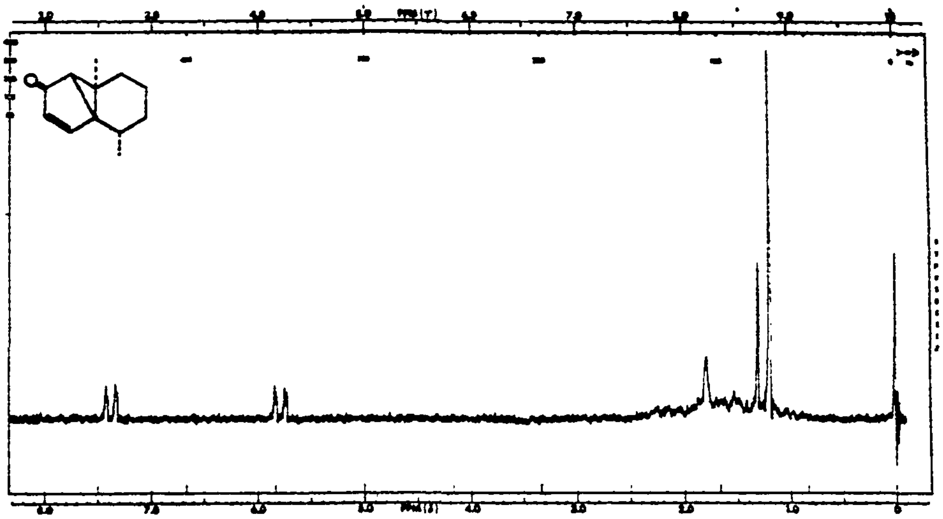

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

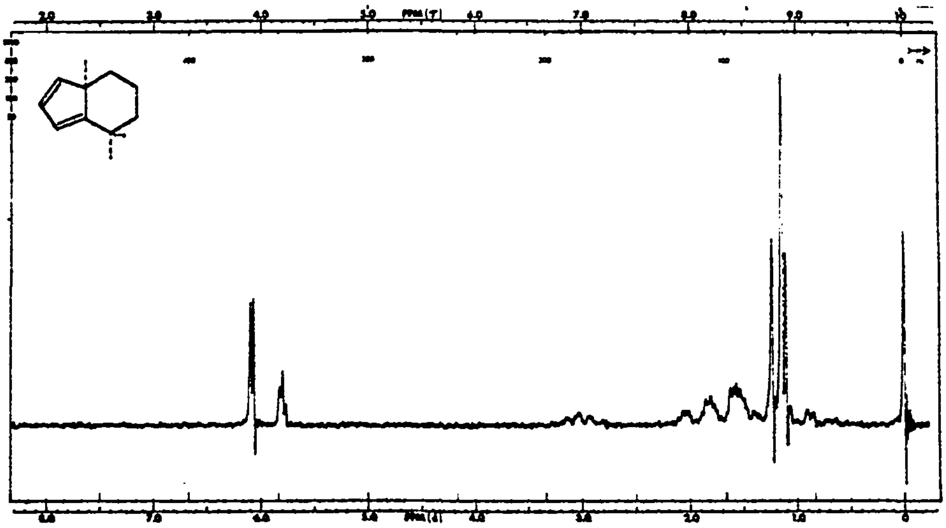
Figure 21. Nuclear magnetic resonance spectra

Top--5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone (CCl_4)

Middle--3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane (CCl_4)

Bottom--4,8-dimethyl-15-oxa-tetracyclo [7.4.1.1.$^{10,13}0^{3,8}$]pentadeca-2,11-dien-14-one ($CDCl_3$)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

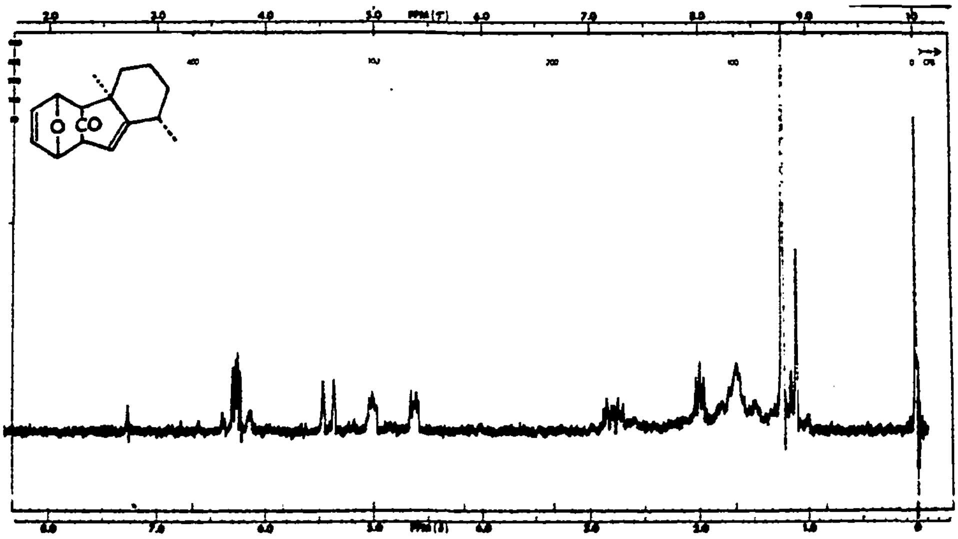

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
0
O
CO
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 22. Nuclear magnetic resonance spectra (C_6D_6)

Top--3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane

Middle--3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane
100 Mc expansion: 578.4-584.6 Hz;
597.5-622.6 Hz

Bottom--3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane
100 Mc expansion: 574.8-584.6;
597.5-622.6 Hz
irradiation allylic methine (297 Hz)

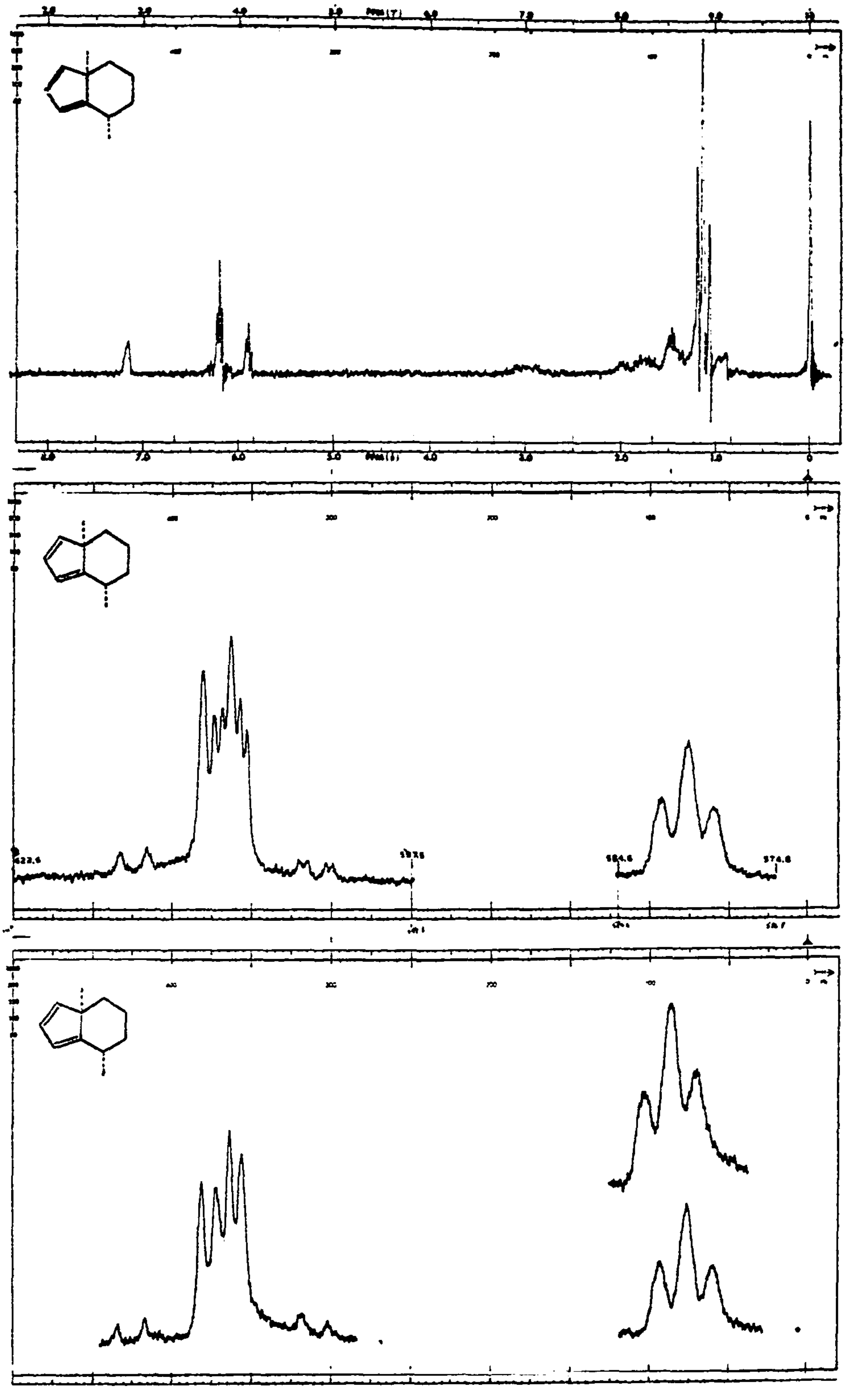

2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0
622.6
597.5
584.6
574.6

Figure 23. Simulated nuclear magnetic resonance spectrum

3a,7-Dimethyl-$\Delta^{1,7:2,3}$-perhydroindane
100 Mc expansion: 597.5-622.6 Hz
irradiation allylic methine (297 Hz)

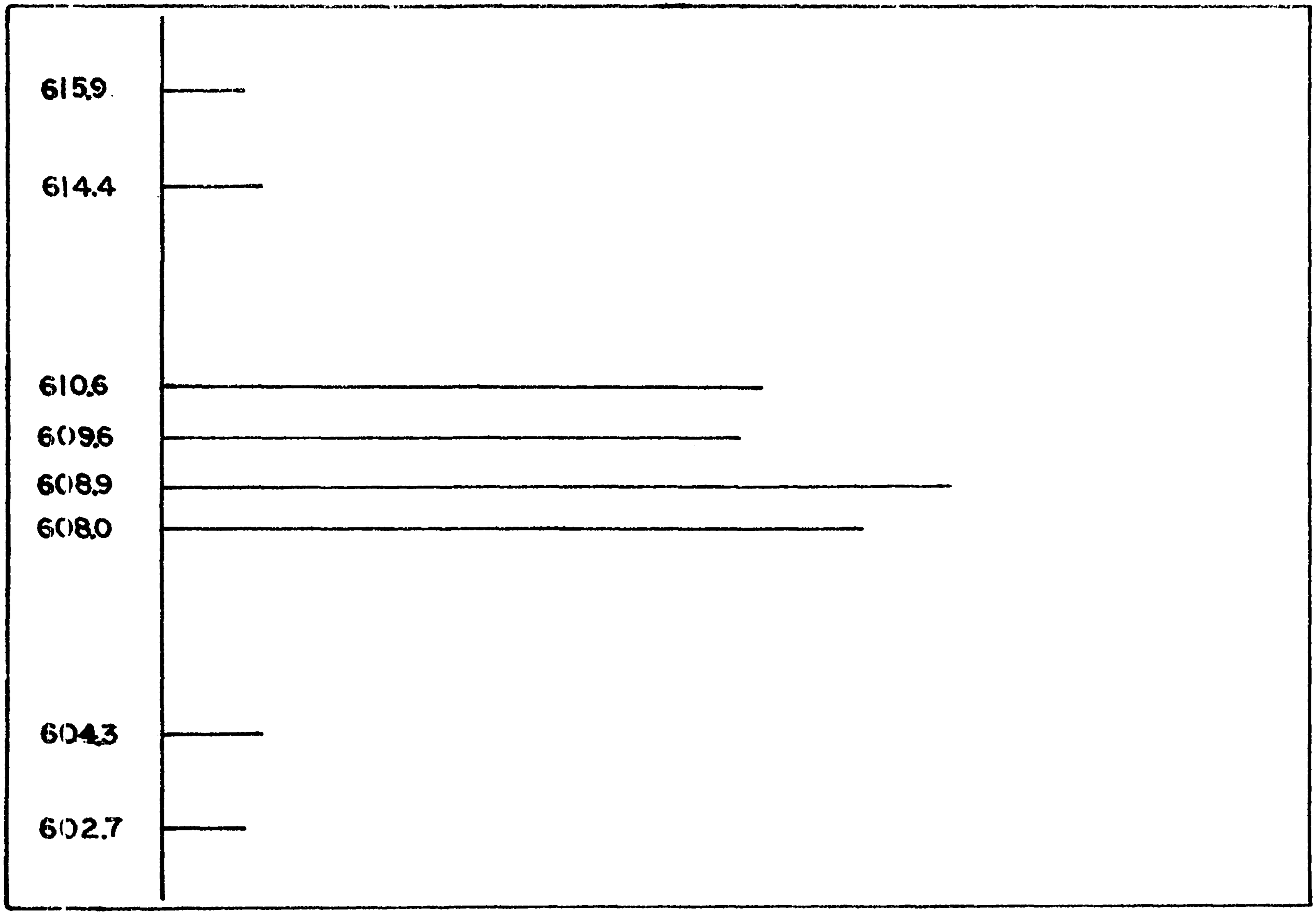

615.9
614.4
610.6
609.6
608.9
608.0
604.3
602.7

Figure 24. Simulated nuclear magnetic resonance spectrum

3a,7-Dimethyl-$\Delta^{1,7:2,3}$-perhydroindane 100 Mc expansion: 574.8-584.6 Hz

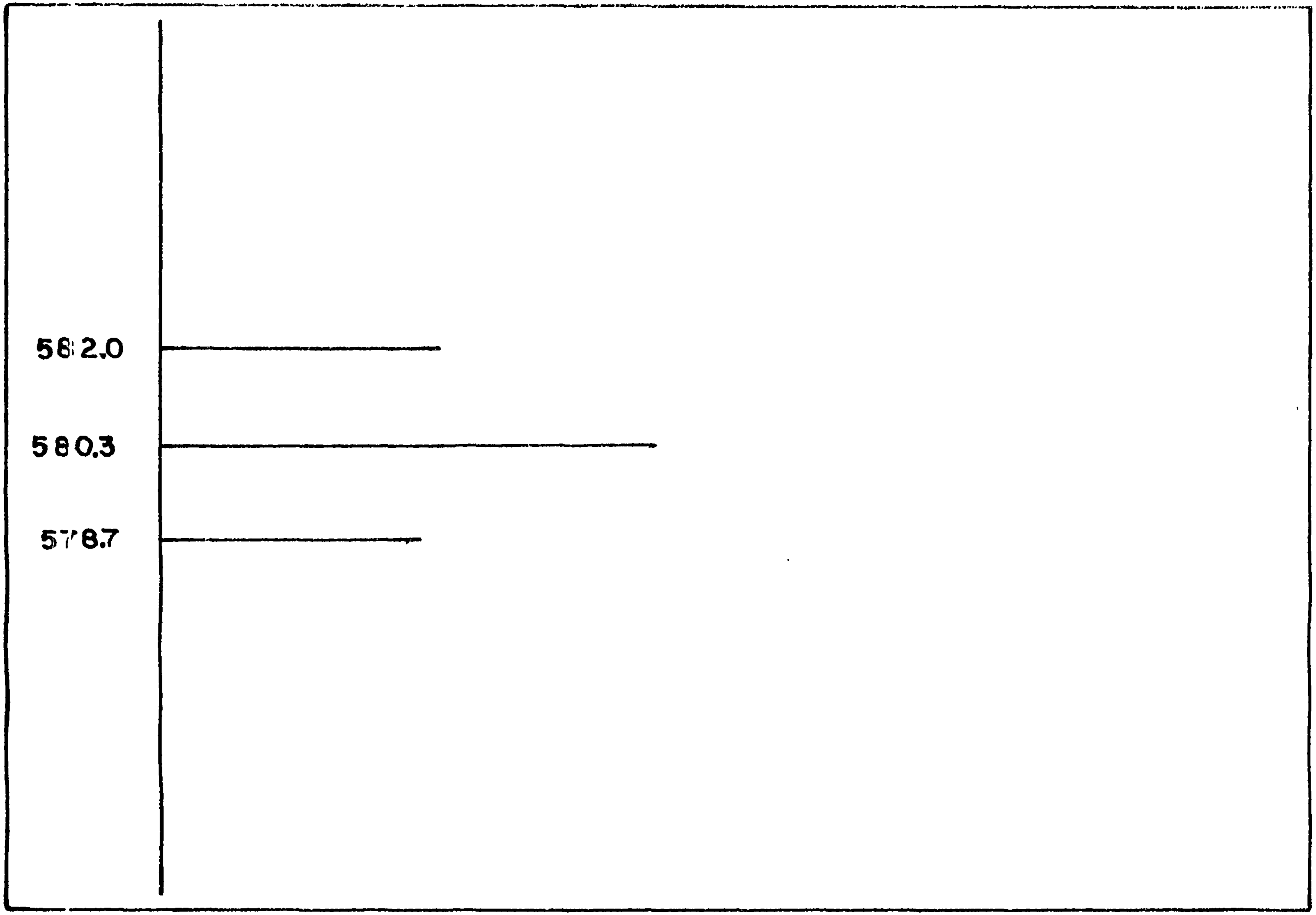

582.0
580.3
578.7

Figure 25. Mass spectrum (70 ev)

3a,7-Dimethyl-$\Delta^{1,7:2,3}$-perhydroindane

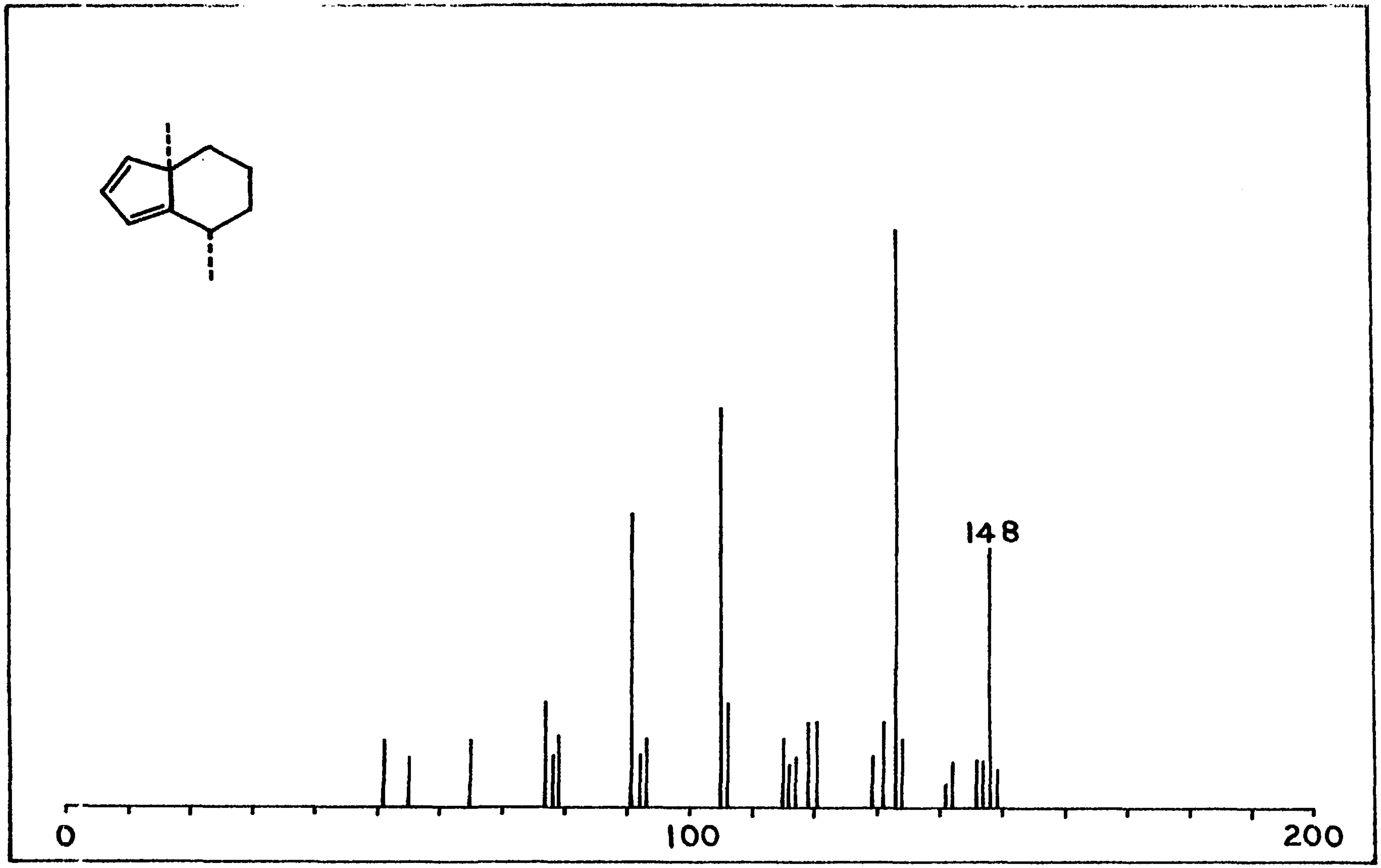
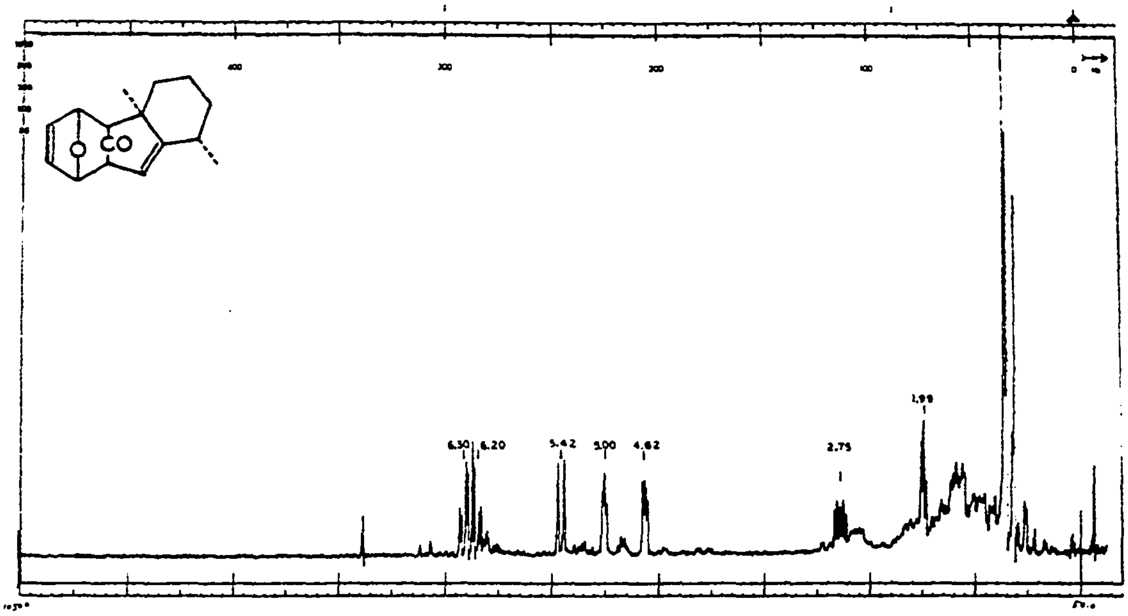

148
0
100
200

Figure 26. Nuclear magnetic resonance spectra ($CDCl_3$)

Top--4,8-dimethyl-15-oxa-tetracyclo [7.4.1.1.^{10,13}0^{3,8}]pentadeca-2,11-diene-14-one

Bottom--4,8-dimethyl-15-oxa-tetracyclo [7.4.1.1.^{10,13}0^{3,8}]pentadeca-2,11-diene-14-one
double resonance data


400
300
200
100
0
CO
O
6.30
6.20
5.42
5.00
4.62
2.75
1.99

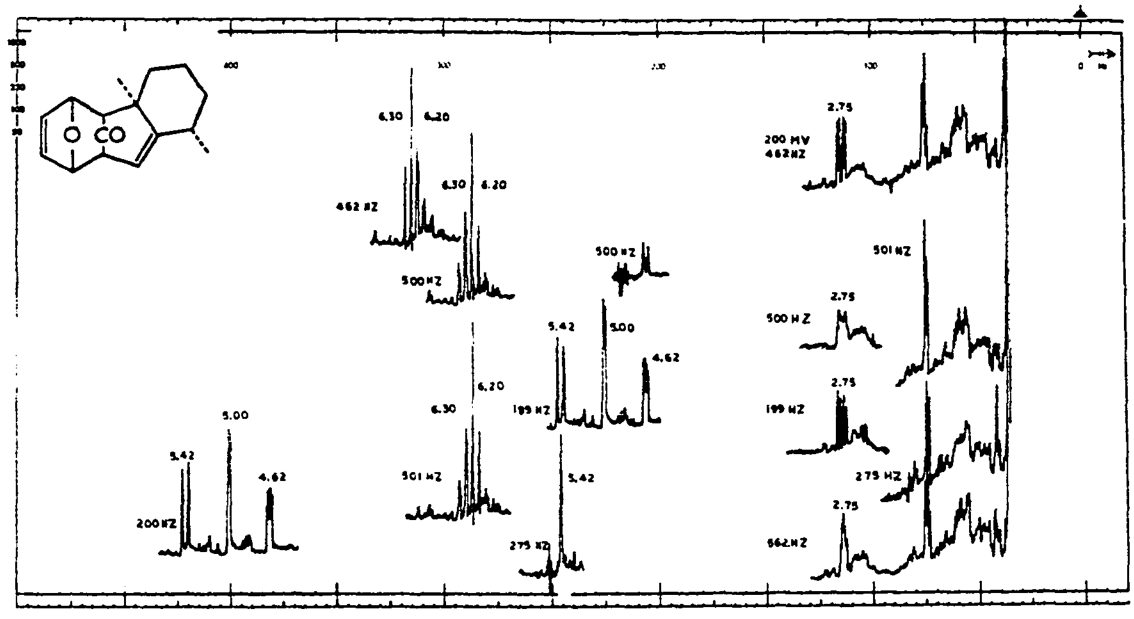

400
300
200
100
0
CO
O
6.30
6.20
462 HZ
500 HZ
500 HZ
5.42
5.00
4.62
199 HZ
200 HZ
501 HZ
275 HZ
2.75
200 MV
462 HZ
501 HZ
500 HZ
199 HZ
275 HZ
662 HZ

Figure 27. Mass spectrum (70 ev)

4,8-dimethyl-15-oxa-tetracyclo[7.4.1.1.^{10,13}0^{3,8}]pentadeca-2,11-dien-14-one

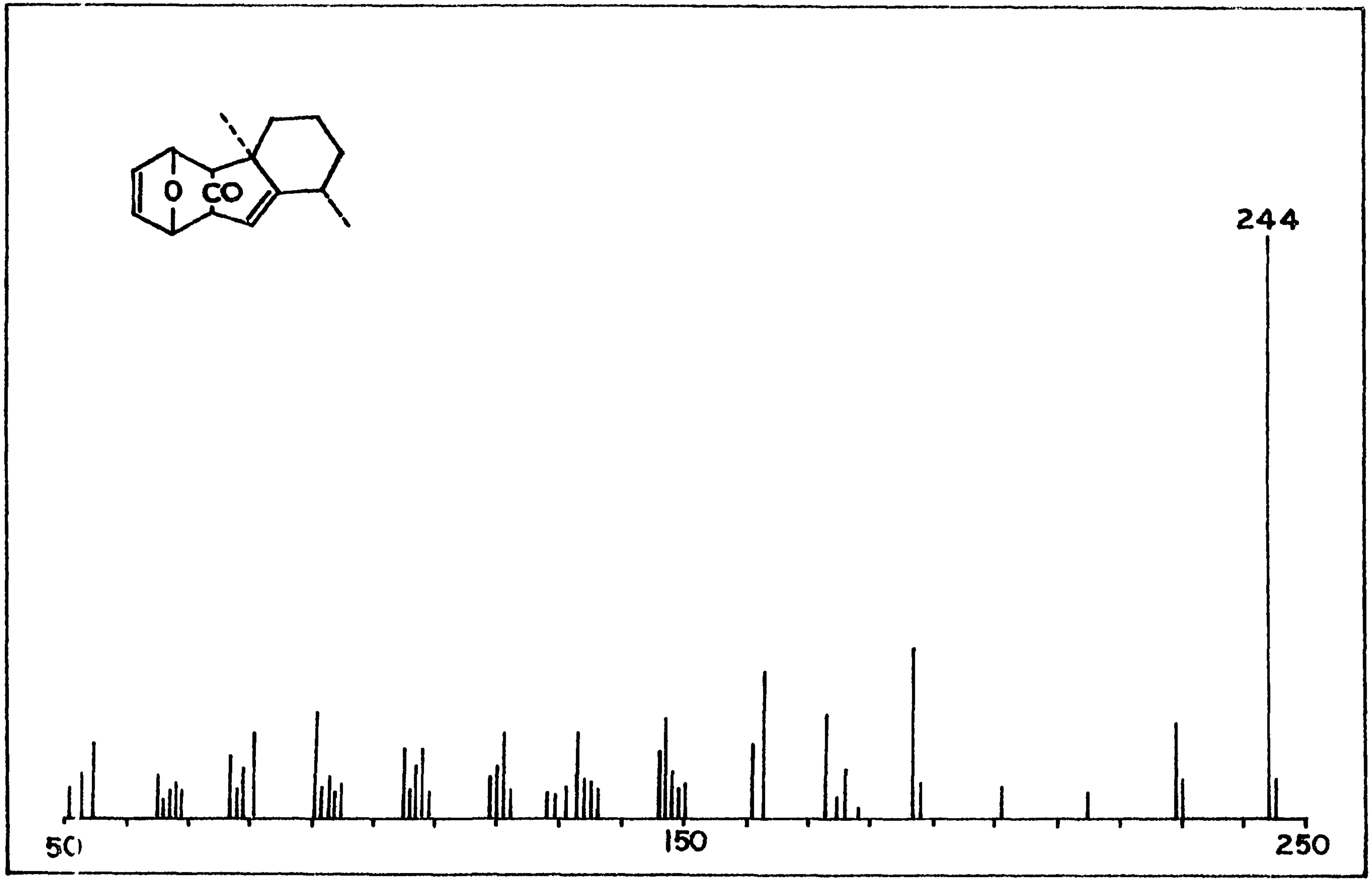
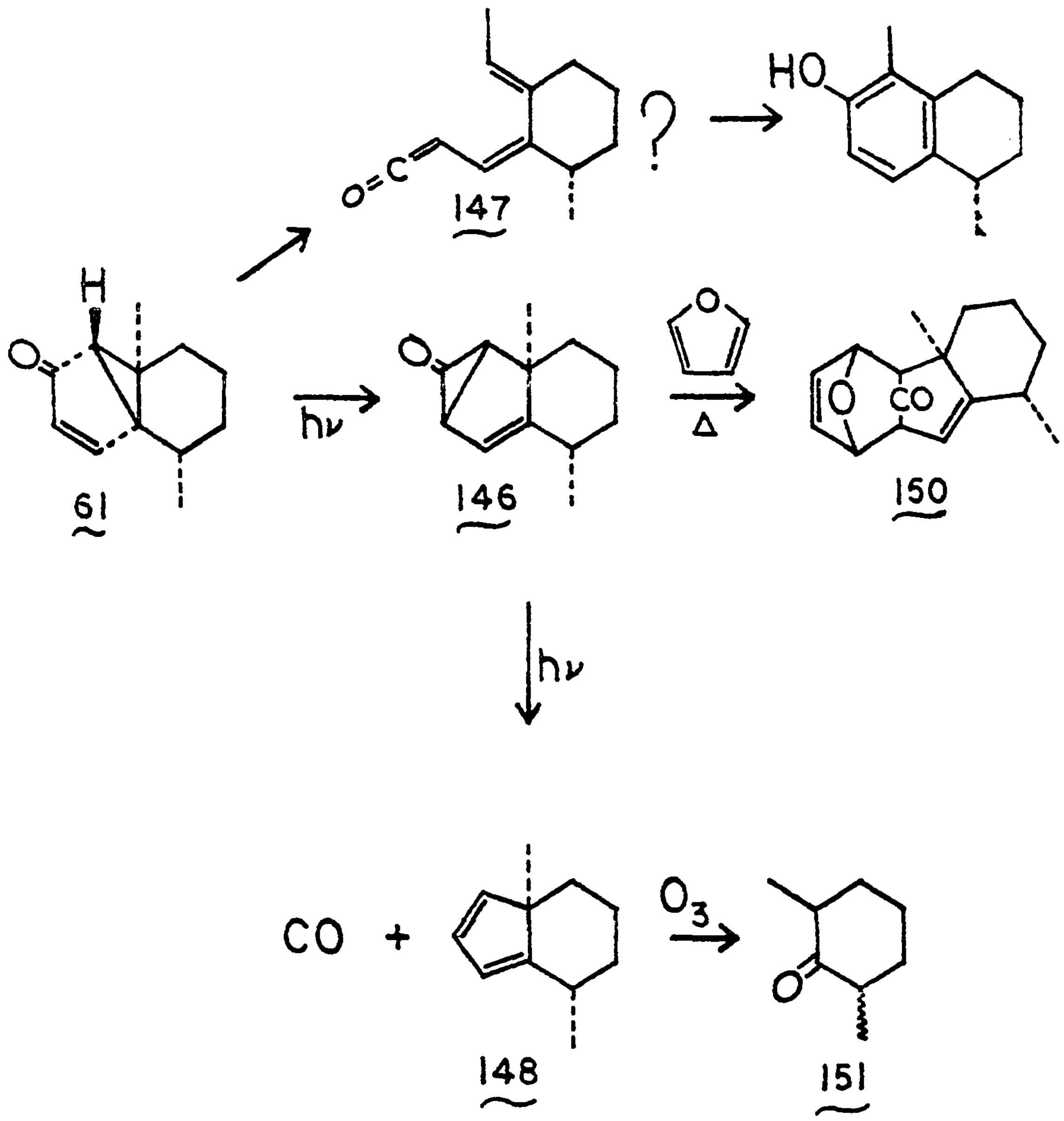

O
CO
244
50
150
250

Figure 28. A summary of the photochemistry of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone


O=C
147
?
HO
H
O
61
hν
146
Δ
CO
150
hν
CO +
148
O$_3$
O
151

following assignments were made based upon the intrepretation of the double resonance experiments. Two doublets of doublets ($J_{11,12}$ = 6.0 Hz, $J_{12,13}$ = 1.5 Hz, $J_{10,11}$ =1.5 Hz) appeared at δ 6.30 and δ 6.20 and were assigned to the protons at positions eleven and twelve respectively. A one proton doublet ($J_{1,2}$ = 6.0 Hz) was observed at δ 5.42 and the two oxa-bridgehead protons ten and thirteen appeared as multiplets at δ 5.00 and δ 4.62 respectively. The protons at positions one and nine appeared as a multiplet δ 2.75 ($J_{1,13}$ = 2 Hz) and a triplet ($J_{9,10} \simeq J_{1,9}$) at δ 1.99. The two methyl groups appeared as a singlet, δ 1.23 and a doublet (J = 7.5 Hz). Six methylene protons appeared between δ 2.4 and δ 0.8. It was not possible to make any stereochemical assignments from this data or from models which were used to simulate the transition state during adduct formation.

8aα-Carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-
2-(4aH)-naphthalenone (56)

Irradiation of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone was shown by Kropp (39) to involve a formal 1,2-migration of a carbethoxy group which gave 1-carbethoxy-5,6,7,8-tetrahydro-2-naphthol in a manner formally analogous to the formation of thymol from umbellulone.

Irradiation of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone at -190° resulted in formation of a ketene derivative (152) with an absorption at 2116 cm^{-1} and a new species obtained in a low steady state concentration with absorptions at 1825 and 1810 cm^{-1} (Figure 29). A trace of carbon monoxide and a blue colored species were formed during the irradiation. The appearance of the ketene derivative absorption at 2116 cm^{-1} and carbon monoxide absorption at 2138 cm^{-1} increased steadily with longer irradiation times while the carbonyl absorption at 1709 cm^{-1} decreased steadily with time (Figure 30). A slight decrease in the intensities of the absorption bands at 1810 and 1825 cm^{-1} occurred at longer irradiation times. It was not possible to determine if an induction period for formation of carbon monoxide occured during the preliminary stages of the irradiation. The irradiation was discontinued when nearly all of the starting material had been destroyed as judged by the decrease in intensity of the absorption at 1709 cm^{-1}. 1-Carbethoxy-5,6,7,8-tetrahydro-2-naphthol was not observed as a photoproduct during the irradiation period. No absorptions at 1670 and 1630 cm^{-1} were detected during the low temperature irradiation.

When the cold, irradiated sample was allowed to warm, rather eratic changes occurred in some of the absorptions

(Figure 31).

The carbon monoxide absorption at 2138 cm^{-1} decreased sharply and then more gradually until it had completely disappeared at -60°. The absorption of the ketene derivative increased slightly and then remained nearly constant during the warmup until the sample temperature reached -110°. Disappearance of this absorption was nearly complete at -60°. During this warmup process, a new absorption at 1660 cm^{-1} appeared. The two absorptions at 1810 and 1825 cm^{-1} remained nearly constant throughout this process.

A rigorous investigation of the structures of the ketene derivative and the intermediate with absorptions at 1810 and 1825 cm^{-1} was not carried out. By analogy with umbellulone, lumisantonin and 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone, the following mechanistic scheme is proposed (Figure 32). The ketene derivative is believed to be a diene-ketene similar to that diene-ketene obtained from umbellulone upon low temperature irradiation. Thermal electrocyclic closure of this diene-ketene derivative followed by tautomerization would give the 2-naphthol derivative obtained by Kropp (39). This naphthol was detected in the crude photomixture by tlc after the sample was warmed to room temperature.

The formation of carbon monoxide in this low

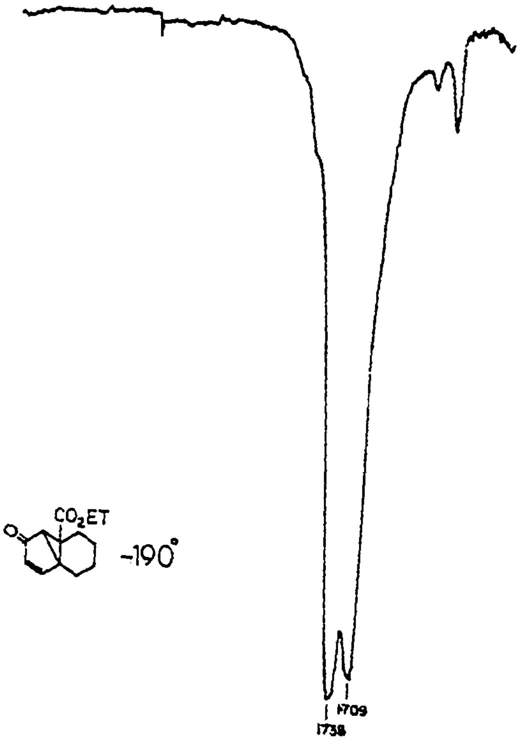
Figure 29. Low temperature infrared spectra (neat)

Top left--8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

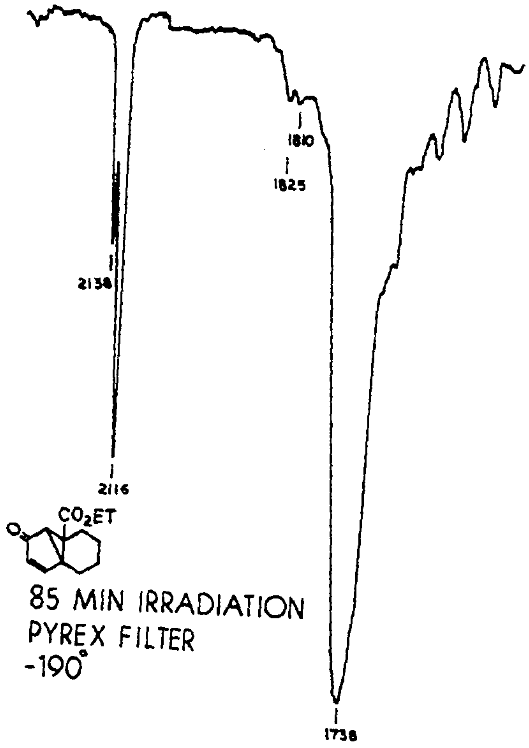
Top right--8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone irradiated through Pyrex

Bottom left--5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

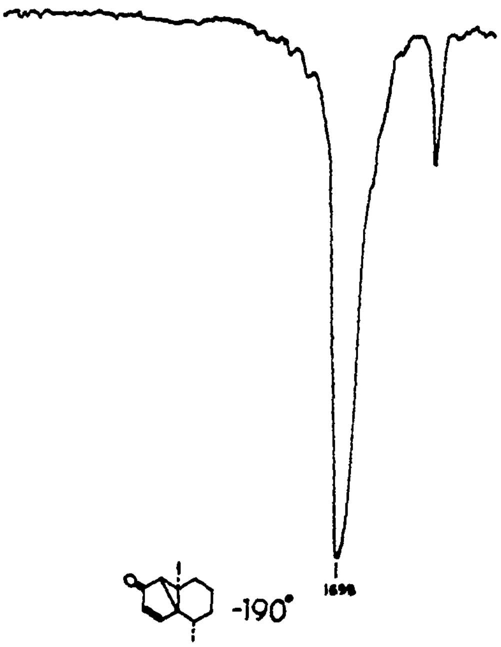
Bottom right--5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone irradiated at 253.7 nm



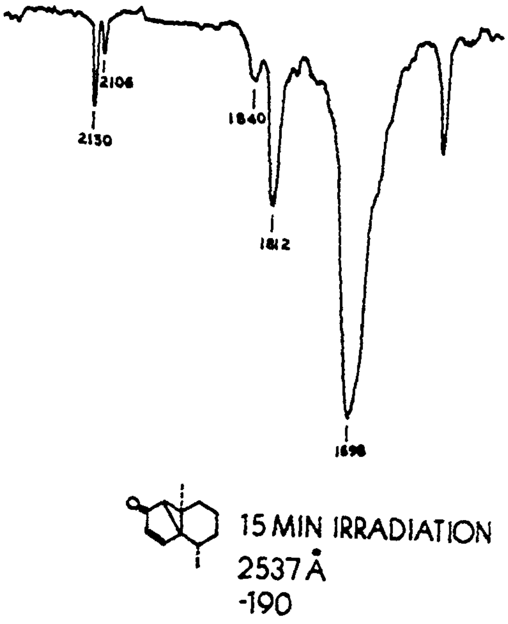
-190°



85 MIN IRRADIATION
PYREX FILTER
-190°



-190°



15 MIN IRRADIATION
2537 Å
-190

Figure 30. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

+ - 2138 cm^{-1}

| - 2116 cm^{-1}

● - 1825, 1810 cm^{-1}

▲ - 1698 cm^{-1}

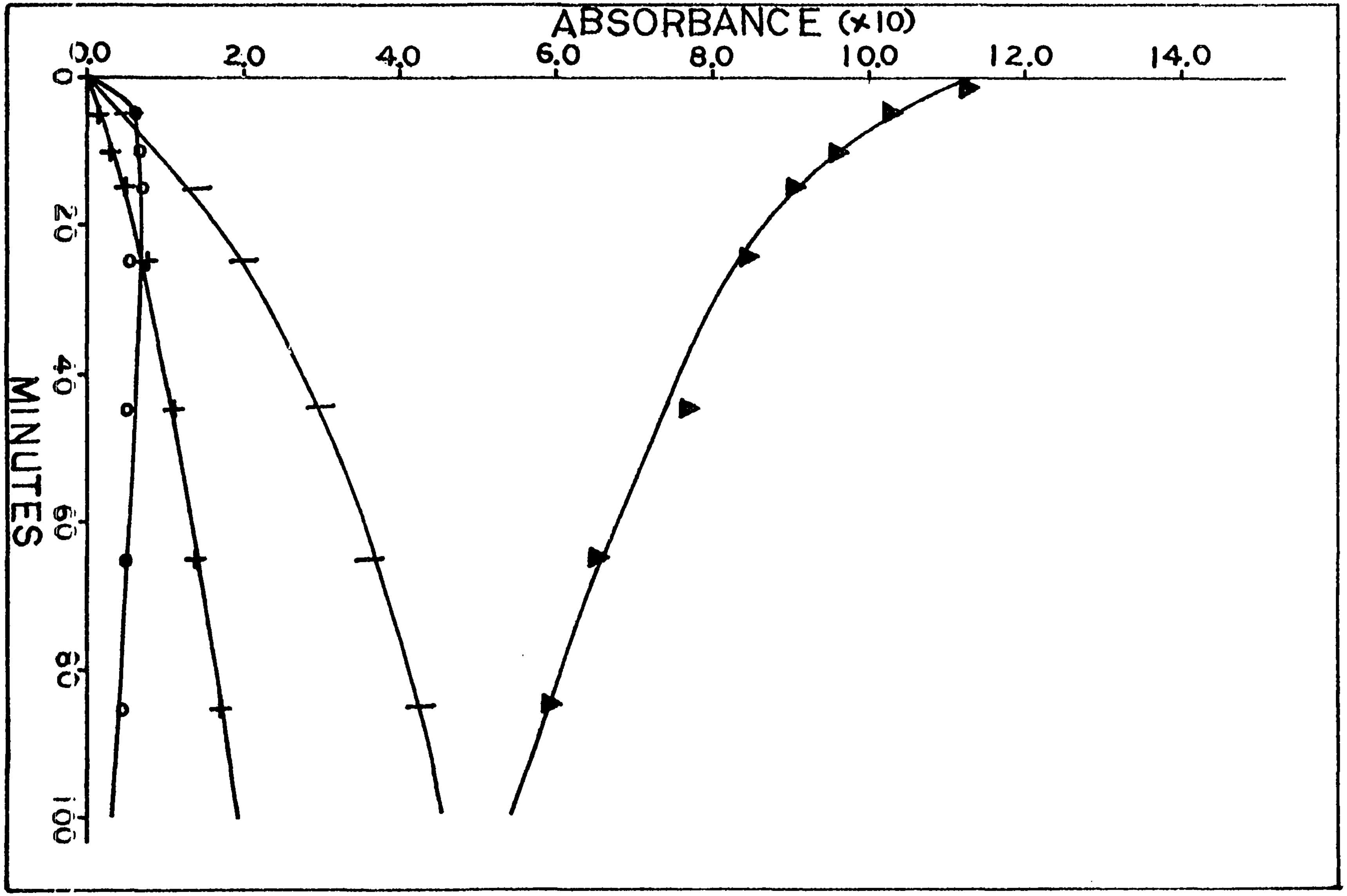

ABSORBANCE (×10)
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
MINUTES
0
20
40
60
80
100

Figure 31. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the spectra obtained while warming a cold, irradiated sample of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

▲ - 2138 cm^{-1}

● - 2116 cm^{-1}

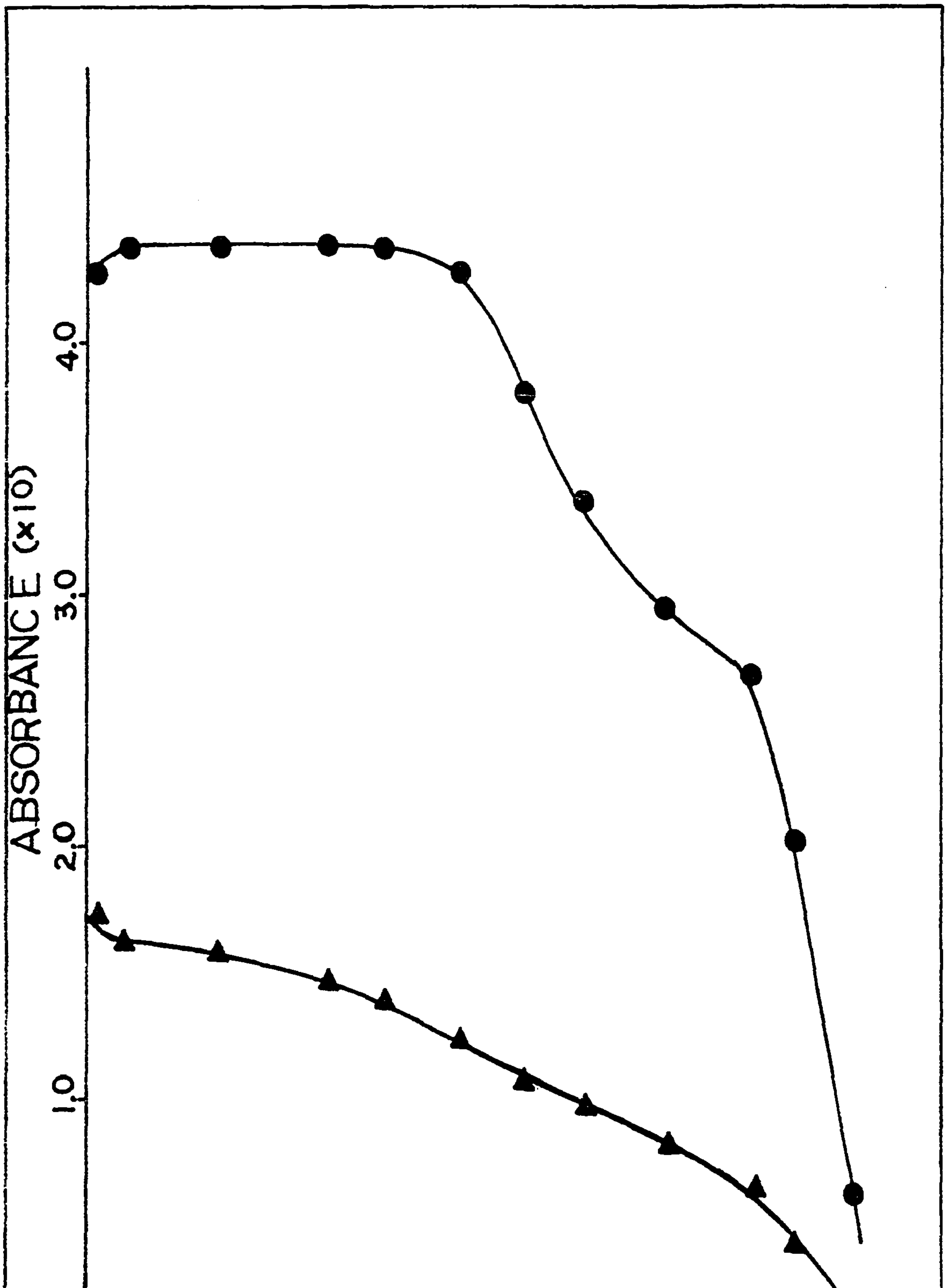
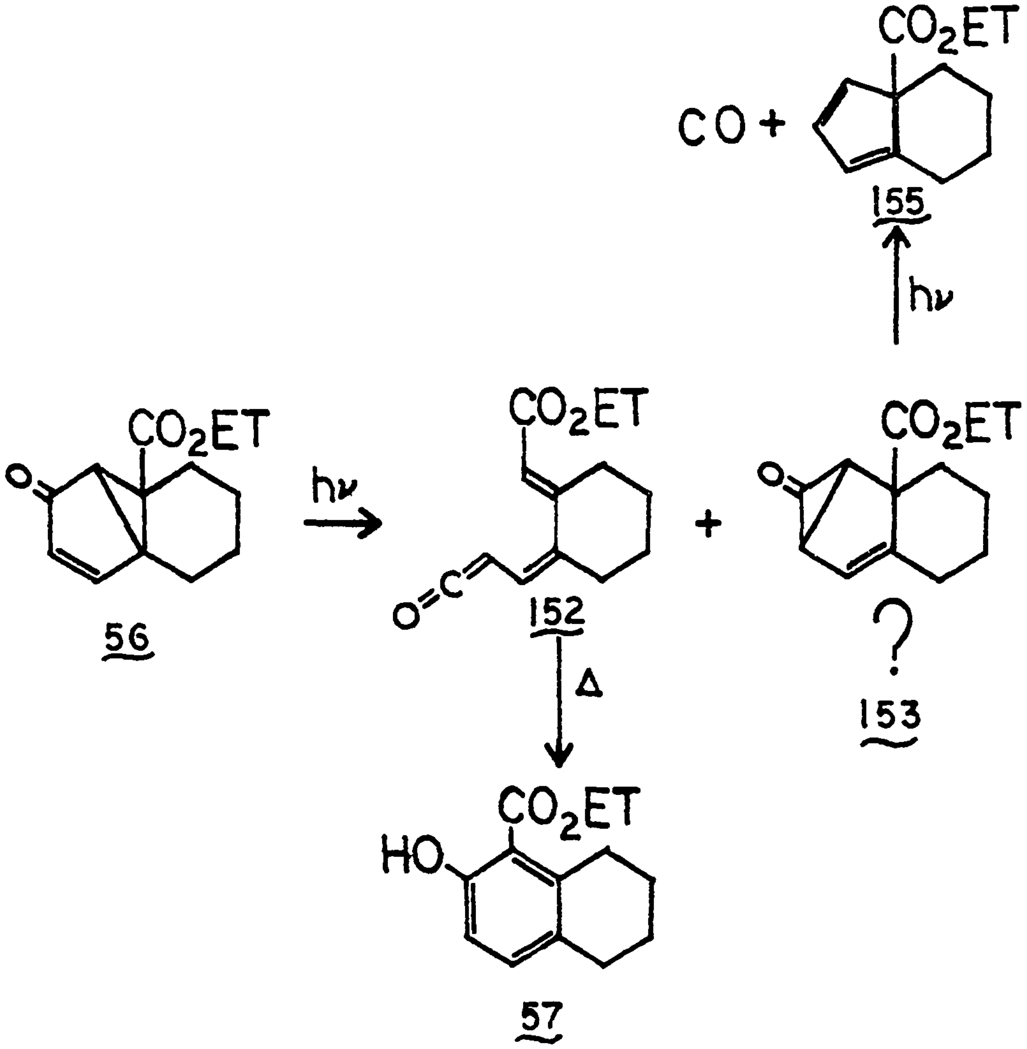
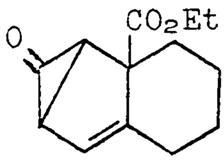

ABSORBANCE (x10)
4.0
3.0
2.0
1.0
0.0
-160
-130
-100
-70
TEMPERATURE (°C)

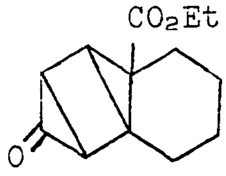
Figure 32. A summary of the photochemistry of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone


CO +
CO₂ET
155
hν
CO₂ET
O
56
hν
CO₂ET
O=C
152
+
CO₂ET
O
?
153
Δ
CO₂ET
HO
57

temperature experiment may occur as the result of a biphotonic process which involves a cyclopropanone derivative. Two possible structures for this proposed cyclopropanone are (153) and (154). By analogy with



153

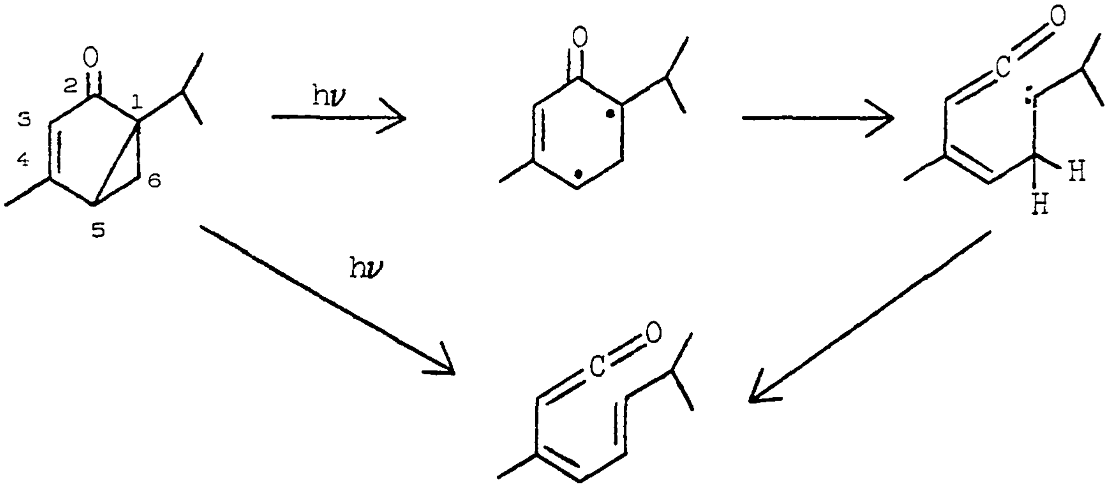


154

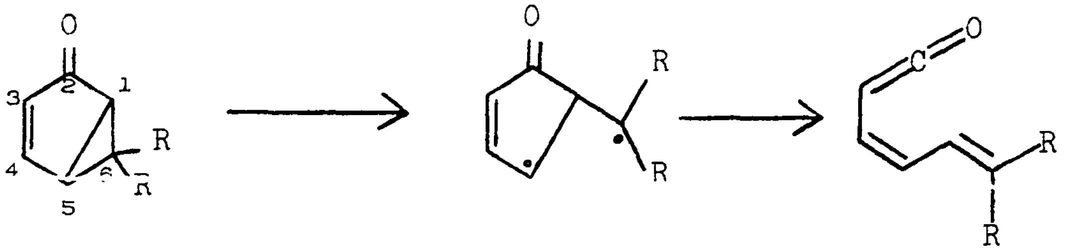
5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone, structure (153) is favored. Photodecarbonylation of this intermediate would be an efficient reaction which would lead to a perhydroindane derivative (155). This reaction pathway may account for as much as 10% of the total reaction.

A detailed investigation of the excited states involved in the photochemistry of the bicyclo[3.1.0]systems mentioned in this thesis has not been carried out. Lumisantonin and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one have been studied by Fisch and Richards (28, 29) and Zimmerman and Schuster (20). In low conversion irradiation studies the triplet state of each system obtained by sensitized irradiation displayed behavior which was identical to that displayed by the reactive state achieved by direct irradiation. These two examples indicate that a triplet excited state may be involved in each of the reactions of bicyclo[3.1.0]hexenones investigated at low temperature. Fisch and Richards suggested that in the case of lumisantonin, the triplet state may be of the n,π^* type.

It is difficult to formulate an all inclusive mechanism which can be used to describe the behavior of each individual bicyclo[3.1.0]hexenone in a predictive fashion at low temperatures, but it is instructive to consider some possibilities for the modes of ketene formation and cyclopropanone formation. The structures of the ketene derivatives that are formed upon irradiation of bicyclo[3.1.0] hexenones are strongly influenced by the substitution pattern on the bicyclo[3.1.0] nucleus. A comparison of the structures of the diene-ketene derivatives obtained upon irradiation of umbellulone, lumisantonin and 8a α-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone to the structures of the diene-ketenes obtained from 6,6-disubstituted bicyclo[3.1.0]hexenones show that two modes of ketene formation occur. Fission of the 1,2-bond of the bicyclo[3.1.0] nucleus is common to both types of reaction sequences. The moment at which fission of the 1,2-bond occurs on the time scale of the complete reaction sequence is not known, but Dauben (78) has shown that α-cleavage between a carbonyl group and a cyclopropane ring is not a favorable process in bicyclo[4.1.0]heptan-2-one derivatives. This suggests that bond breaking initially occurs at the 1,5-bond or 5,6-bond followed by rupture of the 1,2 bond. The formation of the ketene from umbellulone



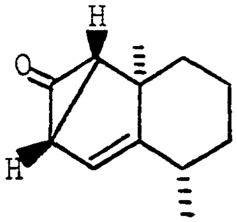
and related compounds involves cleavage of the 1,5-bond and 1,2-bond. In these examples where 1,5-bond cleavage is important, substituents at the 1- and 5-positions should facilitate this mode of fragmentation. In the examples of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones, cleavage of the 5,6-bond occurs. 6,6-Disubstitution appears to strongly favor this type of cleavage. The

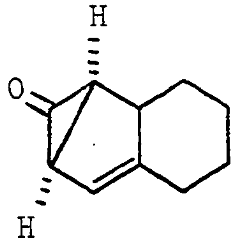


reasons for these observed differences in behavior are not clear. These effects are further complicated by stereochemical changes in more complex bicyclo[3.1.0] hexenone systems. Such a difference is exemplified in the cases of α-lumisantonin and 6-epi-lumisantonin (28, 42).

In contrast to the behavior of these bicyclo[3.1.0] hex-3-en-2-one derivatives, $5\alpha,8a\alpha$-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone gives only a trace of ketene upon irradiation. A major amount of a cyclopropanone derivative is formed at low temperatures. This is the first example of a bicyclo[3.1.0]hex-3-en-2-one going directly to a cyclopropanone. Upon warming, the cyclopropanone undergoes sigma-symmetric heterolysis of the bond opposite the carbonyl group at -120° to give a zwitterion (167) which can be trapped by furan as a 1,3-1,4-dipolar addition adduct. The heterolysis of the cyclopropanone bond is a symmetry allowed process. The zwitterion may also be trapped as the furan adduct at -80° or at room temperature.

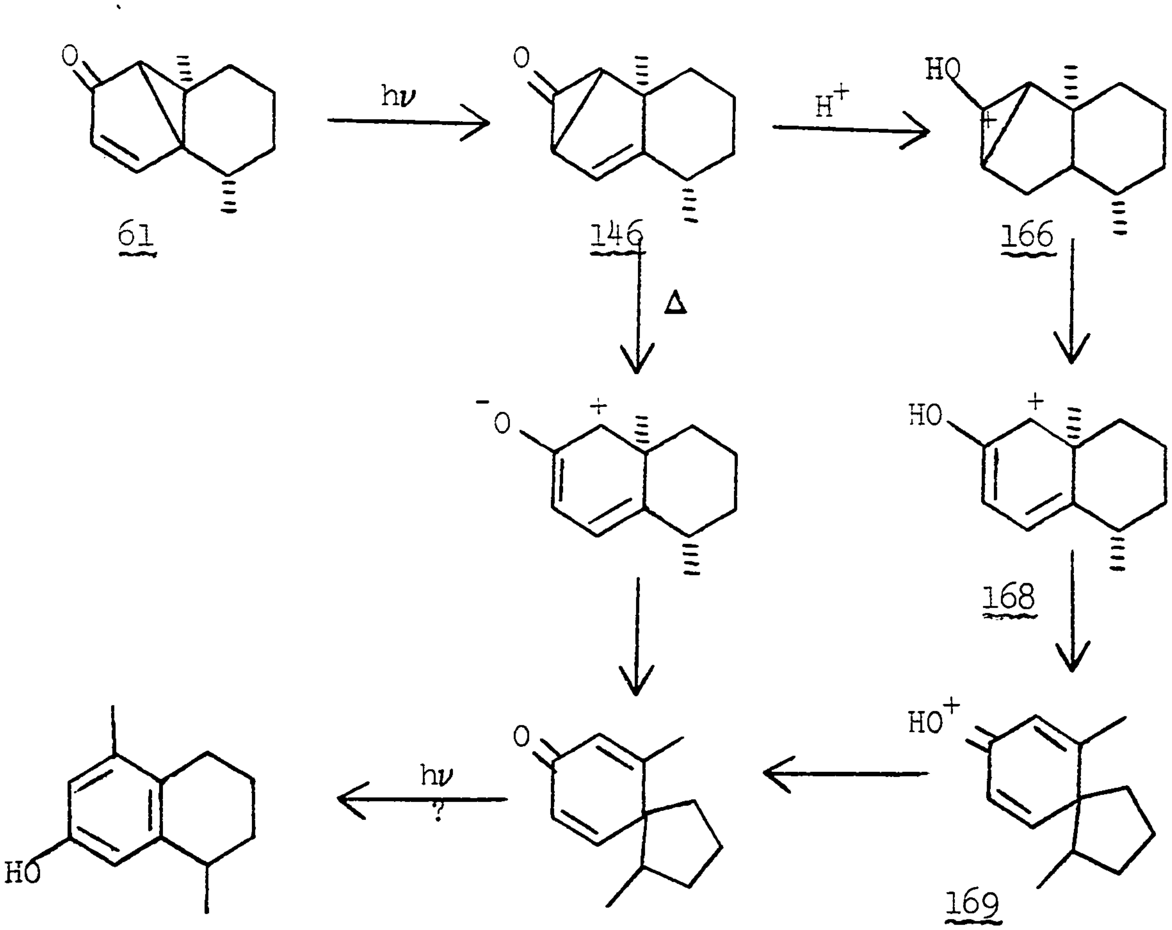
The formation of the cyclopropanone (146) from (61) can be envisioned formally as a $2\pi + 2\sigma$ cycloaddition or a [1,3]-sigmatropic rearrangement (79, 80). Such a rearrangement is symmetry allowed if it occurs in a suprafacial sense. Either process would lead to the stereochemical structure (171). Either one of two stereoisomeric cyclopropanones (171) or (172) might be formed if photochemical opening of the common bond in the bicyclo[3.1.0]hex-3-en-2-one occurred followed by electron demotion and thermal electrocyclic reaction of (167) to (146). A distinction between these possible modes of reaction cannot be made.


171

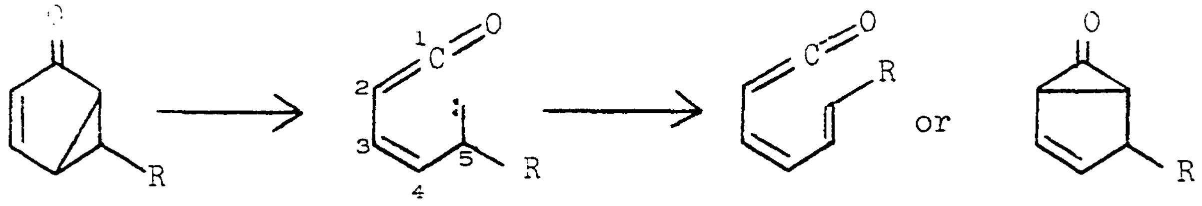

172

The zwitterion (167) or its protonated form (168) are ideal precursors for the formation of the naphthol derivative (62) obtained by Kropp (41) in his room temperature investigations of (61). A spirodienone (170) may be involved in this overall transformation. Analogy for this ring contraction process has been documented for 6-*epi*-lumisantonin and O-acetyl-1-dehydrotestosteron derivatives (42, 47).

van Tamelen (81) suggested that a ketene-carbene intermediate could be a key intermediate in the transformation of lumisantonin to the ketene which ultimately gave



photosantonic acid. Application of this idea to the rearrangements of umbellulone, lumisantonin, 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone (56) and 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone (61) provides a novel way of envisioning ketene formation and cyclopropanone formation. Migration of a substituent from position five to position six would give a diene-ketene derivative while insertion of the carbene into the carbon-carbon double bond would result in the formation of a cyclopropanone. Lumisantonin,



umbellulone and ketone (56) give nearly exclusive migration of the substituent at position five to position six. Ketone (61) follows the pathway which results in insertion of the carbene into the carbon-carbon double bond of the ketene. A small amount of diene-ketene is also formed. The general usefullness of this mechanistic scheme where a ketene-carbene partitions between reaction pathways does not seem clear in view of data presently available.

2,4,6-Cyclooctatrienone

In 1961, Buchi and Burgess (54) reported that 2,4,6-cyclooctatrienone (92) was transformed into bicyclo[4.2.0]-octa-4,7-dien-2-one (91) upon irradiation in pentane and to a mixture of stereoisomeric methyl 2,4,6-octatrienoates (94) when the irradiation was performed in methanol.

Irradiation of 2,4,6-cyclooctatrienone ($\lambda > 360$ nm) led to the formation of two primary photoproducts, a triene-ketene derivative (108) and a species with a carbonyl absorption at 1731 cm^{-1} (Figures 33 and 35). Bicyclo[4.2.0]-

octa-4,7-dien-2-one could not be detected in the spectra of this cold, irradiated sample. After an irradiation period of twenty minutes, the photoreaction had nearly stopped. At this point, the intensities of the absorption bands at 2113 and 1731 cm^{-1} were nearly identical and a pronounced decrease in the intensities of the absorption bands of the starting material was observed. There was no detectable change in the composition of the cold, photomixture upon standing in the dark.

The triene-ketene derivative and the 1731 cm^{-1} transient behaved quite differently upon warming. Virtually no changes occurred in the spectra as the sample temperature was allowed to increase to -130°.

As the sample temperature rose above -130°, the 1731 cm^{-1} species rapidly disappeared with simultaneous appearance of a new species with an absorption band at 1709 cm^{-1}. An increase in the intensity of the starting material absorption bands was also observed during the disappearance of the 1731 cm^{-1} species. Complete disappearance of the 1731 cm^{-1} species had occurred once the cell temperature reached -95°. No change in the intensity of the triene-ketene absorption at 2113 cm^{-1} was observed. As the sample was allowed to warm above -80°, a pronounced decrease in the intensity of the triene-ketene absorption occurred with a concomitant increase in the intensities of the absorption bands of 2,4,6-cyclooctatrienone. The disappearance of the triene-ketene derivative correlated well with the electrocyclization to starting material. This facile cyclization could have occurred only if the two central double bonds of the triene-ketene possessed cis stereochemistry. The structures of the triene-ketene derivative and the 1731 cm^{-1} species could only be partially inferred from this spectral data. Complete characterization of the intermediates was possible by performing selective low temperature trapping experiments.

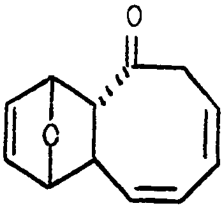
A sample of 2,4,6-cyclooctatrienone which contained methanol (ca. 25%) was irradiated at -190° in a manner similar to that employed for neat 2,4,6-cyclooctatrienone. The infrared spectrum of this cold, irradiated sample appeared to be identical to that of the cold, irradiated sample of 2,4,6-cyclooctatrienone except for the incorporation of methanol absorption bands. When the sample was allowed to warm, the behavior described for neat 2,4,6-cyclooctatrienone was observed until the sample temperature reached -80°. Instead of intramolecular cyclization of the triene-ketene back to starting material, addition of methanol occurred to the ketene with formation of a new absorption band at 1739 cm^{-1}. This is the expected position for the absorption of a nonconjugated carbonyl group of an ester. In contrast to this result, the methyl 2,4,6-octatrienoates reported by Buchi (54) possessed carbonyl absorption bands at 1725 cm^{-1}.

In an attempt to isolate this new ester with absorption at 1739 cm^{-1} a preparative scale trapping experiment was performed at -190°. 2,4,6-Cyclooctatrienone was irradiated in a methanol-ether glass and allowed to warm to room temperature. The infrared spectrum of this crude irradiation mixture revealed an intense absorption at 1739 cm^{-1}. Isolation of this ester by preparative glpc resulted in thermal isomerization to one of the conjugated esters obtained by Buchi. These results suggest that 1,2-addition of methanol to the triene-ketene is followed by thermal or photochemical isomerization to the more thermodynamically stable isomer.

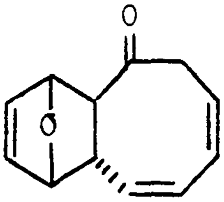
The structure of the ketene obtained at low temperatures is therefore concluded to be the linear triene-ketene postulated by Buchi. The stereochemistry of the two central double bonds was concluded to be *cis*. *trans* Stereochemistry at either of these double bonds would prohibit facile thermal cyclization of the triene-ketene to 2,4,6-cyclooctatrienone. The addition of methanol to the triene-ketene would not be expected to change the stereochemistry of either of the central double bonds.

The structure of the 1731 cm^{-1} species was established in the following way. Because of the high frequency absorption of the carbonyl group and the high reactivity of this transient, it was concluded that the 1731 cm^{-1} species might be a stereoisomer of 2,4,6-cyclooctatrienone, *e.g.*, *trans,cis,cis*-; *cis,trans,cis*-; or *cis,cis,trans*-2,4,6-cyclooctatrienone. Corey (56) and Eaton (57) showed that 2-cycloheptenone and 2-cyclooctenone undergo *cis*-*trans* isomerization when irradiated. *trans*-2-Cyclooctenone was stable at room temperature. An enhanced reactivity of these strained *trans* isomers was observed when they were treated with dienes like furan or cyclopentadiene. Stereoisomeric Diels-Alder adducts were then obtained. If the 1731 cm^{-1} species was one of the *trans* stereoisomers of 2,4,6-cyclooctatrienone, it might also possess a propensity to form Diels-Alder adducts with furan or cyclopentadiene. Trapping experiments were therefore carried out at room temperature and at -190°.

Irradiation of 2,4,6-cyclooctatrienone in furan at room temperature gave three products. Bicyclo[4.2.0]-octa-4,7-dien-2-one was obtained in approximately 60% yield from this irradiation mixture. The other two components were obtained in nearly equal yield. The crude mixture was easily separated by column chromatography on silica gel. Some of the bicyclo[4.2.0]-octa-4,7-dien-2-one isomerized back to starting material during chromatography but this did not prevent clean separation and isolation of the two crystalline adducts. The structures of these two adducts, (157) and (158), were assigned on the basis of the following spectral evidence and chemical transformations.



157



158

The mass spectra (Figures 41 and 45) of adducts (157) and (158) showed molecular ions at m/e 188 and correct element analyses calculated for $C_{12}H_{12}O_2$ were obtained. The infrared spectra (Figures 39 and 43) of both adducts showed strong carbonyl at 1715 cm^{-1}. The absorptions in the fingerprint region of the infrared spectra were quite different.

The nmr spectra of the furan adducts along with double resonance experiments were very useful for assigning the overall structures and stereochemistry. The nmr spectrum (Figure 40) of adduct (157) displayed a nearly collapsed two proton AB pattern centered at δ 6.41 and was assigned to the protons at positions eleven and twelve. Comparison of this spectrum with spectra of other furan-type Diels-Alder adducts supported this assignment. A four proton multiplet occurred between δ 6.29 and δ 5.45. The general appearance of this four-proton pattern along with its chemical shift and similarity to the diene moiety of *cis,cis*-1,3-cyclooctadiene permitted assignment of these absorptions to the four vinyl protons at positions five through eight. The two bridgehead protons at positions one and ten appeared as a broadened doublet and a broadened singlet at δ 5.01 and δ 4.73 respectively. Anet has shown that in 7-oxa-2-norbornene derivatives, coupling to the bridgehead positions occurs only when the protons are in the *exo* configuration and that these protons occur downfield relative to the *endo* protons. The proton at position two was split into a doublet of doublets ($J_{1,2}$ = 4.0 Hz, $J_{2,9}$ = 7.5 Hz) centered at δ 3.37. The assignment of these couplings was based upon data from double resonance experiments. Irradiation of the signal at δ 5.01 resulted in collapse of the proton at position two to a doublet. Similarly, irradiation of the proton absorption at δ 3.37 resulted in collapse of the absorption at δ 5.01 to a broad singlet. This perturbation also resulted in collapse of a similar one proton absorption at δ 2.54 which consisted of a doublet of doublets ($J_{8,9}$ = 3.7, $J_{2,9}$ = 7.5 Hz). This doublet of doublets was assigned to the proton at position nine. The remainder of the spectrum consisted of an AB part of an ABX system centered at δ 3.11. This pattern amounted to two protons which were assigned to those at position four. An analysis of this pattern was not necessary to complete remaining part of the spectrum.

The nmr spectrum (Figure 44) of adduct (158) showed some similarities to the spectrum obtained for adduct (157), especially for the bridgehead proton absorptions at positions one and ten. The protons at positions eleven and twelve appeared as a symmetrical eight line pattern which consisted of two doublets of doublets ($J_{11,12}$ = 5.7 Hz, $J_{1,12}$ = $J_{10,11}$ = 1.8 Hz) at δ 6.57 and δ 6.31. The complete assignment of protons at positions eleven and twelve was not determined by double resonance experiments. A complex unresolved pattern of four protons which appeared between δ 6.21 and δ 5.47 was assigned to the four vinyl protons at positions five through eight. A broadened singlet and a doublet ($J_{9,10}$ = 4 Hz) at δ 5.20 and δ 4.95 were assigned to the protons at positions one and ten. The fact that only one of these protons experienced significant coupling supports the structural assignment with only one proton in the exo configuration. The two protons at position three gave rise to a multiplet between δ 3.59 and δ 2.97. The one remaining proton at δ 2.77 appeared as a doublet ($J_{2,9}$ = 8.0 Hz). This higher field position relative to the proton at position nine is consistent with the endo stereochemistry at this position.

Chemical evidence for these proposed structures was obtained in the following way. Irradiation of cis-2-

cyclooctenone (127) at room temperature in the presence of furan gave two Diels-Alder adducts. Both adducts were formed by thermal addition of furan to trans-2-cyclooctenone (75). Separation and purification of the two adducts was achieved by column chromatography on silica gel followed by short path distillation. The two adducts possess spectral properties which were very similar to those adducts obtained by Corey (56).

The structures of the two adducts were assigned in the following way. Both adducts gave correct element analyses calculated for $C_{12}H_{16}O_2$ which corresponds to a one-to-one adduct of furan and 2-cyclooctenone. The infrared spectra (Figures 39 and 43) of both adducts showed strong carbonyl absorptions at 1690 cm^{-1}. The nmr spectra (Figures 40 and 44) of adducts (159) and (160) possessed interesting similarities to the nmr spectra of adducts (157) and (158).

The protons at positions eleven and twelve in adduct (159) appeared as a nearly collapsed two proton AB pattern centered at δ 6.38. The two bridgehead protons at positions one and ten appeared as a doublet ($J_{1,2}$ = 4 Hz) and a broadened singlet at δ 4.88 and 4.38 respectively. Since only one of these two bridgehead protons experienced significant coupling, it was concluded that only one of the two protons at positions two and nine exists in the _exo_ configuration. A one proton multiplet set apart from the remaining eleven methylene protons between δ 2.55 and δ 1.20 was assigned to the proton at position two. This downfield shift from the remaining protons was expected, since _exo_ protons in 7-oxa-2-norbornene derivatives occur approximately 0.5 ppm downfield from the corresponding _endo_ protons.

The nmr spectrum of adduct (160) possessed remarkable similarities to adduct (158) obtained from 2,4,6-cyclooctatrienone. The protons at positions eleven and twelve appeared as a symmetrical eight line pattern which consisted of two sets of doublets of doublets ($J_{11,12}$ = 5.8 Hz, $J_{1,2} = J_{10,11}$ = 1.8 Hz) at δ 6.42 and δ 6.21. The two bridgehead protons at δ 5.04 and δ 4.69 occurred as a broadened singlet and a broadened doublet ($J_{9,10}$ = 4 Hz). The proton at position one was assigned to the singlet at δ 5.04 and the proton at position ten to the doublet. The remainder of the twelve protons appeared between δ 2.95 and δ 0.51 and were not resolved well enough for intrepretation.

The salient feature common to the spectra of all four compounds is that they show that only one of the two possible bridgehead protons in positions one and ten are significantly coupled to the other two bridgehead protons at positions two and nine. It can therefore be concluded that all four adducts are derived from intermediates which possess trans stereochemistry at the reactive carbon-carbon double bond.

The comparative structural relationships between adducts (157) and (158) and adducts (159) and (160) was established by catalytic hydrogenation of all four adducts with prereduced Adam's catalyst. Adducts (157) and (159) gave an identical perhydroderivative as did adducts (158) and (160). The identity of each set of adducts was shown by comparative spectral data and glpc retention times.

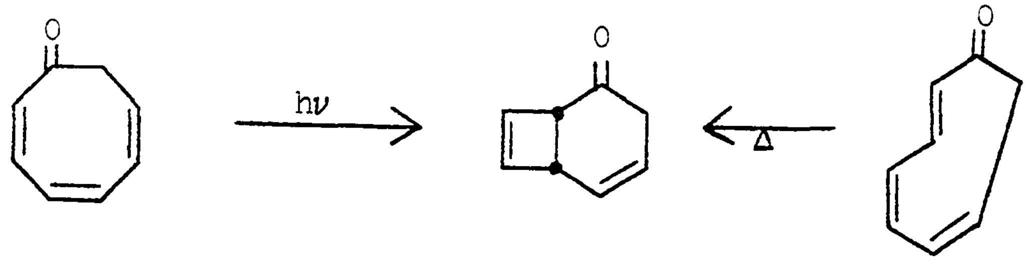
The mass spectra (Figures 42 and 46) of both new perhydroadducts (161) and (162) showed molecular ions at m/e 194. Element analyses calculated for $C_{12}H_{18}O_2$ were obtained for both adducts and the infrared spectra (Figures 39 and 43) showed strong carbonyl absorptions at 1690 cm^{-1}. The nmr spectrum (Figure 40) of perhydroadduct (161) was readily distinguished from the spectrum (Figure 44) of perhydroadduct (162). Adduct (161) showed a poorly resolved one proton triplet at δ 4.53 and a one proton doublet at δ 4.03. A rigorous assignment of these proton absorptions was not possible, however, a tentative assignment of the proton at position one to the triplet and the proton at position ten to the doublet is plausible. A partially resolved triplet at δ 3.58 probably belonged to the proton at position two. The remaining thirteen protons between δ 2.50 and δ 1.10 were not resolved.

Adduct (162) obtained from adducts (158) and (159) showed a one proton doublet (J = 4 Hz) at δ 4.74 which was assigned to the proton at position one. A second one proton absorption appeared as a poorly resolved triplet at δ 4.28 which was assigned to the proton at position ten. The remainder of the spectrum consisted of a sixteen proton unresolved pattern between δ 2.80 and δ 1.10.

Attempts to isomerize adducts (159) and (160) with base met with only partial success. Adduct (159) cleanly isomerized to the more stable adduct with both protons in the *endo* configuration. A complete characterization of this isomer was not obtained. It could readily be observed from the nmr spectrum of this adduct that the proton absorption at δ 4.88 in the starting material collapsed from a doublet to a singlet, so both protons at positions one and ten appeared as singlets. Adduct (160) did not behave similarly but appeared to undergo more complex transformations upon treatment with base and was not investigated in greater detail. No attempts to isomerize adducts (159) or (160) were performed because of the high probability that both would rearrange to α,β-unsaturated ketones.

Low temperature experiments were performed to show that formation of adducts (157) and (158) occurred by way of thermal addition of furan to photochemically generated trans,cis,cis-2,4,6-cyclooctatrienone. A sample of 2,4,6-cyclooctatrienone which contained about 25% furan by volume was irradiated at low temperatures in a manner similar to that used for neat 2,4,6-cyclooctatrienone. The behavior of the sample upon irradiation appeared identical to that observed for 2,4,6-cyclooctatrienone. Upon warming the 1731 cm^{-1} transient in the presence of furan, two Diels-Alder adducts (157) and (158) were formed. Within the limits of detection by infrared spectroscopy, no furan adducts were formed during the low temperature irradiation. A preparative scale irradiation of 2,4,6-cyclooctatrienone in furan-ether-isopentane at -190° followed by tlc analysis of the mixture obtained by warming the cold, irradiated solution of furan and 2,4,6-cyclooctatrienone showed that two adducts with R_f values identical to the adducts (157) and (158) were present in the solution. Bicyclo[4.2.0]octa-4,7-dien-2-one could not be detected in this mixture by tlc or glpc. In a similar low temperature experiment with 2,4,6-cyclooctatrienone in the absence of furan, this bicyclic isomer could not be detected by tlc or glpc. It was assumed that dimers or oligomers were formed by way of trans,cis,cis-2,4,6-cyclooctatrienone. No attempt was made to characterize these new compounds.

The formation of bicyclo[4.2.0]octa-4,7-dien-2-one at room temperature could conceivably occur by way of direct photochemical closure across positions two and five with a disrotatory motion of "p" orbitals at these atoms or it could result from a thermal electrocyclic closure of trans,cis,cis-2,4,6-cyclooctatrienone with a conrotary motion of the "p" orbitals at positions two and five. Inspection of the basic set of orbitals in each transition



state shows that disrotatory closure is allowed photochemically and the conrotatory closure is allowed thermally. The basic set of orbitals in the transition state of the disrotatory closure has no nodes and involves four pi electrons. One node occurs in the basis set of orbitals for the transition state of the conrotatory closure which still involves four pi electrons. If the ring closure to the bicyclic isomer is a concerted process, the conrotatory process would follow a thermal reaction pathway. The mode of closure of 2,4,6-cyclooctatrienone could not be determined from the stereochemistry at the bridgehead positions of bicyclo[4.2.0]octa-4,7-dien-2-one because photochemical closure of cis,cis,cis-2,4,6-cyclooctatrienone or thermal closure of trans,cis,cis-2,4,6-cyclooctatrienone would lead to the same stereochemistry in the resulting product. Buchi (54) demonstrated that the two hydrogen atoms at positions one and six were cis in the bicyclic isomer obtained by irradiation of 2,4,6-cyclooctatrienone. Photochemical closure of trans,cis,cis-2,4,6-cyclooctatrienone was not considered as a likely possibility because of the exceedingly high thermal reactivity of this isomer at room temperature. The steady state concentration of trans,cis,cis-2,4,6-cyclooctatrienone would be expected to be unusually low relative to cis,cis,cis-2,4,6-cyclooctatrienone and it would not be expected to compete effectively with cis,cis,cis-2,4,6-cyclooctatrienone for light at 360 nm. Distortion of the eight membered ring by the trans 2,3-double bond would probably destroy the conjugation of the 2,3-double bond with the carbonyl group. Eaton (75) has shown that the carbonyl group of trans-2-cyclooctenone exhibits properties of a non-conjugated chromophore.

A choice in favor of one of the two possible modes for formation of bicyclo[4.2.0]octa-4,7-dien-2-one, i.e., thermal electrocyclic closure of thermal electrocyclic closure of trans,cis,cis-2,4,6-cyclooctatrienone instead of photochemical closure of cis,cis,cis-2,4,6-cyclooctatrienone was made in view of the following information. Bicyclo[4.2.0]octa-4,7-dien-2-one was not detected as a photoproduct when 2,4,6-cyclooctatrienone was irradiated as a neat film at room temperature or in a rigid glass at low temperatures. 1,3-Cycloheptadiene and 2-pyrone undergo facile photochemical closure to their corresponding cyclobutene derivatives at low temperatures (82). This information suggests that bicyclo[4.2.0]octa-4,7-dien-2-one is not formed directly from a photoexcited state of *cis*,*cis*,*cis*-2,4,6-cyclooctatrienone, but that it may be formed by thermal electrocyclic closure of *trans*,*cis*,*cis*-2,4,6-cyclooctatrienone. Liu (73) has shown that thermal electrocyclic closure of *trans*,*cis*-1,3-cyclooctadiene gives *cis*-bicyclo[4.2.0]oct-7-ene.

To test this hypothesis, two possible mechanistic schemes representing the formation of bicyclo[4.2.0]octa-4,7-dien-2-one and adducts (**157**) and (**158**) were considered.

$$K_C \xrightarrow{\phi' Ia} K_B$$

$$K_C \xrightarrow{\phi Ia} K_T$$

$$K_T \xrightarrow{k_1} K_B$$

$$K_T \xrightarrow{k_{-1}} K_C$$

$$\text{furan} + K_T \xrightarrow{k_2} K_A$$

K_C is 2,4,6-cyclooctatrienone, K_B is bicyclo[4.2.0]octa-4,7-dien-2-one, K_T is trans,cis,cis-2,4,6-cyclooctatrienone, K_A is the sum of adducts (157) and (158), Ia is the light intensity, ϕ' is the quantum yield for formation of bicyclo[4.2.0]octa-4,7-dien-2-one and ϕ is the quantum yield for cis,trans isomerization. An examination of these two mechanistic schemes indicated that a distinction between them might be possible by investigating the effects of varying furan concentrations on the yields of each of these products.

If it is assumed that the only reactive intermediate responsible for the formation of bicyclo[4.2.0]octa-4,7-dien-2-one and adducts (157) and (158) is K_T, then a comparison of the rates of formation of these compounds gives the following expression. This expression predicts

$$\frac{K_A}{K_B} = \frac{k_2[\text{furan}][K_T]}{k_1[K_T]}$$

that the ratio of the yields of adducts (157) and (158) to the yield of bicyclo[4.2.0]octa-4,7-dien-2-one should vary in a linear fashion with changes in the furan concentration. However, if adducts (157) and (158) are formed from trans,cis,cis-2,4,6-cyclooctatrienone and bicyclo[4.2.0]octa-4,7-dien-2-one is formed directly from an excited state of cis,cis,cis-2,4,6-cyclooctatrienone, then the following expression gives the ratio of adducts

$$\frac{K_A}{K_B} = \frac{k_2[\text{furan}][K_T]}{\phi' Ia}$$

$$[K_T] = \frac{\phi Ia}{k_{-1} + k_2[F]}$$

(157) and (158) to bicyclo[4.2.0]octa-4,7-dien-2-one. By substituting the expression for the steady state concentration of K_T into the previous equation followed by inversion and rearrangement of terms gives an equation

$$\frac{K_B}{K_A} = \frac{\phi' k_{-1}}{\phi k_2[\text{furan}]} + \frac{\phi'}{\phi}$$

which predicts that the ratio of bicyclo[4.2.0]octa-4,7-dien-2-one to adducts (157) and (158) should vary in a linear fashion when plotted against the reciprocal of the furan concentrations.

Irradiation of 2,4,6-cyclooctatrienone in the presence of varying concentrations of furan showed that the ratio of the yield of adducts (157) and (158) to the yield of bicyclo[4.2.0]octa-4,7-dien-2-one varied in a linear fashion as a function of furan concentration (Figure 47). When the ratio of the yield of bicyclo[4.2.0]octa-4,7-dien-2-one to the yield of adducts (157) and (158) was plotted versus the reciprocal of furan concentration, a non-linear relationship was observed (Figure 48). This data strongly supports the intermediacy of trans,cis,cis-2,4,6-cyclooctatrienone during the formation of bicyclo[4.2.0]octa-4,7-dien-2-one.

A summary of the photochemistry of 2,4,6-cyclooctatrienone is shown in Figure 49.

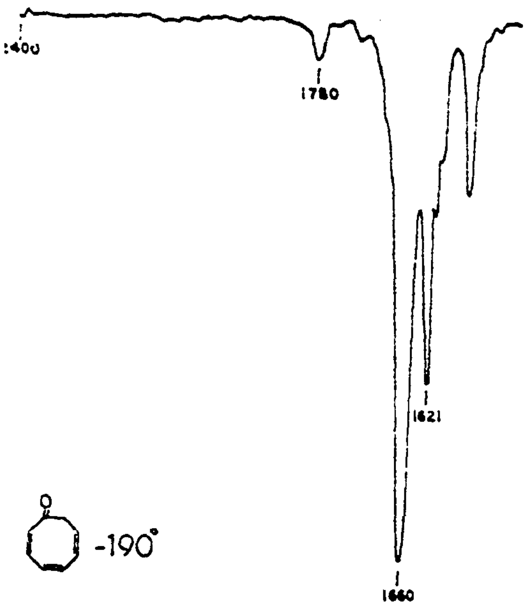
Figure 33. Low temperature infrared spectra (neat)

Top left--2,4,6-cyclooctatrienone (-190°)

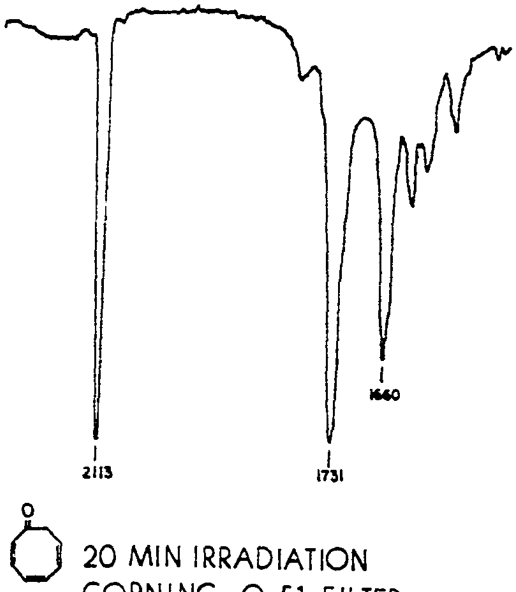
Top right--2,4,6-cyclooctatrienone (-190°) irradiated through a Corning 0-51 filter

Bottom left--2,4,6-cyclooctatrienone irradiated through a Corning 0-51 filter and warmed to -127°

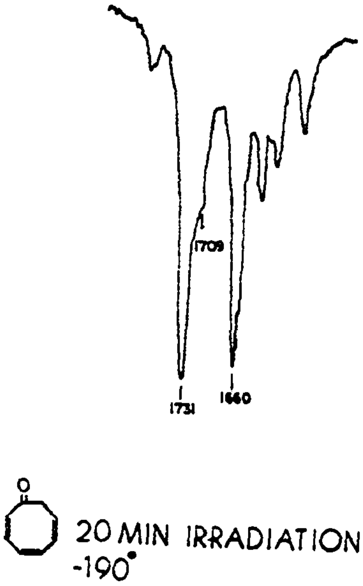
Bottom right--2,4,6-cyclooctatrienone irradiated through a Corning 0-51 filter and warmed to -107°



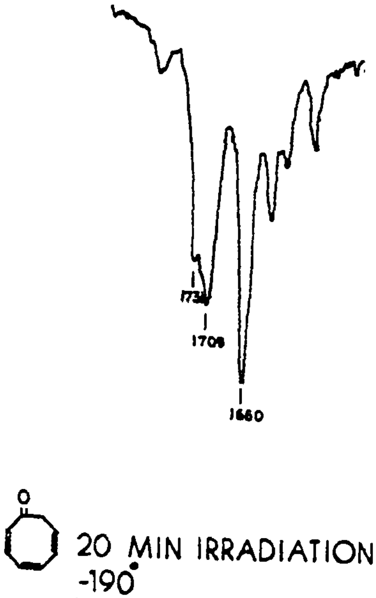
-190°



20 MIN IRRADIATION
CORNING O-51 FILTER
-190°



20 MIN IRRADIATION
-190°
WARMED TO -127°



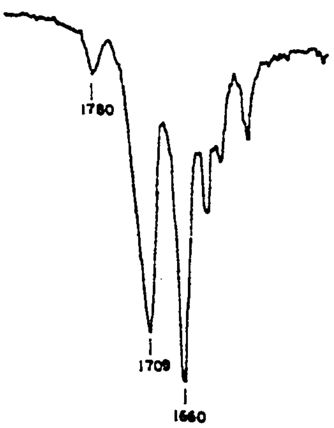
20 MIN IRRADIATION
-190°
WARMED TO -107°

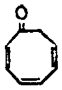
Figure 34. Low temperature infrared spectra

Top left--2,4,6-cyclooctatrienone irradiated through a Corning 0-51 filter and warmed to -95°

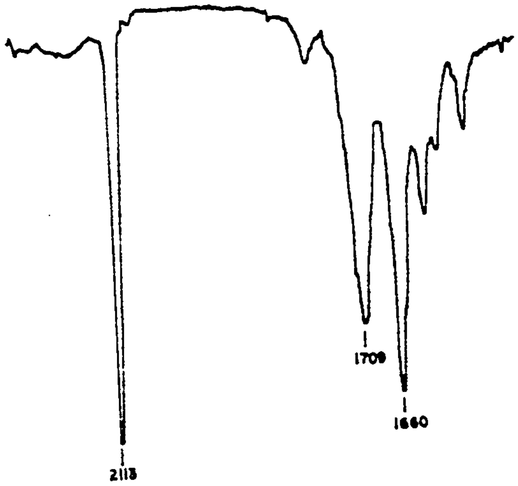
Top right--2,4,6-cyclooctatrienone irradiated through a Corning 0-51 filter, warmed to -95° and cooled to -190°

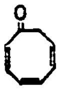
Bottom left--2,4,6-cyclooctatrienone irradiated through a Corning 0-51 filter, warmed to -55° and cooled to -190°



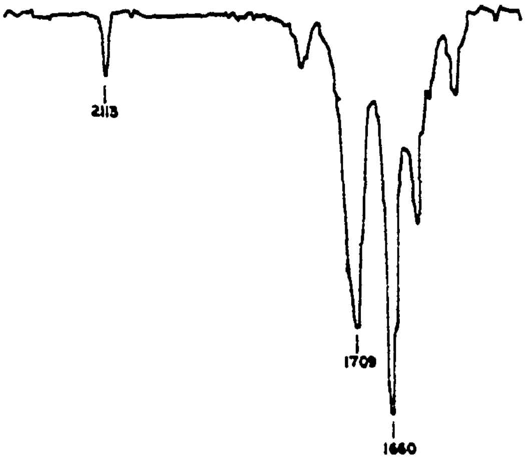


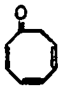
20 MIN IRRADIATION
-190
WARMED TO -95°





20 MIN · IRRADIATION
-190°
WARMED TO -95°
COOLED TO -190°





20 MIN IRRADIATION
-190°
WARMED TO -55°
COOLED TO -190°

Figure 35. A plot of absorbances of selected infrared absorption bands versus time obtained from the infrared spectra of a cold, irradiated sample of 2,4,6-cyclooctatrienone

| - 2113 cm^{-1}

● - 1731 cm^{-1}

▲ - 1660 cm^{-1}

▮ - 1624 cm^{-1}

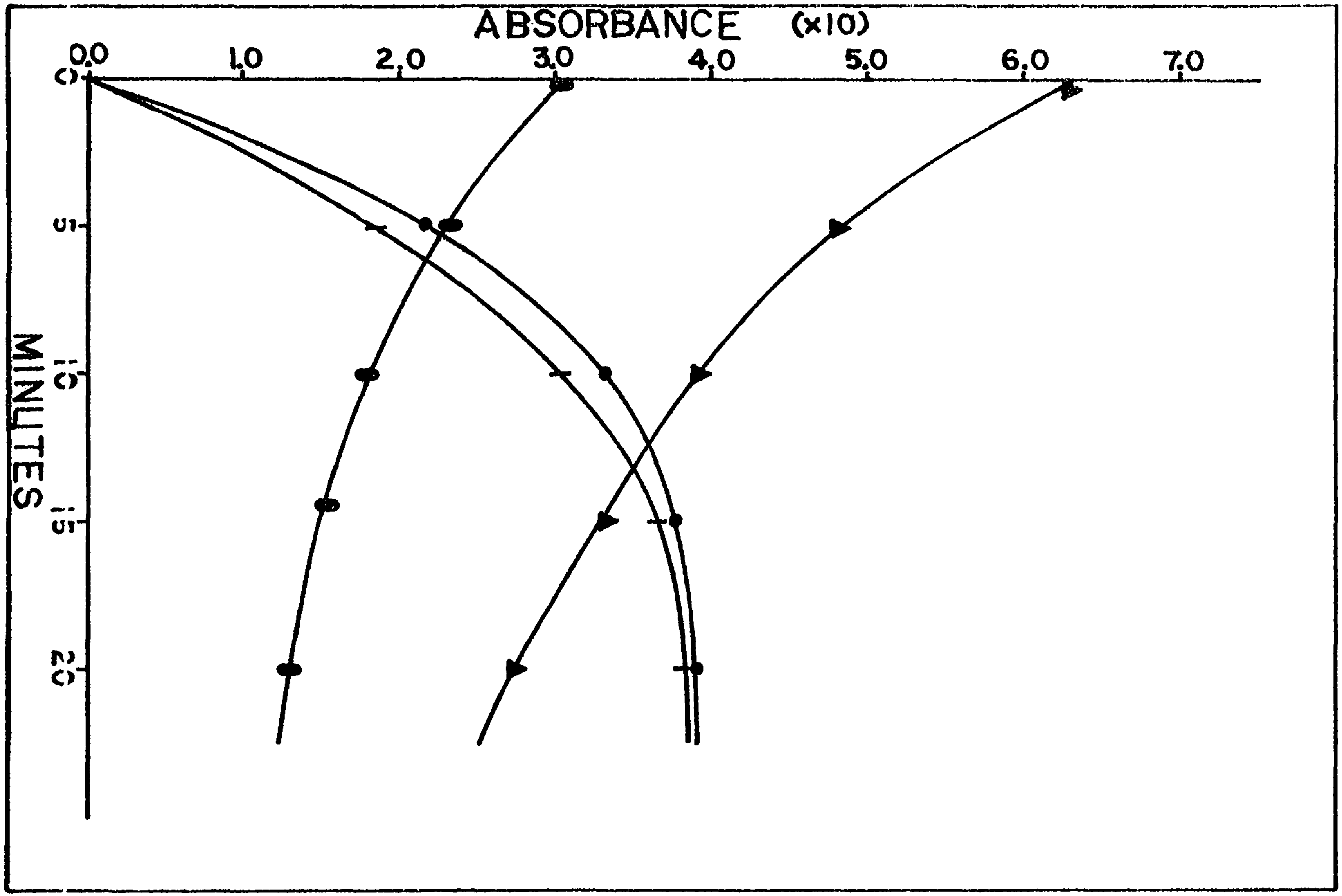

ABSORBANCE (x10)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
MINUTES
0
5
10
15
20

Figure 36. A plot of absorbances of selected infrared absorption bands versus temperature which were calculated from the spectra obtained by warming a cold, irradiated sample of 2,4,6-cyclooctatrienone

| - 2113 cm^{-1}

● - 1731 cm^{-1}

⬮ - 1709 cm^{-1}

▲ - 1668 cm^{-1}

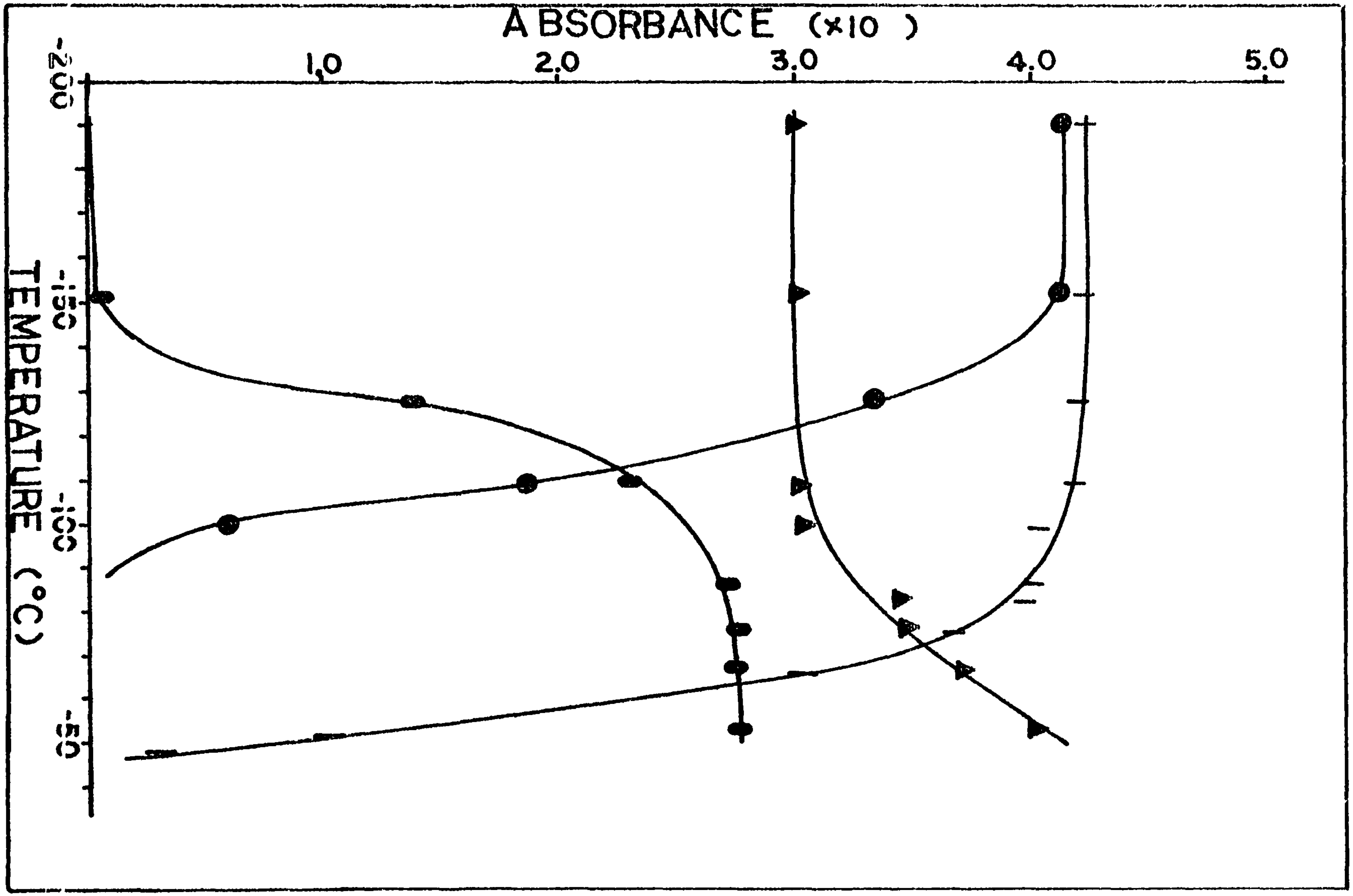
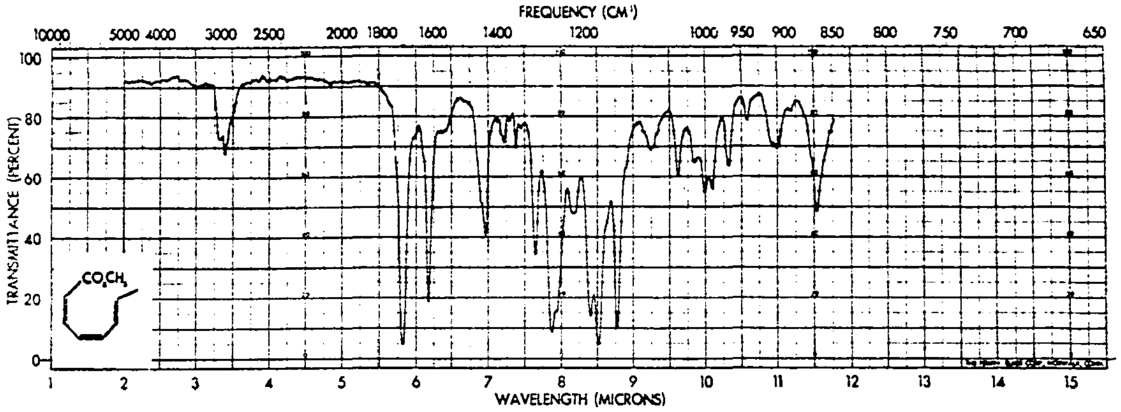

ABSORBANCE (×10)
1,0
2,0
3,0
4,0
5,0
-200
-150
-100
-50
TEMPERATURE (°C)

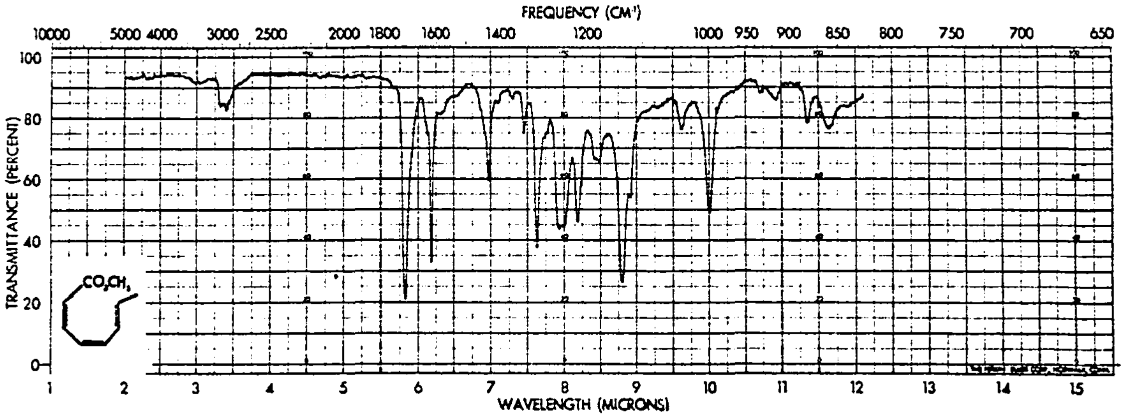
Figure 37. Infrared spectra (neat)

Top--methyl 2,4,6-octatrienoate (stereochemistry unspecified)

Middle--methyl 2,4,6-octatrienoate (stereochemistry unspecified)

Bottom--bicyclo[4.2.0]octa-4,7-dien-2-one


FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
CO₂CH₃
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
CO₂CH₃
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

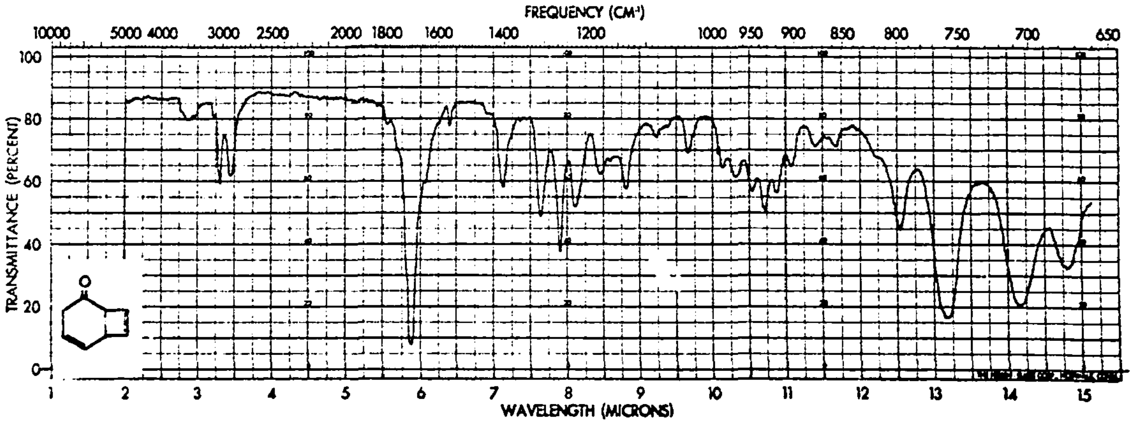
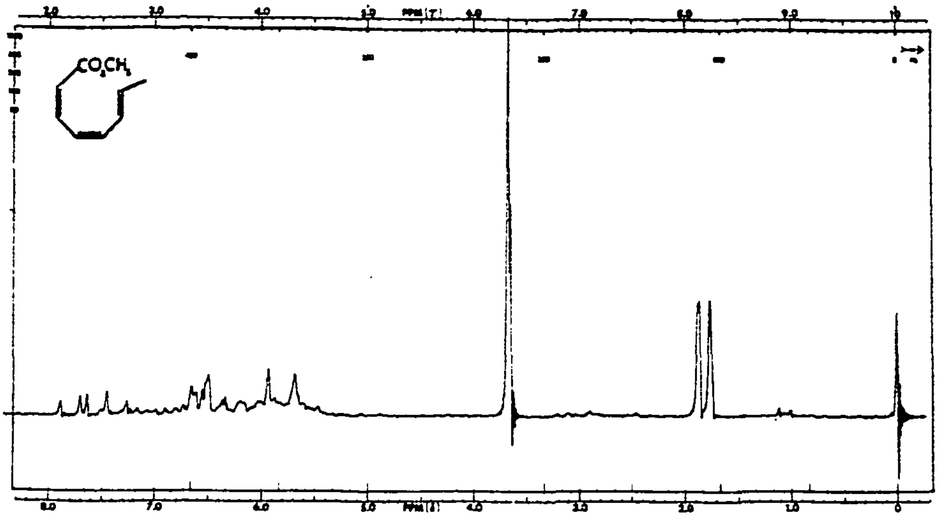

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
O
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

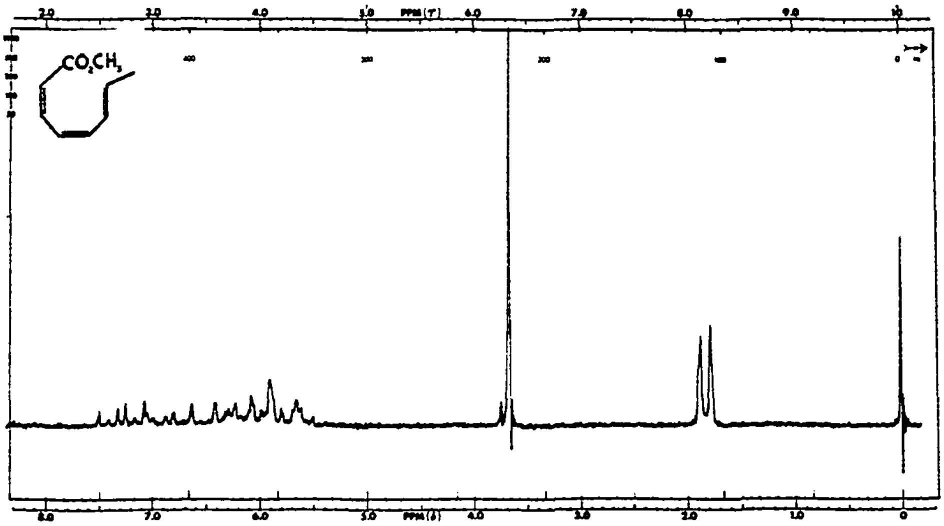
Figure 38. Nuclear magnetic resonance spectra (CCl_4)

Top--methyl 2,4,6-octatrienoate (stereochemistry unspecified)

Middle--methyl 2,4,6-octatrienoate (stereochemistry unspecified)

Bottom--bicyclo[4.2.0]octa-4,7-dien-2-one


CO$_2$CH$_3$
2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0


CO$_2$CH$_3$
2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0

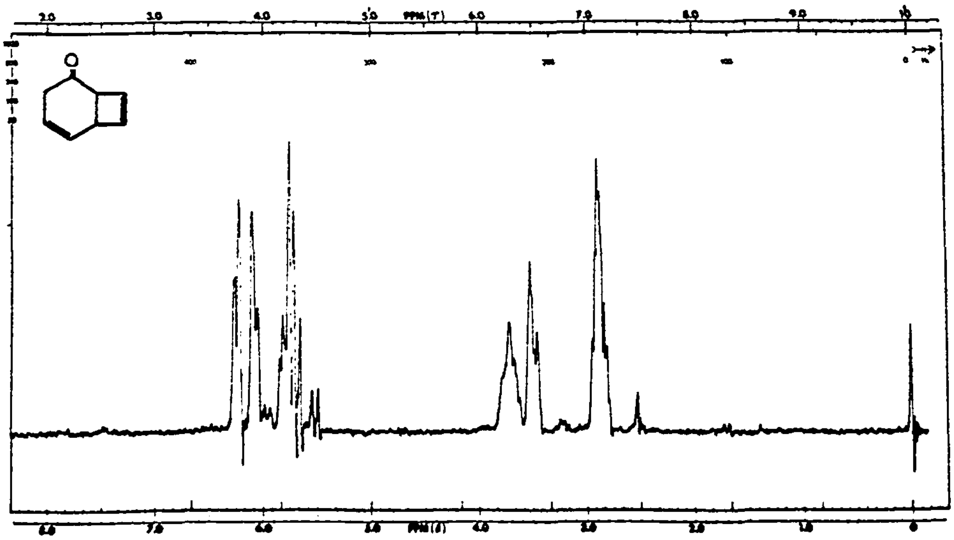
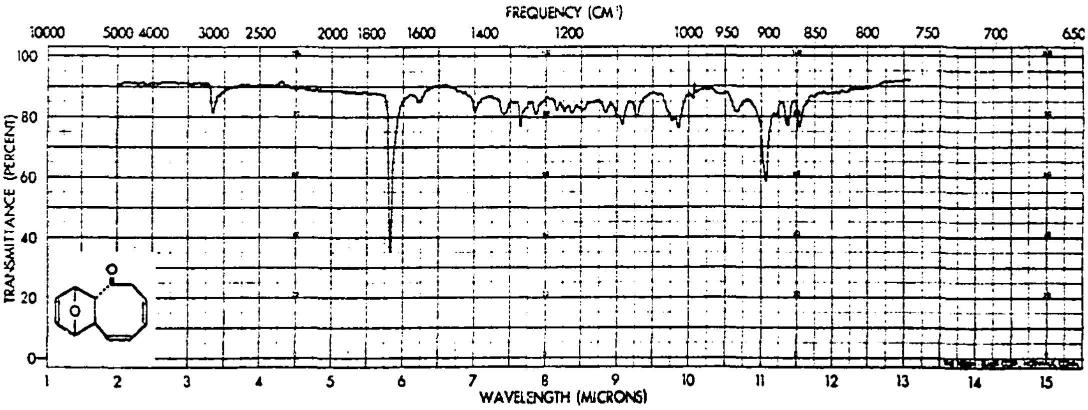

O
2.0
3.0
4.0
5.0
PPM(τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM(δ)
4.0
3.0
2.0
1.0
0

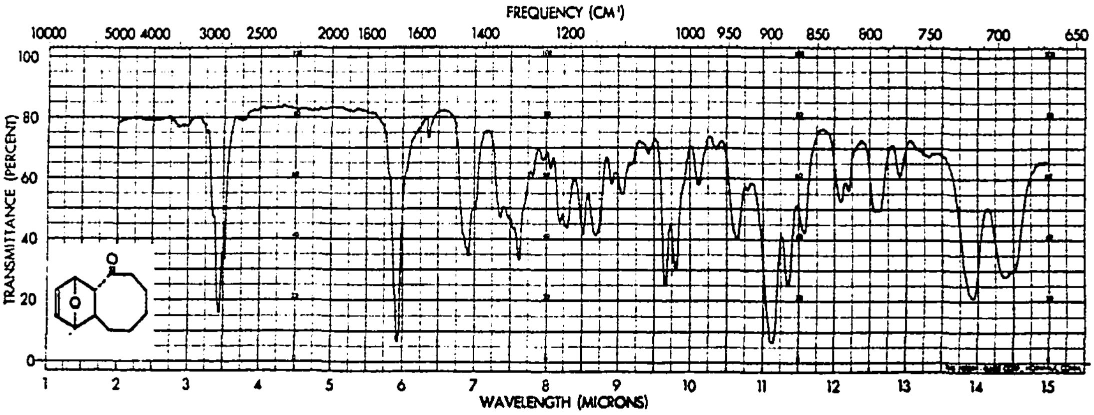
Figure 39. Infrared spectra (CCl_4)

Top--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

Middle--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-11-en-3-one

Bottom--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-3-one


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


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

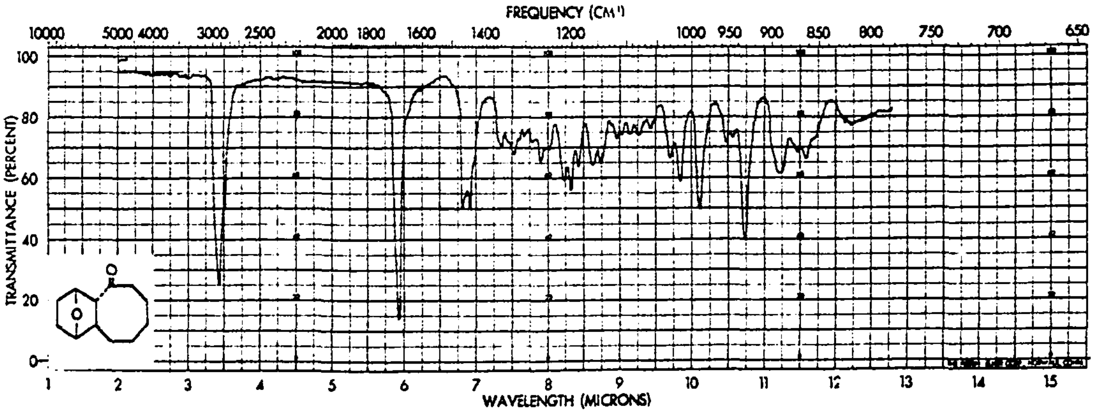
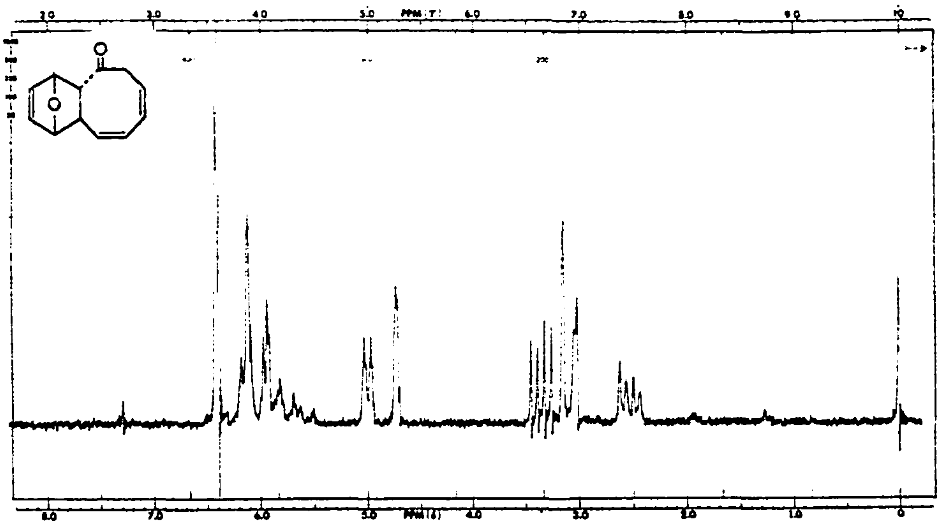

FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
O
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

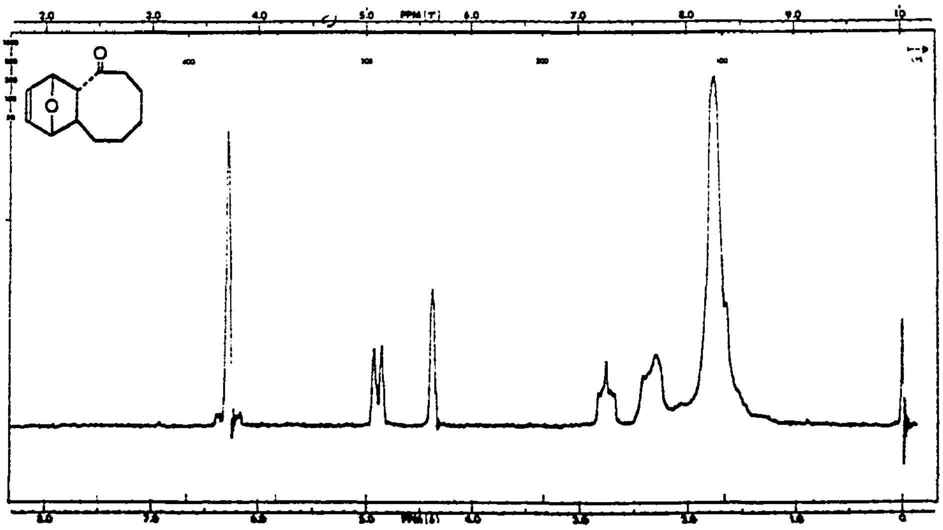
Figure 40. Nuclear magnetic resonance spectra ($CDCl_3$)

Top--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

Middle--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-11-en-3-one

Bottom--1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-3-one


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

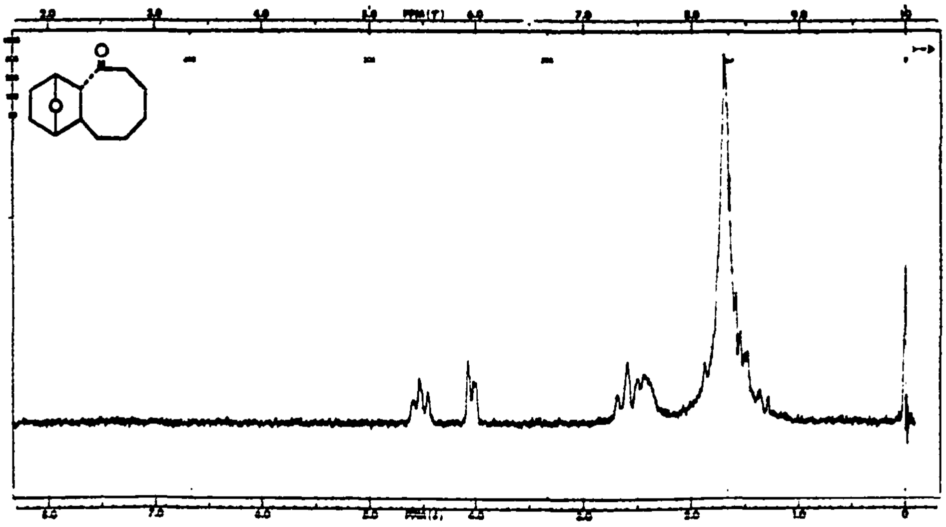

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 41. Mass spectrum (70 ev)

1(RS), 2(RS), 9(RS), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

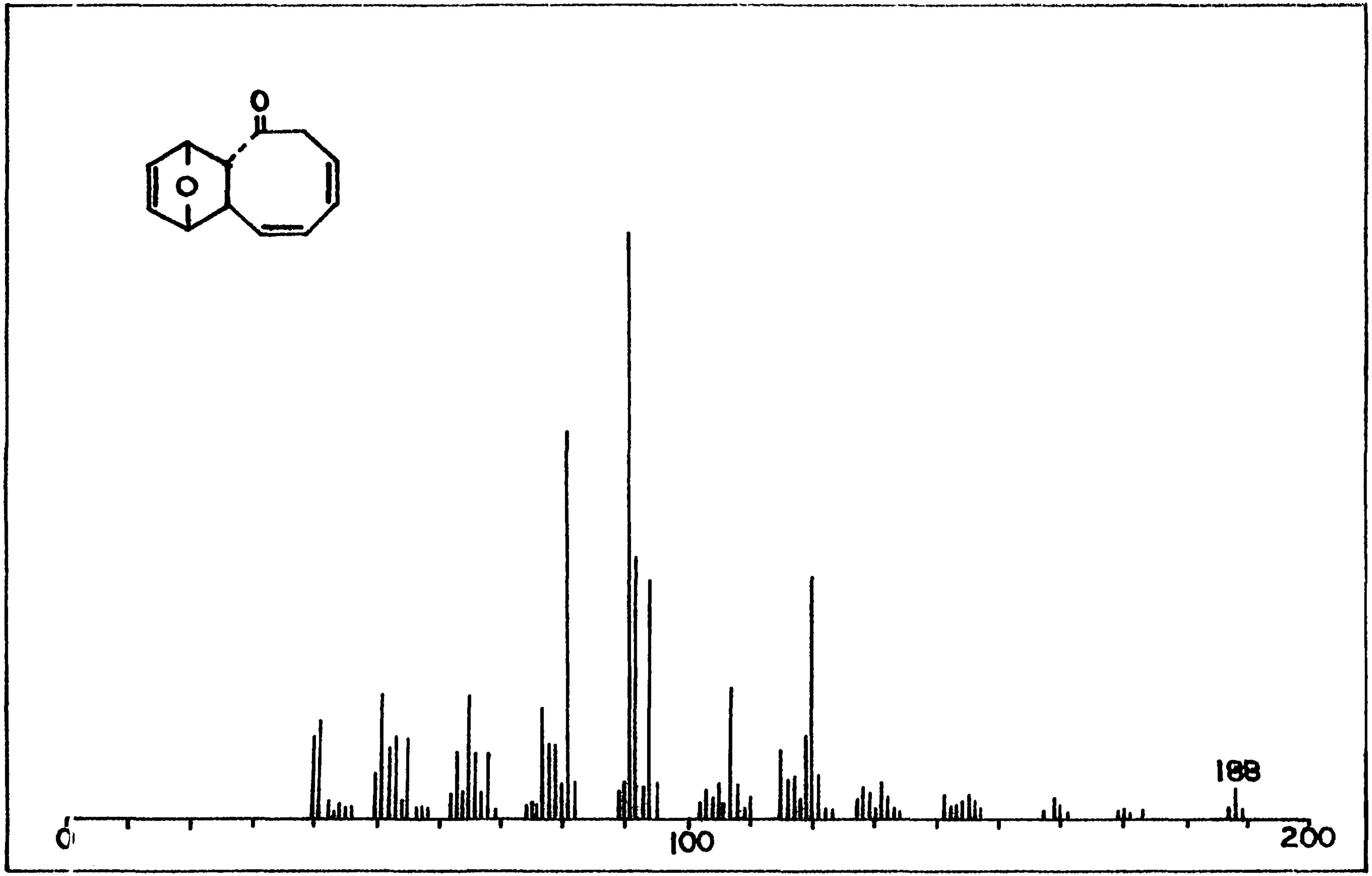

O
O
188
0
100
200

Figure 42. Mass spectrum (70 ev)

1(RS), 2(RS), 9(RS), 10(SR)-13-oxatricyclo[8.2.1.$0^{2,9}$]trideca-3-one

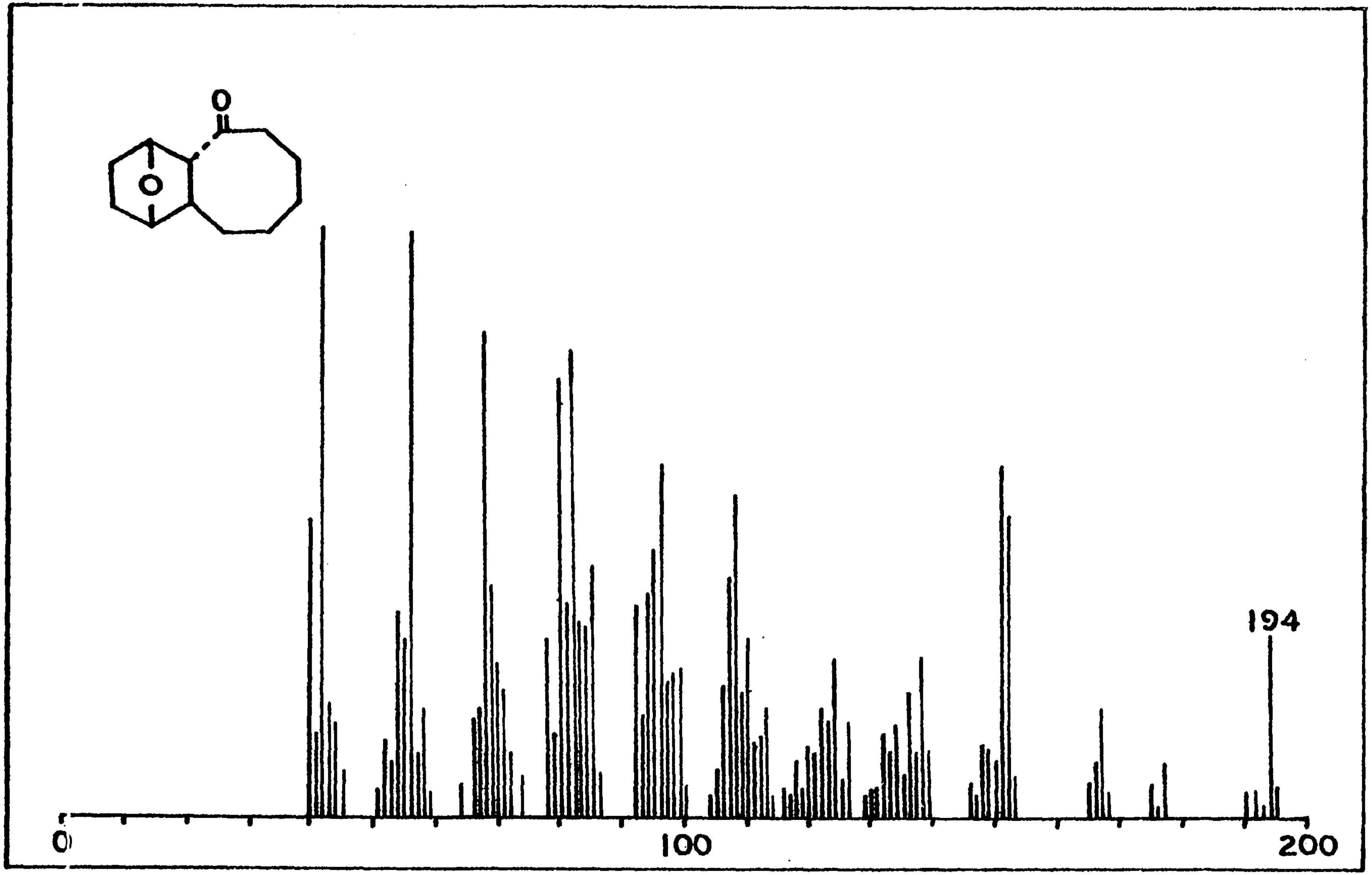
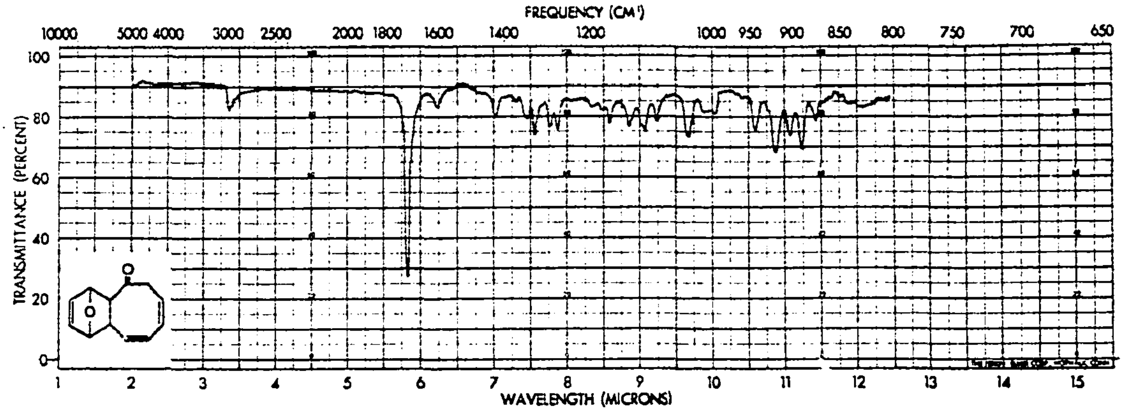

O
O
194
0
100
200

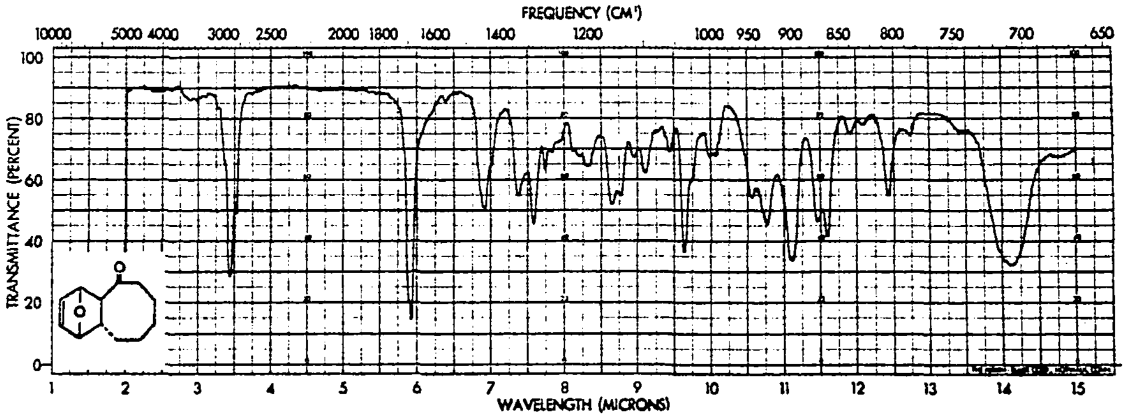
Figure 43. Infrared spectra (CCl_4)

Top--1(RS), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

Middle--1(RS), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-11-en-3-one

Bottom--1(RS), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-3-one


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


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

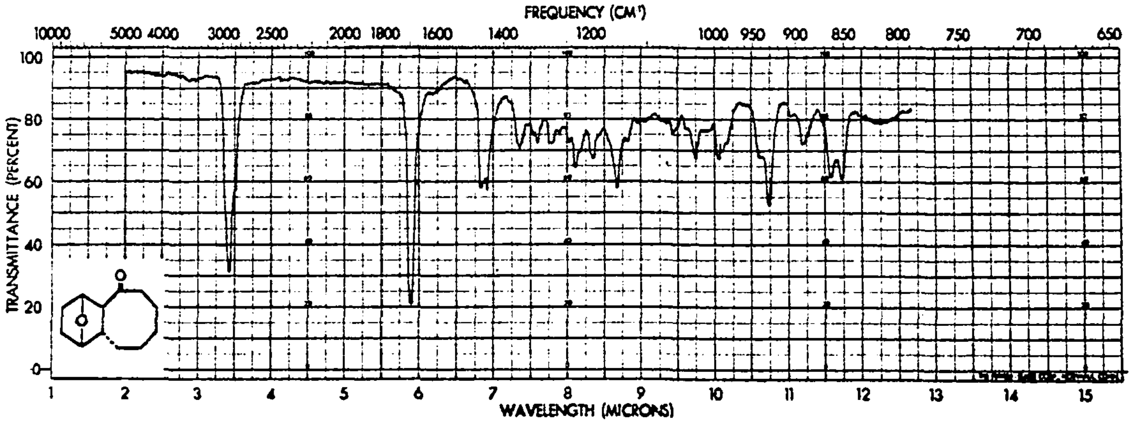
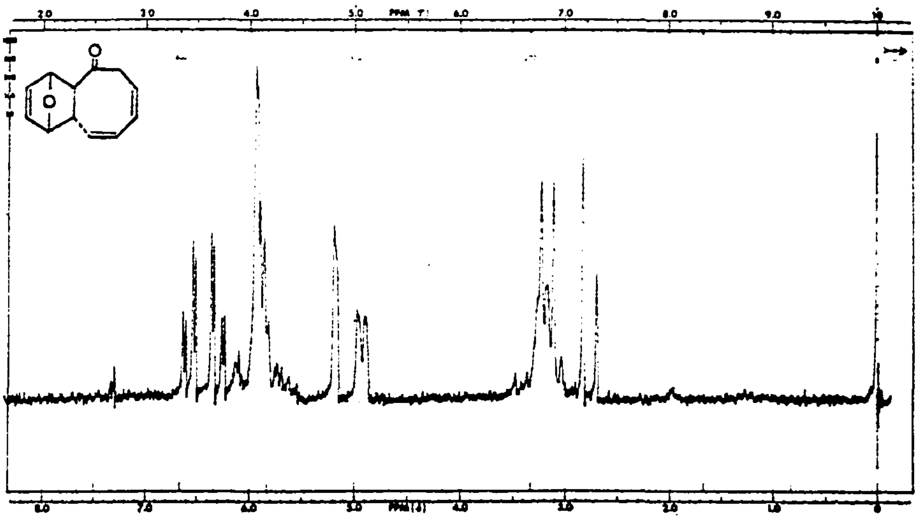

FREQUENCY (CM⁻¹)
10000
5000 4000
3000 2500
2000 1800
1600
1400
1200
1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
0
20
40
60
80
100
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
O

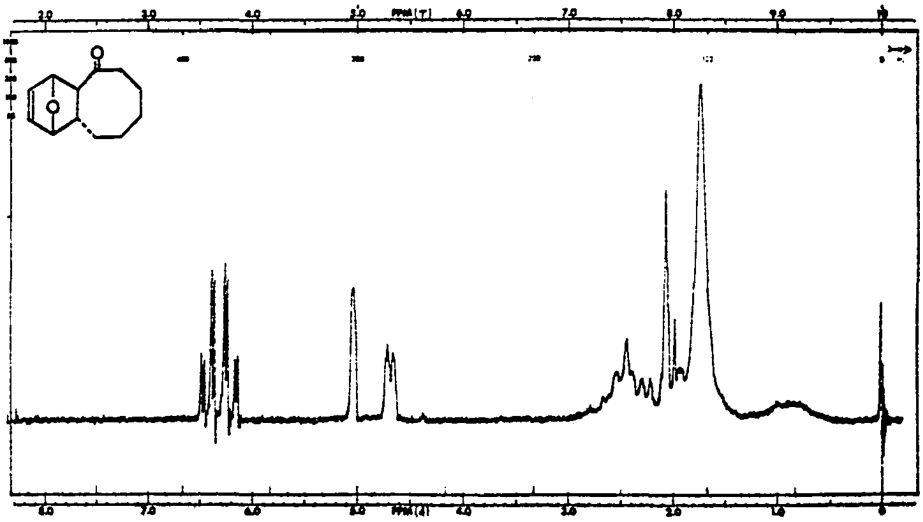
Figure 44. Nuclear Magnetic Resonance Spectra ($CDCl_3$)

Top--1(RS), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

Middle--1(RS), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-11-en-3-one

Bottom--1(SR), 2(SR), 9(SR), 10(SR)-13-oxa-tricyclo[8.2.1.$0^{2,9}$]trideca-3-one


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

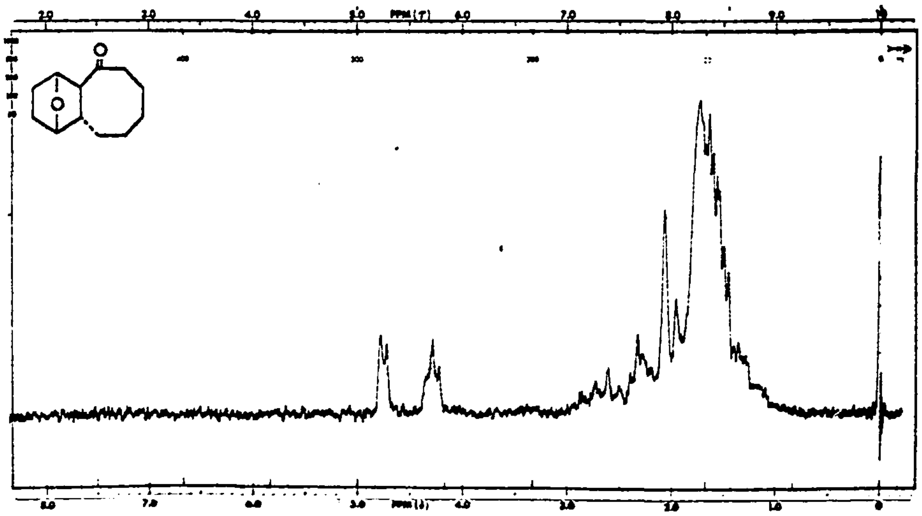

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 45. Mass spectrum (70 ev)

1(RS), 2(SR), 9(SR), 10(SR)-13-oxatricyclo[8.2.1.$0^{2,9}$]trideca-5,7,11-trien-3-one

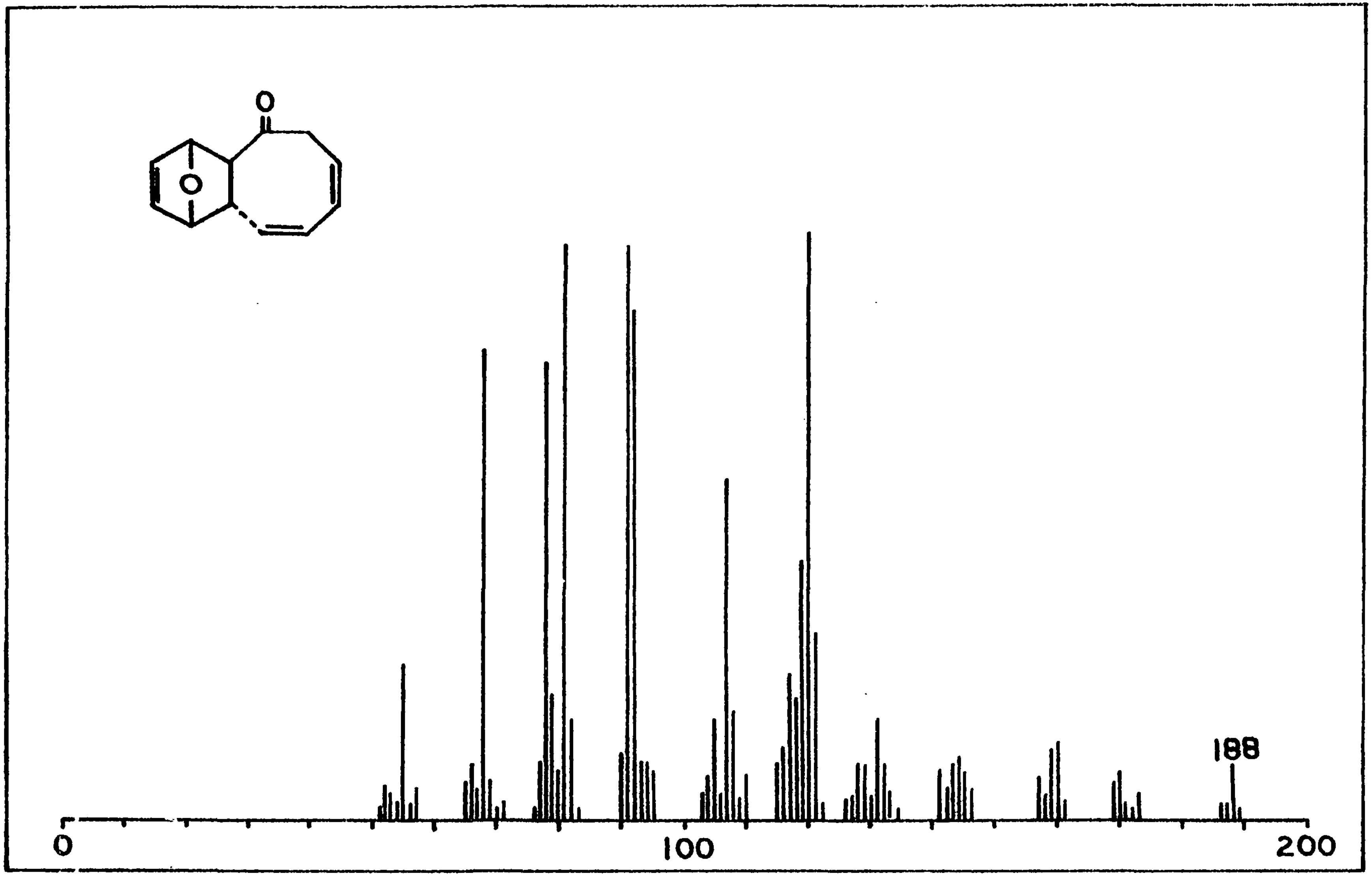

O
O
188
0
100
200

Figure 46. Mass spectrum (70 ev)

1(RS), 2(SR), 9(SR), 10(SR)-13-oxatricyclo[8.2.1.$0^{2,9}$]trideca-3-one

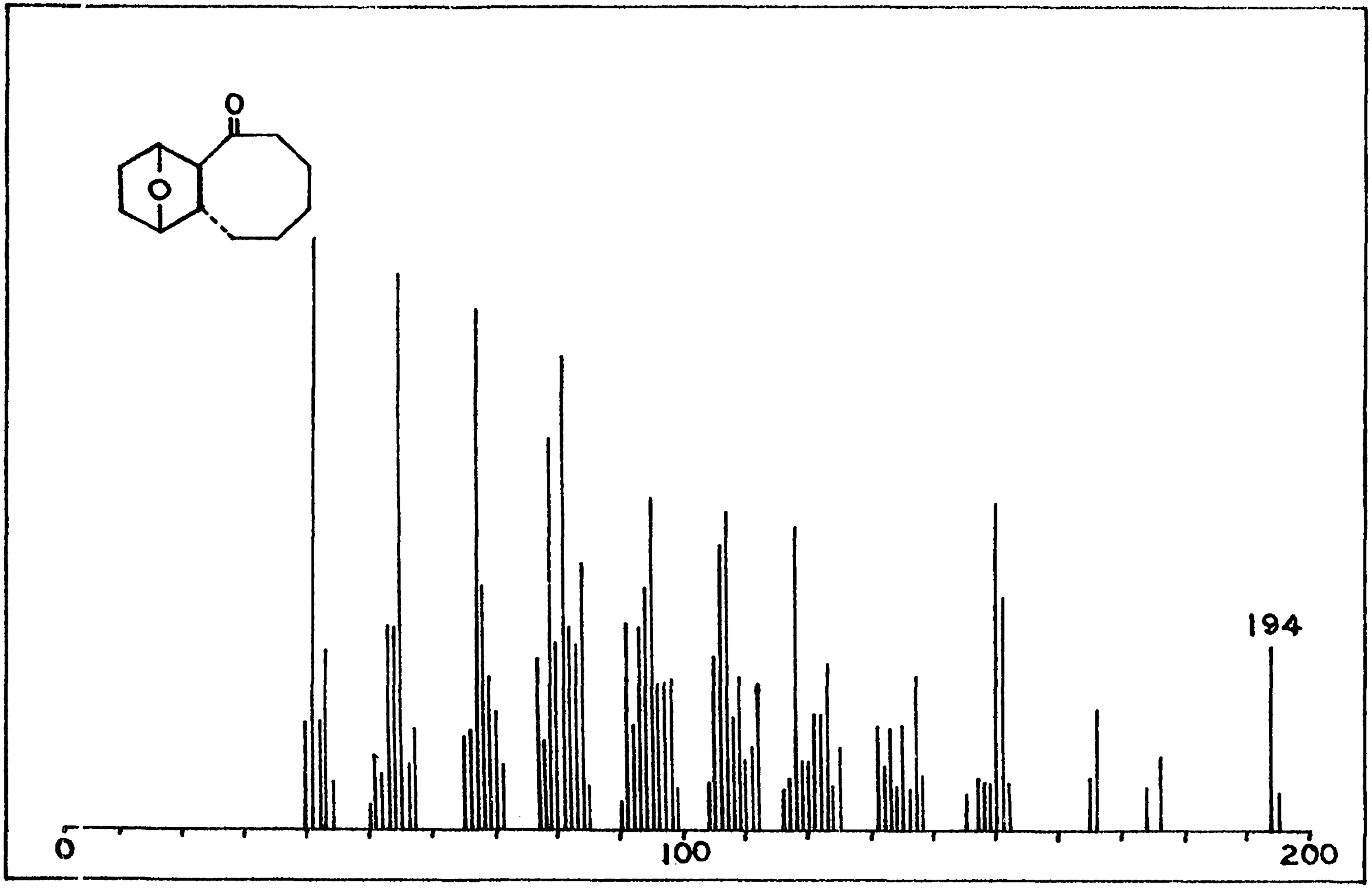

O
O
194
0
100
200

Figure 47. A plot of the ratio of the sum of the moles of adducts (157) and (158) to the moles of bicyclo[4.2.0]octa-4,7-dien-2-one versus furan concentration

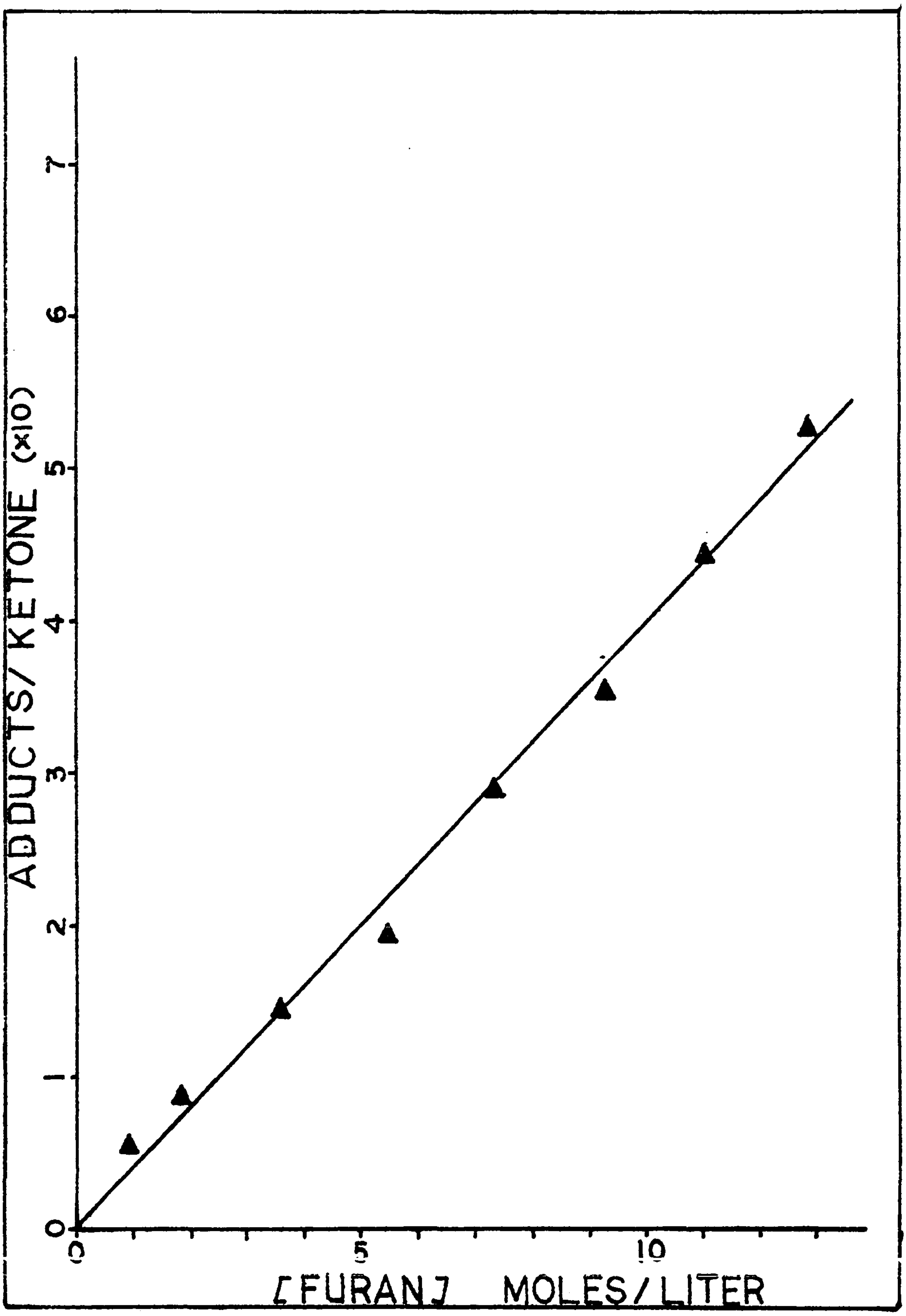

ADDUCTS/ KETONE (x10)
0
1
2
3
4
5
6
7
0
5
10
[FURAN] MOLES/LITER

Figure 48. A plot of the ratio of the moles of bicyclo-[4.2.0]octa-4,7-dien-2-one to the sum of the moles of adducts (157) and (158) versus the reciprocal of the furan concentration

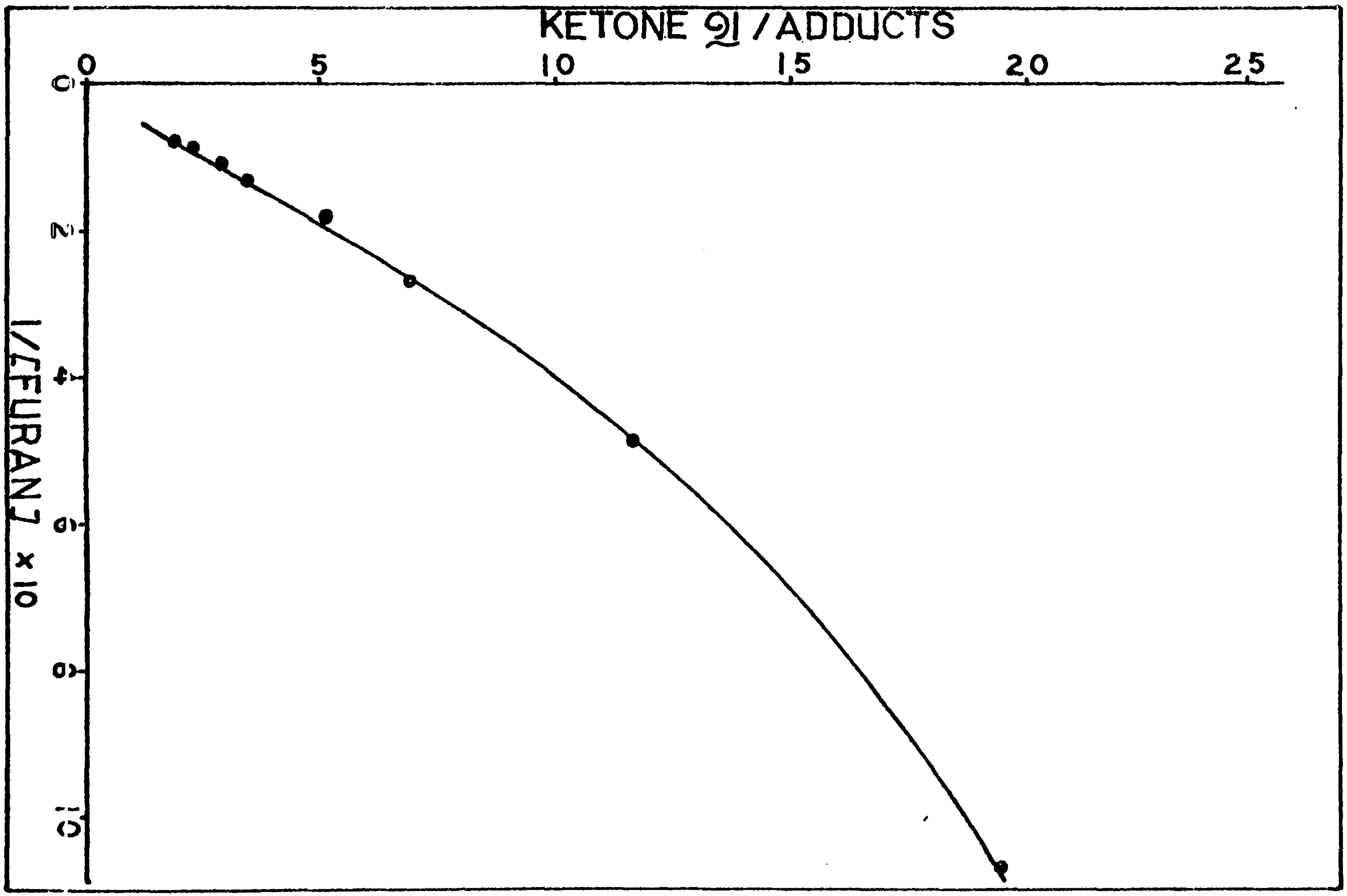
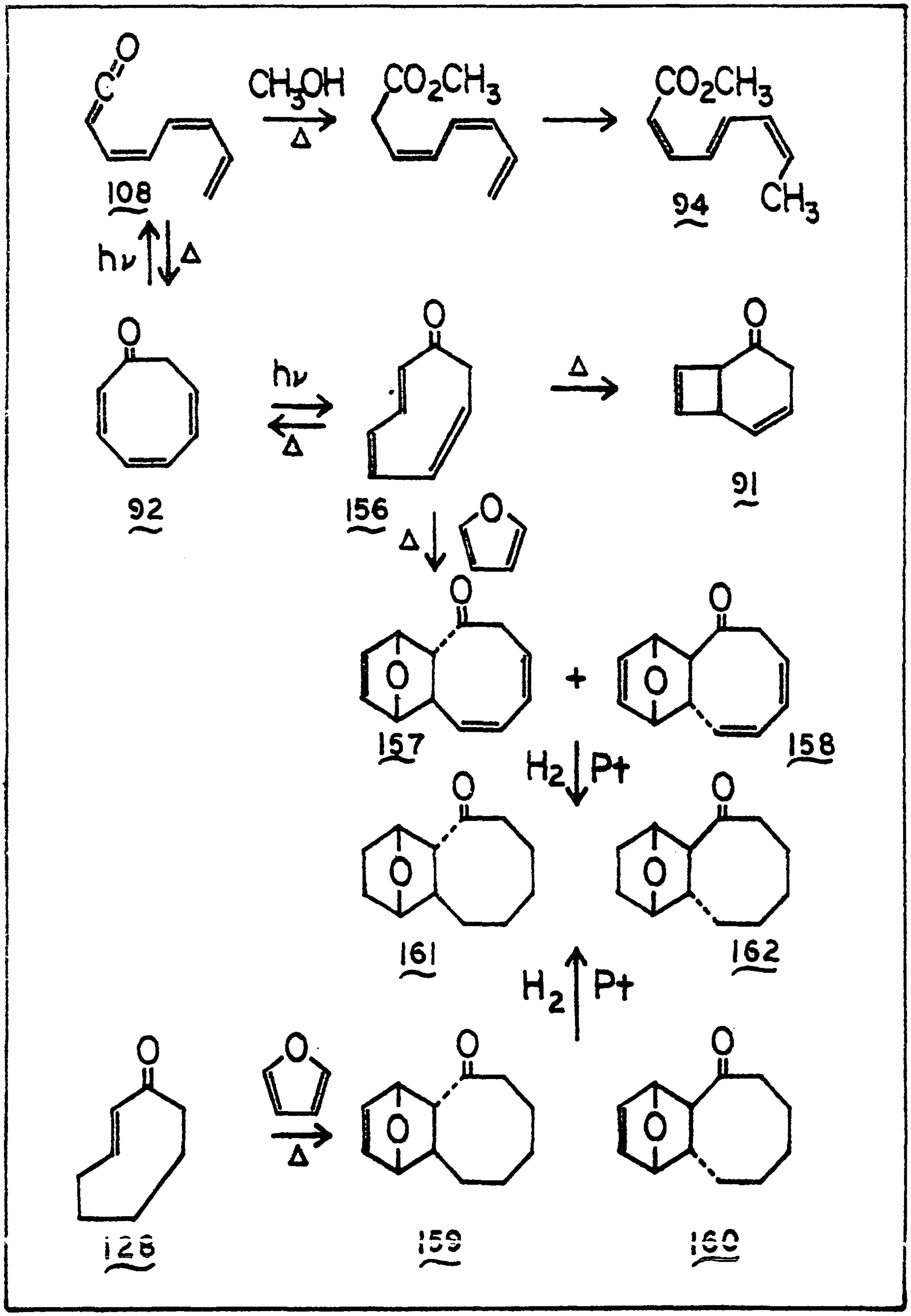

KETONE 91 / ADDUCTS
0
5
10
15
20
25
0
2
4
6
8
10
1/[FURAN] x10

Figure 49. A summary of the photochemistry of 2,4,6-cyclooctatrienone

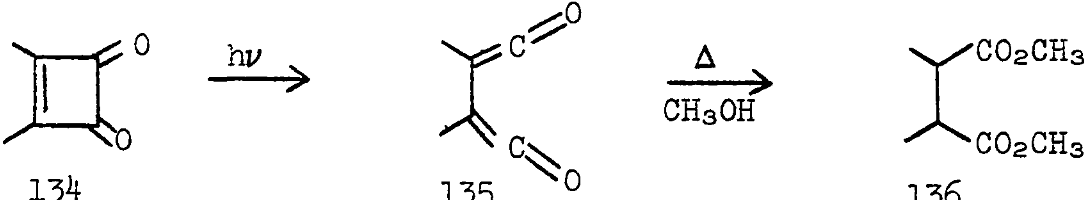


108
CH$_3$OH
Δ
CO$_2$CH$_3$
CO$_2$CH$_3$
94
CH$_3$
hν
Δ
92
hν
Δ
156
Δ
91
Δ
157
+
158
H$_2$
Pt
161
162
H$_2$
Pt
Δ
128
159
160

SUMMARY

2,3-Dimethylcyclobutenedione, umbellulone, lumisantonin, 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)-naphthalenone, 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone and 2,4,6-cyclooctatrienone undergo one or more primary photochemical reactions, e.g., α-cleavage, electrocyclic ring opening, sigmatropic shifts, and cis,trans isomerization upon irradiation. Ketene derivatives, cyclopropanone derivatives and highly strained cyclic trans isomers are formed by these processes. These intermediates were investigated by low temperature infrared spectroscopy. Ensuing thermal reactions of these photogenerated intermediates ultimately led to stable products by competing intramolecular and intermolecular processes.

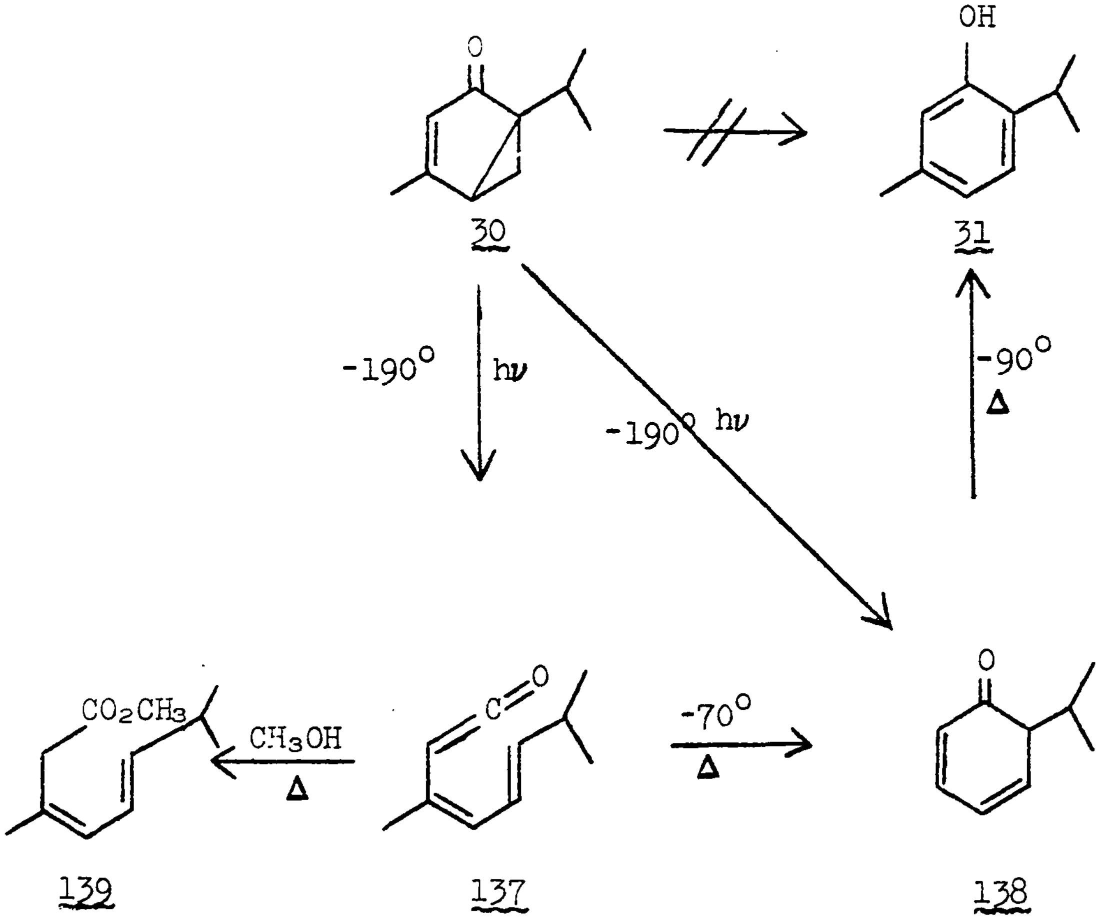
2,3-Dimethylcyclobutenedione undergoes photochemical electrocyclic ring opening to give a diketene derivative



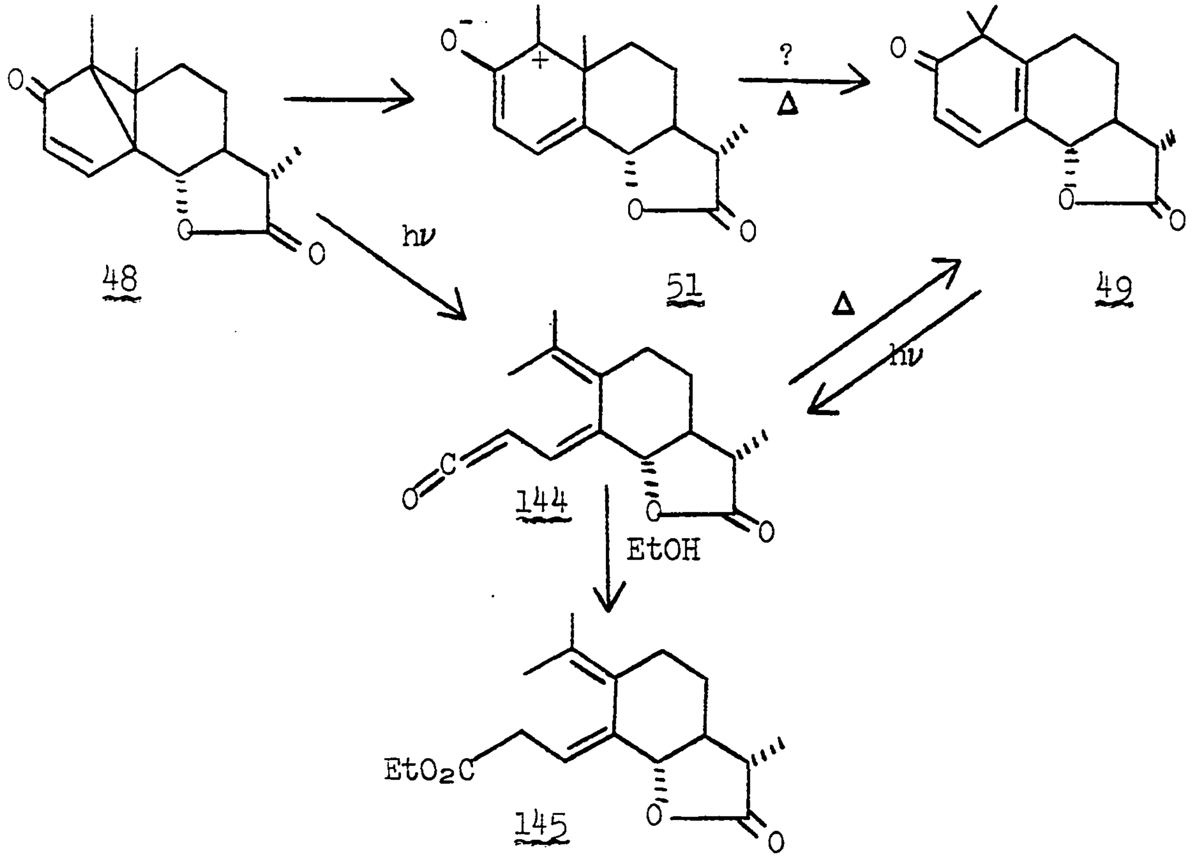
134 135 136

which can be trapped by methanol to give meso and racemic dimethyl 2,3-dimethylsuccinate.

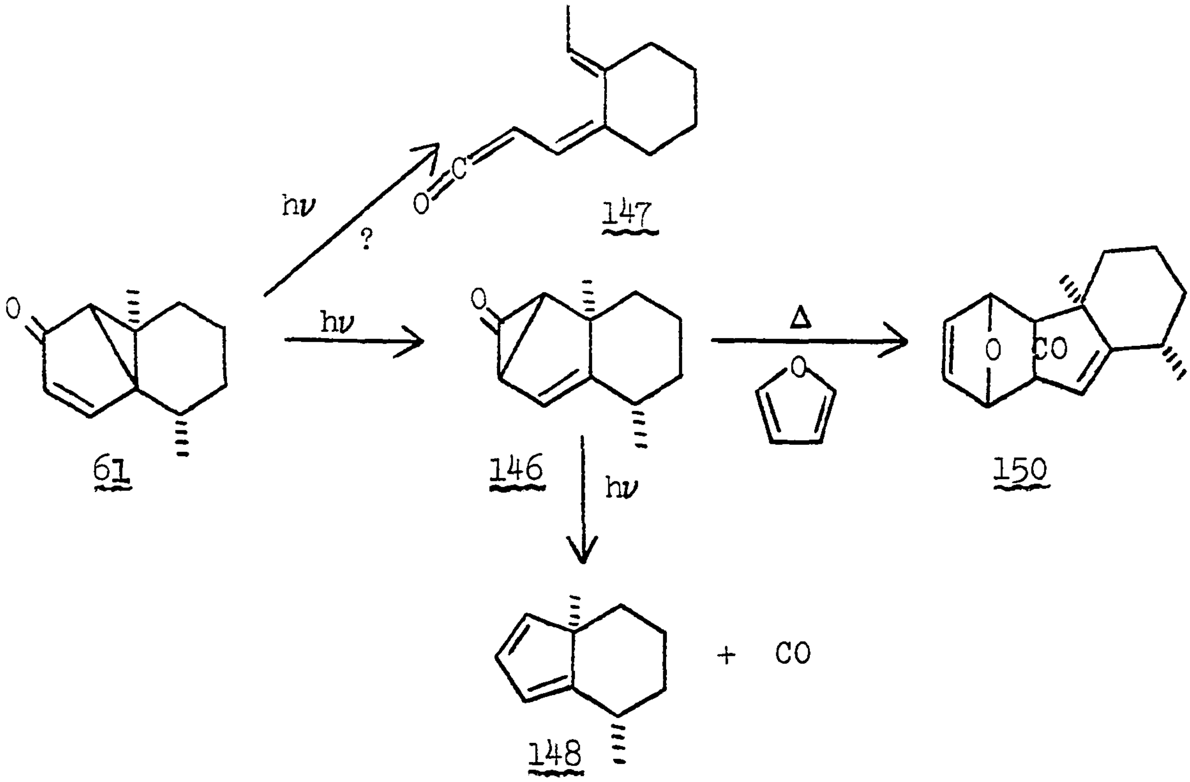
Umbellulone gives two intermediates, a diene-ketene derivative and 3-methyl-6-isopropylcyclohexa-2,4-dienone upon irradiation at low temperatures. Formation of thymol was not observed during the low temperature irradiation, but both intermediates give thymol upon warming. The diene-ketene was trapped at low temperatures and characterized as the methyl ester.



Lumisantonin and mazdasantonin gave a single diene-ketene upon low temperature irradiation which could be trapped at room temperature, or at low temperatures with protonic solvents. Lumisantonin also gives a characteristic blue species which is believed to be a zwitterion. The importance of this blue species in the photochemistry of lumisantonin is not clearly established. 5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone and 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone also give blue species with thermal properties similar to that species obtained from lumisantonin.



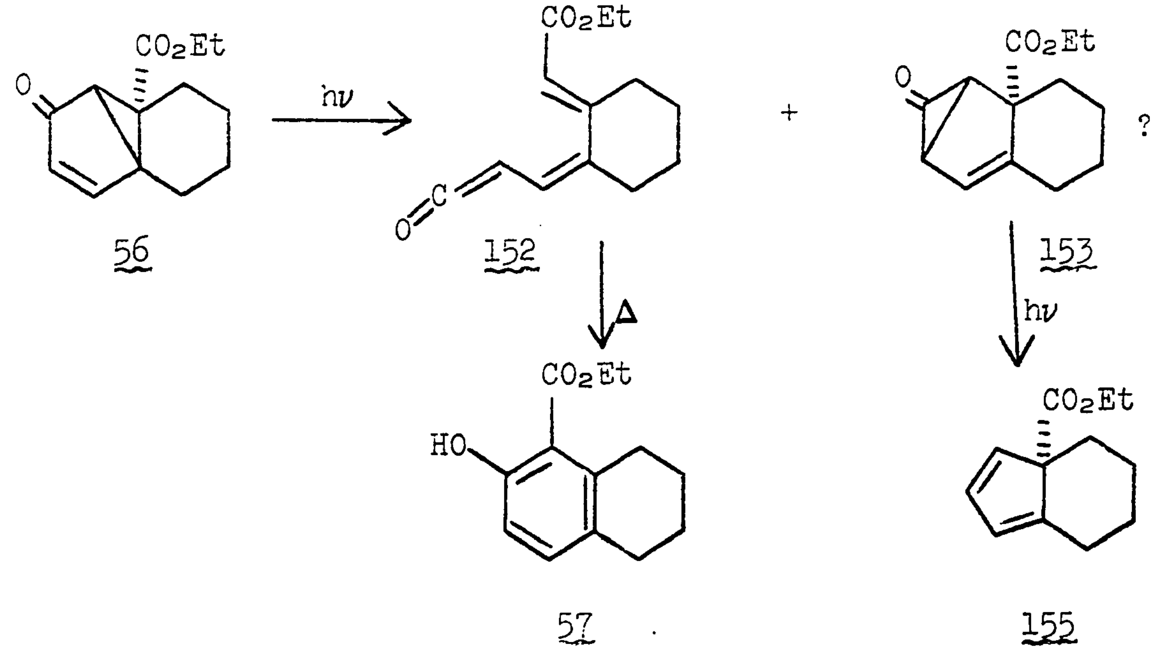
Irradiation of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone at low temperatures gives a cyclopropanone derivative which undergoes photodecarbonylation upon prolonged irradiation. A trace of a ketene



derivative is also formed which is probably a diene-ketene derivative similar to those obtained from umbellulone and lumisantonin. Upon warming the cyclopropanone derivative, heterolytic ring opening occurs to give a zwitterion which may be trapped as a 1,3-dipolar adduct in the presence of furan. This adduct may be formed at low temperatures directly from the cyclopropanone derivative or at room temperature by irradiating the lumiketone in the presence of furan.

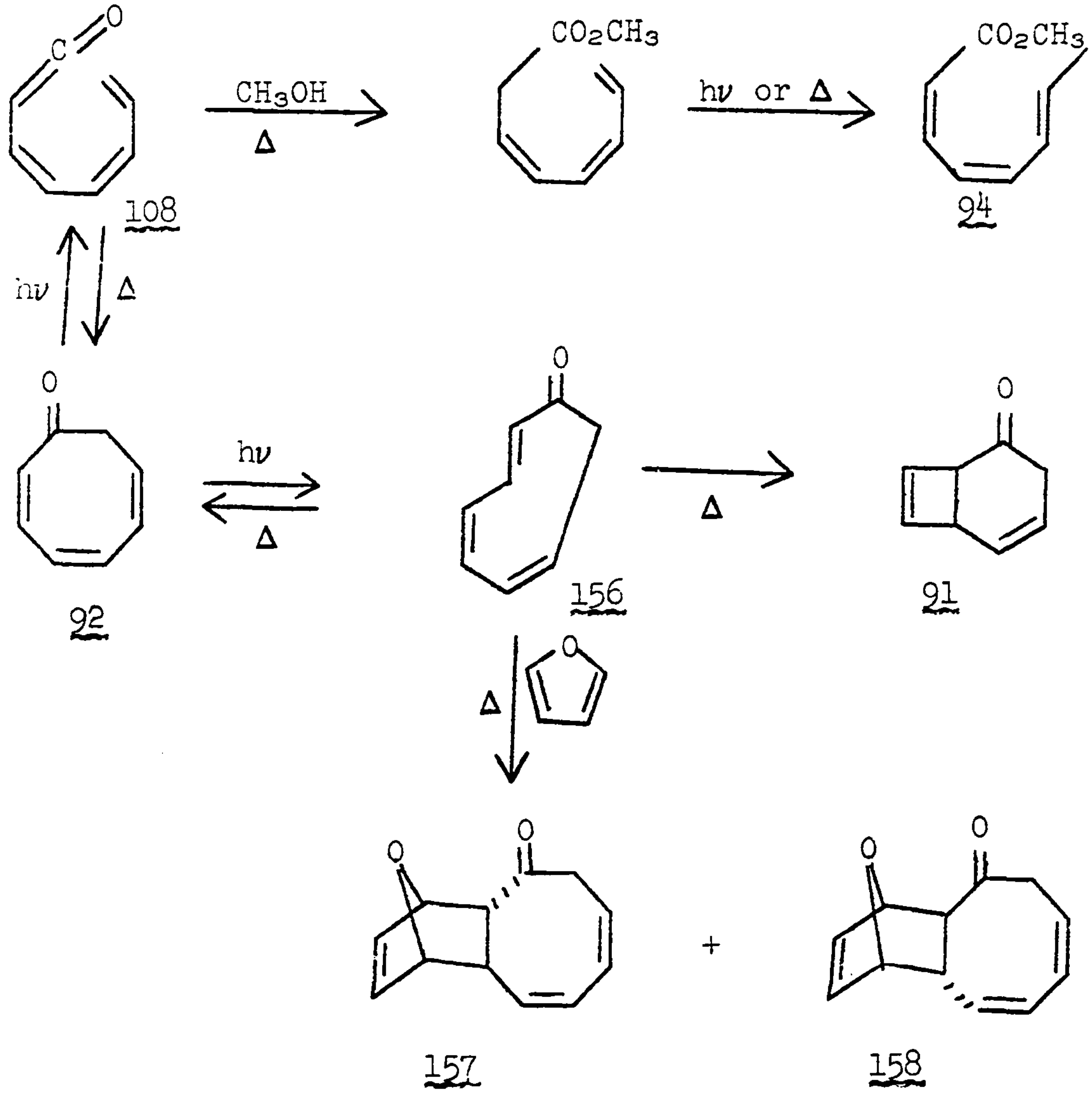
8aα-Carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-

(4aH)-naphthalenone behaves similarly to umbellulone and lumisantonin upon low temperature irradiation. A diene-ketene derivative is obtained which gives 1-carbethoxy-5,6,7,8-tetrahydro-2-naphthol upon warming. A small amount of a cyclopropanone may be formed which also undergoes photodecarbonylation upon prolonged irradiation.



2,4,6-cyclooctatrienone undergoes cis-trans isomerization and electrocyclic ring opening to give trans, cis, cis-2,4,6-cyclooctatrienone and hexatrienylketene upon low temperature irradiation. Upon warming, hexatrienyl ketene gives 2,4,6-cyclooctatrienone and trans, cis, cis-2,4,6-cyclooctatrienone probably dimerizes. In the presence of dienes, e.g., furan, two Diels Alder adducts are formed which result from addition of trans, cis, cis-2,4,6-cyclooctatrienone to furan. Trans, cis,cis-2,4,6-

Cyclooctatrienone was shown to be an intermediate in the conversion of 2,4,6-cyclooctatrienone to bicyclo [4.2.0] octa-4,7-dien-2-one.



In each of these examples, photo-thermal reactions pathways are involved in the overall transformations. These results indicate that photo-thermal reaction pathways may be prevalent in many photoinitiated reactions and suggest that additional low temperature studies in other systems be performed. In some cases, low temperature photochemical transformations may provide a means of carrying out useful synthetic procedures.

EXPERIMENTAL

General Instruments and Methods

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. Nuclear magnetic resonance spectra were obtained with Varian Associates Model A60 and Model HA100 spectrometers. TMS was employed as an internal standard. All spectra were obtained in carbon tetrachloride or deuteriochloroform solution. Infrared spectra were obtained with a Perkin-Elmer Model 21, a Beckman IR-12, or a Beckman IR-9 spectrometer. Mass spectra were obtained with an Atlas CH-4 mass spectrometer. Analytical and preparative gas-liquid partition chromatography was performed on an Aerograph Model A90P. Thermal conductivity detectors were employed. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

Low Temperature Infrared Spectroscopy Unit

The low temperature photochemical reactions which were studied by infrared spectroscopy were performed in a liquid nitrogen cooled infrared cell, Model WX 1A, obtained from Air Products and Chemicals, Allentown, Pennsylvania. The cell consisted of a vacuum shroud, a cooling unit and a sample holder.

The vacuum shroud was fitted with two sodium chloride windows (0.25 in. by 1.75 in. diameter) and two gas inlet ports. The gas inlet ports were sealed with gas chromatography type septums. The sodium chloride windows were sealed to the metal shroud with lubricated Neoprene "O" rings. The vacuum within the shroud securely held the windows in position during operation.

The cooling unit was fitted with a copper-constantan thermocouple (30 gauge) temperature sensing probe which was attached during operation to the sample holder. During operation the unit was evacuated by a conventional vacuum system mounted on a portable vehicle and attached to the cell through the cooling unit.

The sample holder consisted of two metal plates designed to accommodate round sodium chloride plates (25 x 4 mm). One metal plate was fitted with a brass screw which permitted attachment to the cooling unit. The two metal plates, which were held together by five small screws were used to sandwich the sodium chloride plates in a rigid vertical position parallel to the windows of the vacuum shroud.

General Procedure for Low Temperature Irradiations Using the Air Products Infrared Unit

The samples studied were either liquids or solids and could be conveniently studied by preparing a film of the compound between two polished sodium chloride plates followed by mounting the plates in the metal cell holder of the Air Products low temperature infrared spectroscopy unit. An infrared spectrum of this sample at room temperature was then recorded on a Beckman IR-12 spectrometer.

The cell was then cooled with liquid nitrogen to -190° and at the same time gradually evacuated to prevent condensation of moisture and carbon dioxide. A careful balance between cooling and evacuation was necessary to prevent loss of sample. The infrared spectrum of the sample at -190° was then recorded. A slight increase in intensity of all the peaks in the spectrum was observed upon cooling. Also peaks were better resolved and occassionally split into doublets upon cooling.

The low temperature unit was then removed from the spectrometer and transferred to the irradiation unit where the cold sample was irradiated. Cut off filters for the irradiation unit were chosen so that the $n \longrightarrow \pi^*$ absorption band could be selectively irradiated. A Pyrex filter (2950 Å) and a Corning 0-51 filter (3600 Å) were most useful for this purpose.

At the end of the irradiation period, the low temperature unit was transferred to the Beckman IR-12 where the infrared spectrum of the cold, irradiated mixture was recorded. The spectrum of the sample was recorded within one or two minutes after each irradiation period. This sequence was usually repeated several times and for various lengths of time depending upon the behavior during irradiation of the compound under investigation.

At the conclusion of the irradiation period the liquid nitrogen was removed from the cooling unit of the cell. The temperature of the sample within the cell was continuously monitored with a thermocouple and potentiometer while specific regions of the spectrum were repeatedly scanned. The regions 2000-2200 cm^{-1} and 1500-1850 cm^{-1} were most commonly used to observe changes of reactive intermediates upon warming. It was generally useful to cool the unit back to -190° at certain stages of the warmup for comparison spectra. If two or more reactive intermediates were present which displayed different reactivities, several warmups and cooling cycles could be performed to study each intermediate selectively.

General Procedure for Low Temperature Preparative Scale Trapping Experiments

Preparative scale trapping experiments of the photogenerated intermediates were performed at -80° and -190°. Only one type of apparatus was needed to carry out these experiments. A quartz Dewar flask, a photochemical reaction vessel and a high intensity light source were used. The quartz Dewar flask was constructed with a transparent window on one side of the flask while the remaining parts were silver plated. During a typical experiment, the flask was filled with about one half liter of coolant, i.e., liquid nitrogen or Dry Ice-ethanol. The reaction vessel consisted of a quartz or Pyrex tube (20 mm diameter) which could be immersed in the coolant and placed next to the transparent window. Twenty milliters of solution could be conveniently irradiated under these conditions. If the experiment was performed at -190°, it was necessary to periodically warm the reaction vessel until the rigid glass melted so that mixing could occur. Prolonged irradiation of a rigid matrix resulted in the formation of concentration gradients.

For prolonged irradiations, it was necessary to use a Liquid Nitrogen Automatic Level Controller, obtained from American Instruments Co., Inc., Silver Springs, Maryland, U.S.A. A twelve liter resevoir of liquid nitrogen was used along with a thermistor probe which permitted detection of changing levels of the liquid nitrogen in the quartz Dewar. The thermistor was connected to a solenoid valve which operated to regulate the flow of liquid nitrogen from the resevoir through a glass delivery tube to the quartz Dewar flask.

The irradiations were performed with an apparatus constructed from a design of Moore and Ketchum (83). A Westinghouse 800 watt high pressure mercury vapor lamp was used as the light source. Quartz convex lens were used to focus the light onto the sample.

Investigation of 2,3-Dimethylcyclobutenedione

Low temperature irradiation of neat 2,3-dimethylcyclobutenedione (134)

2,3-Dimethyl-1,2-cyclobutenedione (~5 μl) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then mounted in the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A Pyrex filter was used throughout the periods of irradiation. The sample was irradiated for five, seven, eight and ten minute intervals for a total of thirty minutes. The results of the irradiation and warmup are shown in Figures 2, 3 and 4 and Tables 1 and 2.

Table 1. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of 2,3-dimethylcyclobutenedione

Duration of Irradiation (min)	Absorbances			
	2138 cm^{-1}	2120 cm^{-1}	2090 cm^{-1}	1280 cm^{-1}
0	0.0	0.0	0.0	0.0
5	0.072	0.150	0.204	0.018
12		0.243	0.440	0.041
20		0.408	0.633	0.076

Table 2. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 2,3-dimethylcyclobutenedione

Temperature (°C)	2120 cm^{-1}	2090 cm^{-1}
-170	0.394	0.439
-153	0.394	0.439
-114	0.350	0.428
-107	0.326	0.405
-101	0.296	0.382
- 92	0.260	0.360
- 85	0.243	0.326
- 63	0.176	0.253
- 56	0.146	0.204

Synthesis of 2,3-dimethylcyclobutenedione

2,3-Dimethylcyclobutenedione (134) was prepared by the method of Bloomquist and Vierling (84, 85). A solution of methyl lithium in ether prepared from lithium wire (8 g, 1 mole) and methyl iodide (144 g, 1 mole) was cooled to -50° in an acetone-Dry Ice bath. The flask was fitted with an acetone-Dry Ice condensor. The solution was stirred continuously in an atmosphere of dry argon while perfluorocyclobutene (84 g, 0.55 mole) was passed into the solution through a twelve inch syringe needle. The acetone-Dry Ice bath was removed followed by gradual warming with continuous stirring. At -25° the solution turned from a light violet color to green and then to brown at room temperature. The solution was allowed to stand for three hours followed by addition of 2N hydrochloric acid (300 ml). The product was extracted into ether followed by separation of the aqueous phase which was extracted with three portions of ether. The combined ethereal extracts were dried over sodium sulfate and concentrated with the aid of a rotatory evaporator. The crude 1,2-dimethyl-3,3,4,4,-tetrafluorocyclobutene was used for the next step without further purification.

1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutene (~7 g, 0.045 mole) was added to concentrated sulfuric acid (75 ml). The solution was heated to 70° with continuous stirring for two hours. The mixture was cooled and poured onto crushed ice (300 g). Sodium hydroxide solution (30%, 15 ml) was then added with caution. More crushed ice (100 g) was added followed by extraction of the aqueous solution with four portions of ether (100 ml). The aqueous layer was then saturated with sodium chloride and extracted with ether. The combined ethereal extracts were washed with water, dried over magnesium sulfate and concentrated with the aid of a rotatory evaporator. This crude black liquid was chromatographed on silica gel (200 g) with ether as eluant. The insoluble, non-volatile components were removed by this process. Preparative glpc through 12 ft. by 3/8 in. of 10% Carbowax 20 M on 60-80 mesh Chromosorb W at 170° yielded an analytical sample of 2,3-dimethylcyclobutenedione: ir (film) 1820, 1790, 1765 and 1610 cm^{-1}; nmr (CCl_4) δ 2.31 (s) [lit. (85) ir (film) 1820, 1788, 1762 and 1610; nmr (CCl_4) 2.40].

meso and racemic Dimethyl 2,3-dimethylsuccinate

2,3-Dimethylcyclobutenedione (50 mg, 0.455 mmole) was dissolved in methanol (10 ml), placed in a Pyrex tube, capped with a rubber septum and purged with argon for ten minutes. The solution was irradiated for one and one half hours in a Rayonet reactor at 350 nm followed by removal of the solvent with the aid of a rotatory evaporator.

Preparative glpc through 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 160°, yielded a mixture of meso and racemic dimethyl 2,3-dimethylsuccinate: ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) δ 3.65 (s, 6H), 2.85-2.35 (2H, m), 1.11 (d, 6H). The infrared and nmr spectra of this mixture were superimposable with the spectra obtained from a known sample of meso and racemic dimethyl 2,3-dimethylsuccinate.

Investigation of Umbellulone

Low temperature irradiation of neat umbellulone

Umbellulone (~5 µl) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then mounted into the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A Pyrex filter was used throughout the irradiation. The sample was irradiated in intervals for a total irradiation of two minutes. The results of the irradiations are shown in Figures 6, 7 and 8 and Tables 3 and 4.

Table 3. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of umbellulone

Duration of Irradiation (sec)	Absorbances				
	2107 cm^{-1}	1695 cm^{-1}	1660 cm^{-1}	1630 cm^{-1}	1610 cm^{-1}
0	0	0.728	0.114	0.053	0.375
30	0.260	0.602	0.187	0.154	0.335
45	0.398	0.539	0.199	0.176	0.292
60	0.455	0.514	0.198	0.188	0.296
75	0.526	0.484	0.198	0.204	0.286
90	0.593	0.470	0.198	0.208	0.286
105	0.652	0.450	0.198	0.208	0.270
120	0.652	0.432	0.198	0.208	0.250

Table 4. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of umbellulone

Temperature (°C)	2107 cm^{-1}	1695 cm^{-1}	1630 cm^{-1}	1610 cm^{-1}
-144	0.644	0.410	0.230	0.260
-129	0.644	0.410	0.225	0.255
-110	0.644	0.410	0.222	0.200
- 99	0.644	0.410	0.222	0.250

Table 4 (Continued)

Temperature (°C)	Absorbances			
	2107 cm^{-1}	1695 cm^{-1}	1630 cm^{-1}	1610 cm^{-1}
- 85	0.644	0.410	0.212	0.250
- 80	0.644	0.375	0.164	0.250
- 74	0.644	0.347	0.110	0.250
- 72	0.644	0.347	0.083	0.259
- 68	0.602			
- 67	0.584			
- 65	0.549			
- 62	0.532			
- 59	0.501	0.250		
- 53	0.441			
- 34	0.362			
- 24	0.308		0.083	

Irradiation of umbellulone at 25° in methanol

Umbellulone (50 mg, 0.33 mmole) was dissolved in methanol (40 ml), placed in a Pyrex tube, capped with a rubber septum, purged with argon for fifteen minutes and irradiated for one hour in a Rayonet reactor at 300 nm. Tlc analysis showed complete destruction of starting material and formation of one new product. The solvent was removed with the aid of a rotatory evaporator. Preparative glpc on 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 170°, of the crude photomixture gave an analytical sample of thymol. The nmr and infrared spectra of this sample were superimposable with those spectra obtained from an authentic sample of thymol.

Irradiation of umbellulone at -80° in methanol

Umbellulone (25 mg, 0.165 mmole) was dissolved in methanol (7 ml), placed ina Pyrex culture tube, capped with a rubber septum and degassed with argon for fifteen minutes. This sample was placed in a Dewar flask designed with a transparent Pyrex window, colled to -80° with ethanol-Dry Ice and irradiated for one hour in a Rayonet reactor at 300 nm. The Dewar was removed from the reactor and the sample was allowed to warm to room temperature. Thymol was the only phenolic product obtained as judged by glpc retention times and comparative R_f values obtained by tlc.

Irradiation of umbellulone in a rigid, methanol containing glass at -190°

Umbellulone (15 mg, 0.10 mmole) was mixed with methanol (5 µl) until a homogenous solution was obtained. A sample of this solution was placed between two sodium chloride plates which were separated by a circular spacer (0.012 mm). The two salt plates were then mounted in the Air Products low temperature infrared unit. The infrared spectrum of this solution was obtained after the unit was cooled to -190°. The sample was then irradiated through a Pyrex filter for eight minutes. The carbonyl absorption bands of the diene-ketene (137) and cyclohexadienone (138) were clearly observable. The low temperature unit was then allowed to warm gradually while the temperature of the sample was monitored and the regions between 1600-1800 cm^{-1} and 2000-2200 cm^{-1} were continuously scanned. The diene-ketene absorption band decreased rapidly when the sample temperature reached -90°. At -65°, the ketene was nearly completely destroyed. During this reaction period, a new carbonyl absorption band appeared at 1740 cm^{-1}. This material with an absorption band at 1740 cm^{-1} was not isolated from this sample, but it was isolated and characterized by a preparative scale trapping experiment with methanol.

Irradiation of umbellulone in an ether-methanol rigid glass at -190°

Umbellulone (100 mg, 0.66 mmole) and ether-methanol (4:1, 30 ml) were placed in a Pyrex tube, capped with a rubber septum and purged with argon for fifteen minutes. This solution was quenched to -190° in liquid nitrogen. A rigid, cracked glass formed which was suitably transparent for the irradiation. During irradiation of this sample through the Pyrex window in the Dewar flask, a distinct yellow color formed within the sample. After six hours, the glass was allowed to warm to room temperature. Upon warming, the yellow color quickly disappeared to give a clear, colorless solution. The solvent was removed with the aid of a rotatory evaporator. Analysis of the resulting oil by glpc revealed two major products and umbellulone. The relative retention times of methyl *cis,trans*-dimethylocta-3,5-dienoate, umbellulone and thymol were 1, 1.17 and 7.85 minutes on Carbowax 20 M. Preparative glpc of this mixture through 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb,W, 170°, yielded an analytical sample of *cis,trans*-dimethylocta-3,5-dienoate: ir (film) 1739 cm^{-1}; uv max (CH_3OH) 238 nm (log ϵ 4.42); nmr (CCl_4) δ 6.33-4.95 (m, 3H, olefinic), 3.63 (s, 3H), 3.06 (s, 2H), 3.00-2.10 (m, 1H), 1.84 (s, 3H), 1.00 (d, 6H); mass spectrum 70 (ev) (Figure 11) m/e (rel intensity) 182 (42), 152 (7), 136 (19), 123 (27), 110 (100), 108 (93), 94 (63), 82 (53), 68 (37), 56 (27), 42 (63).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.59; H, 9.99.

Catalytic hydrogenation of methyl 3,7-dimethylocta-3,5-dienoate

Methyl 3,7-dimethylocta-3,5-dienoate (30 mg, 0.165 mmole) in methanol (0.5 ml) was added to platinum oxide (10 mg) in methanol (10 ml) which had been prereduced with hydrogen. The solution was stirred until 3.3×10^{-4} moles of hydrogen were consumed. The solution was then carefully filtered through Celite and concentrated with the aid of a rotatory evaporator. Preparative glpc of this crude tetrahydro-derivative through 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 160°, gave an analytical sample of methyl 3,7-dimethyloctanoate: ir (film) 1740 cm^{-1}; nmr (CCl_4) δ 3.60 (s, 3H), 2.40-2.05 (m, 2H), 2.05-1.05 (μ, 8H), 1.05-0.74 (d, d, J = 6.4, 9H); mass spectrum (70 ev) (Figure 12) m/e (rel intensity) 186 (3), 100 (50), 73 (100).

<u>Catalytic hydrogenation of 3,7-dimethylocta-2,6-dien-1-ol</u>

3,7-Dimethylocta-2,6-dien-1-ol (10.0 g, 0.065 mole) was dissolved in absolute ethanol (20 ml) and added slowly to a mixture of absolute ethanol (100 ml) and platinum oxide (100 mg) which had been prereduced with hydrogen for several minutes. A positive pressure of two psi was maintained while the mixture was stirred for twelve hours. The mixture was filtered through Celite and concentrated on a rotatory evaporator to give 10.2 g of crude 3,7-dimethyl-1-octanol. Preparative glpc of this crude sample through 12 ft. by 3/8 in. 10% Carbowax 20 M on Chromosorb W, 160°, gave an analytical sample of 3,7-dimethyl-1-octanol: ir (film) 3290, 1048 cm^{-1}; nmr (CCl_4) δ 3.56 (t, 2H, J ~ 6.5 Hz), 3.08 (s, 1H), 1.95-1.04 (μ, 10H), 0.89 (d, d, 9H); bp 91-93° (5 mm) [lit. (86) bp 88-89.5 (4 mm)].

Oxidation of 3,7-dimethyl-1-octanol with potassium permanganate

3,7-Dimethyl-1-octanol (6.0 g, 0.0382 mole) was dispersed in a cold solution of sulfuric acid (12.0 g) and water (80 ml). With vigorous stirring, powdered potassium permanganate (9.0 g) was added as fast as it was reduced while the temperature was kept below 25°. Sufficient solid sodium bisulfite was added to dissolve the manganese dioxide, and the solution was thoroughly extracted with ether. The ethereral solution was concentrated to a volume of about 100 ml and then extracted with 20% sodium hydroxide solution. The alkaline extract was covered with hexane and acidified with aqueous sulfuric acid (30%). The liberated acid was taken up in ether, dried over magnesium sulfate and concentrated. Distillation of this extract through a short path distillation apparatus gave a pure sample of 3,7-dimethyloctanoic acid: bp 126-128° (5.5 mm) [lit. (86) bp 128 (6 mm)]; nmr (CCl_4) δ 11.73 (s, 1H), 2.48-2.08 (m, 2H), 2.08-1.09 (μ, 8H), 0.95 (d, d, 9H).

Esterification of 3,7-dimethyl-1-octanoic acid

3,7-Dimethyl-1-octanoic acid (1.0 g, 5.8 mmole) was dissolved in ether (15 ml). To this solution was added an etheral solution of diazomethane prepared in the following way. Ether (50 ml) and aqueous potassium hydroxide (40%) were cooled to 5°. N-Methyl-N-nitrosourea

(5.0 g) was added to this solution in small quantities with stirring over a two minute period. This mixture was allowed to stand for thirty minutes. The ether was decanted and added to the ethereal solution of 3,7-dimethyl-1-octanoic acid until a faint yellow color of diazomethane appeared. The product solution was allowed to stand for thirty minutes, dried over magnesium sulfate and concentrated with the aid of a rotatory evaporator to give crude methyl 3,7-dimethyl-1-octanoate. Distillation of the crude ester gave pure methyl 3,7-dimethyloctanoate (0.82 g): bp 51-53 (0.6 mm); ir (film) 1740 cm^{-1} [lit. (87) bp 53 (0.5 mm); ir (film) 1739 cm^{-1}]; nmr (CCl_4) δ 3.60 (s, 3H), 2.40-2.05 (m, 2H), 2.05-1.05 (μ, 8H), 1.05-0.74 (d, d, J = 6.4 Hz, 9H); mass spectrum (70 ev) m/e (rel intensity) 186 (3), 100 (50), 73 (100).

3-Methyl-5-isopropyl-2-cyclohexenone

Ethyl acetoacetate (210 g, 1.6 mole) was placed in a round bottom flask and cooled to 0° in an ice salt bath. Isobutyraldehyde(55.4 g, 0.77 mole) was then added followed by ethanol (5 ml) and piperidine (2 ml). The contents were then mixed and stored in a refrigerator. Each day for three days, piperidine (3 ml) and ethanol (5 ml) were added. The reaction mixture was poured into acetic acid (600 ml) and sulfuric acid (40 ml). The mixture was refluxed for one hour. A vigorous evolution of carbon dioxide occurred. The mixture was cooled and poured into ice water (2 liter) and the layers separated with ether. The organic layer was stirred with water (1200 ml) and neutralized with sodium carbonate. The ethereal solution was concentrated, dissolved in water (1140 ml), alcohol (60 ml) and sodium hydroxide (130 g). The mixture was heated on a steam bath until the ester dissolved. The solution was heated under reflux for fifteen minutes and then acidified carefully with aqueous sulfuric acid (30%). This was carried out slowly while cooling the flask with ice water. The acid was added at a rate such that the evolution of carbon dioxide could be controlled. The acidified mixture was refluxed fifteen minutes, allowed to cool, and the layers separated. The ethereal solution was dried over magnesium sulfate, filtered, concentrated, and distilled to give 3-methyl-5-isopropyl-2-cyclohexenone: bp 120-123 (15 mm) [lit. (88) bp 120-122 (15 mm)].

3-Isopropyl-5-methylphenol

To 3-methyl-5-isopropyl-2-cyclohexenone (5.0 g) in trimethylbenzene (15 ml) was added palladium on charcoal (10%, 1.5 g). The mixture was heated under vigorous reflux for eight hours with continuous stirring. After cooling to 50°, the catalyst was removed by filtration and washed with four portions of ethyl acetate (5 ml). The solution was extracted with two portions of aqueous sodium hydroxide

(10%, 50 ml). The combined alkaline extracts were washed with pentane (40 ml) and diluted with water (100 ml). Concentrated hydrochloric acid (5 ml) was added. The solution was cooled in an ice bath and acidified with dilute hydrochloric acid. The liberated oil was extracted into ether, dried and concentrated. Preparative glpc through 12 ft. by 3/8 in. 10% Carbowax 20 m on 60-80 mesh Chromosorb W, 190°, gave a pure sample of 3-isopropyl-5-methylphenol: mp 49-50° [lit. (89) mp 49-51°]; nmr (CCl_4) δ 6.85 (s, 1H), 6.50 (s, 1H), 6.44 (s, 2H), 3.05-2.35 (h, 1H), 2.18 (s, 3H), 1.11 (d, 3H, J = 7.0 Hz).

Investigation of Lumisantonin

Low temperature irradiation of neat lumisantonin at -190°

Lumisantonin (~5 mg) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then heated gently on a hot plate to the melting point of lumisantonin. A thin film of lumisantonin formed which crystallized quickly upon cooling. The two sodium chloride plates were then mounted in the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A Pyrex filter was used throughout the irradiation. The sample was irradiated for a total of 204 minutes. Spectra were recorded after 23, 107, 166 and 204 minutes of irradiation. The results of the irradiations and warmups are shown in Figures 6, 14 and 15 and Tables 5 and 6.

Table 5. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of α-lumisantonin

Duration of Irradiation (min)	Absorbances		
	2113 cm^{-1}	1720 cm^{-1}	1700 cm^{-1}
0	0	0.511	0.954
23	0.049	0.487	0.813
107	0.338	0.428	0.690
166	0.748	0.447	0.579
204	1.021	0.380	0.450

Table 6. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of α-lumisantonin

Temperature (°C)	Absorbances		
	2113 cm^{-1}	1700 cm^{-1}	1670 cm^{-1}
-155	1.082	0.489	0.111
-113	1.030	0.539	0.130
-97	0.980	0.591	0.143

Table 6 (Continued)

Temperature (°C)	2113 cm^{-1}	1700 cm^{-1}	1670 cm^{-1}
- 80	0.846	0.597	0.173
- 68	0.756	0.690	0.212
- 49	0.490	0.737	0.238

Preparation of lumisantonin

Santonin (5.0 g, 20.1 mmole) was dissolved in ethanol (1300 ml), placed in a quartz vessel, capped with a rubber septum and purged with argon for fifteen minutes. The solution was then irradiated for eight hours in a Rayonet reactor (253.7 nm). Tlc analysis of this solution showed complete destruction of starting material. The solvent was removed with the aid of a rotatory evaporator followed by chromatography of this oil on silica gel (300 g) packed in hexane. The oil was loaded onto the column in benzene. Elution with ether benzene (1:10, 4 1) gave photosantonin (0.40 g) followed by lumisantonin (0.63 g), mp 152-3°. Recrystallization of lumisantonin from ether-hexane raised the melting point to 153-155° [lit. (28) 153-155].

Low temperature irradiation of neat mazdasantonin at -190°

Mazdasantonin (~5 mg) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then heated gently on a hot plate to the melting point of mazdasantonin. A thin film of mazdasantonin formed between the two plates. The two sodium chloride plates were then mounted into the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in this experimental section for the Air Products low temperature unit. A Pyrex filter was used throughout the irradiation. The results of the warmup of the cold, irradiated sample of mazdasantonin are shown in Table 7.

Table 7. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of mazdasantonin

Temperature (°C)	2111 cm^{-1}	1781 cm^{-1}	1661 cm^{-1}	1630 cm^{-1}
-146	0.648	0.567	0.441	0.348
-131	0.667	0.567	0.439	0.350
-125	0.640	0.576	0.450	0.369
-115	0.648	0.574	0.450	0.369
-104	0.632	0.574	0.458	0.367

Table 7 (Cont.)

Temperature (°C)	Absorbances			
	2111 cm^{-1}	1781 cm^{-1}	1661 cm^{-1}	1630 cm^{-1}
-93	0.632	0.576	0.450	0.369
-84	0.626	0.579	0.450	0.369
-75	0.626	0.562	0.477	0.383
-66	0.597	0.562	0.473	0.392
-58	0.544	0.578	0.473	0.404
-51	0.501	0.578	0.500	0.418
-44	0.438	0.578	0.527	0.428
-37	0.350	0.581	0.521	0.444
-31	0.260	0.581	0.521	0.444
-24	0.176	0.581	0.534	0.444
-20	0.104	0.581	0.534	0.444
-13	0.050	0.581	0.540	0.449

Investigation of 5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

Low temperature irradiation of neat 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (~5 μl) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then mounted in the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A low pressure lamp (2537Å) was used throughout the irradiation. The sample was irradiated in five minute intervals for a total irradiation time of twenty minutes. The results of the irradiations and warmups are shown in Figures 18, 19 and 29 and Tables 8 and 9.

Table 8. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)naphthalenone

Duration of Irradiation (min)	2130 cm^{-1}	2106 cm^{-1}	1840 cm^{-1}	1812 cm^{-1}	1700 cm^{-1}
0	0	0	0	0	0.602
5	0.021	0.016	0.029	0.107	0.365
10	0.047	0.024	0.037	0.133	0.344
15	0.061	0.025	0.041	0.133	0.328

Table 9. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2(4aH)naphthalenone

Temperature (°C)	Absorbances				
	2130 cm^{-1}	2106 cm^{-1}	1840 cm^{-1}	1812 cm^{-1}	1670 cm^{-1}
-166	0.068	0.0358	0.045	0.159	0.162
-158	0.061	0.0358	0.045	0.159	0.161
-141	0.050	0.0358	0.045	0.159	0.161
-130	0.041	0.0358	0.045	0.159	0.161
-123	0.029	0.0358	0.039	0.148	0.161
-115	0.029	0.0282	0.037	0.135	
-109	0.0133	0.0178	0.029	0.107	0.185
-101	0.009	0.0137	0.021	0.099	0.203
- 98	0.0	0.0	0.014	0.075	
- 92	0.0	0.0	0.013	0.057	0.212
- 75	0.0	0.0	0.004	0.031	0.225

Preparation of 2-methyl-6-formylcyclohexanone

To an ice cold suspension of two moles of sodium methoxide in benzene (750 ml) which had been previously degassed with argon was added 2-methylcyclohexanone (100 g, 0.89 mole) and ethyl formate (1 mole). The mixture was allowed to stand at room temperature overnight. The suspension became paste like during this time. Ice water was added carefully with vigorous stirring which ultimately resulted in formation of two layers. The benzene layer was separated from the aqueous layer and then washed with cold dilute sodium hydroxide solution. All of the aqueous layers were combined, washed once with ether and acidified with dilute hydrochloric acid. The resulting oil suspension was saturated with sodium chloride and extracted thoroughly with ether. The ether solution was washed with water and dried over magnesium sulfate. The ether was removed on a rotatory evaporator. Distillation gave 2-methyl-6-formylcyclohexanone (95 g, 67%): bp 93-95° (12 mm) [lit. (90) bp 87.5-92.5 (14 mm)].

2,6-Dimethyl-2-formylcyclohexanone

To a stirred suspension of powdered ignited potassium carbonate (42 g, 0.304 mole) in dry acetone (375 ml) was added methyl iodide (63 g, 0.44 mole) followed by 2-methyl-6-formylcyclohexanone (36 g, 0.258 mole). The mixture was allowed to reflux with stirring for fifteen hours. The mixture was then cooled to 20° and diluted with anhydrous ether (180 ml), allowed to stand for one hour, filtered and concentrated with the aid of a rotatory evaporator. Vacuum distillation gave 2,6-dimethyl-2-formylcyclohexanone (32 g, 0.206 mole): bp 100-105° (12 mm) [lit. (90) bp 101-110 (11 mm)].

4aβ,8α-Dimethyl-5,6,7,8-tetrahydro-2-(4aH)-naphthalenone

2,6-Dimethyl-2-formylcyclohexanone (30.5 g, 0.20 mole) was dissolved in dry acetone (270 ml). Piperidine (18.0 g, 0.212 mole) and glacial acetic acid (12.7 g, 0.212 mole) were carefully added with stirring. The reaction mixture was refluxed eighty four hours, cooled to room temperature and concentrated on a rotatory evaporator. The oil was dissolved in ether (300 ml), washed with dilute hydrochloric acid, water, potassium bicarbonate solution (5%) and water. The ether layer was dried over magnesium sulfate and concentrated with the aid of a rotatory evaporator. The orange oil was added to anhydrous methanol (250 ml) followed by the addition of a solution of potassium hydroxide (15 g, 0.268 mole) in water (15 ml). The reaction mixture immediately turned red and was then refluxed for six hours. The solution was cooled and concentrated followed by addition of ether (200 ml) and water (100 ml). After vigorous mixing, the aqueous layer was separated and extracted with ether. The combined organic layers were washed with water, dried and concentrated to give an orange oil. Crystallization occurredupon addition of hexane to give 4aβ,8α-dimethyl-5,6,7,8-tetrahydro-2-(4aH)-naphthalenone (8.5 g): mp 58.5-59° [lit. (91) 59.5-60.5].

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

4aβ,8α-Dimethyl-5,6,7,8-tetrahydro-2-(4aH)-naphthalenone (1.30 g, 8.65 mmole) was placed in a quartz tube, dissolved in p-dioxane (90 ml, previously distilled from lithium aluminum hydride), capped with a rubber septum, degassed with argon for ten minutes and irradiated in a Rayonet reactor (1.5 hours, 253.7 nm). The solvent was removed to give the crude photoproduct (1.39 g). Preparative glpc on 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 185°, gave pure lumiketone: ir (CCl_4) 1694, 1575 cm^{-1}; nmr (CCl_4) δ 7.38 (d, d, 1H), 5.78 (d, d), 1.24 (d, 3H, J = 7 Hz), 1.20 (s, 3H) [lit. (41) ir (CCl_4) 1693, 1578 cm^{-1}; nmr (CCl_4) δ 7.38 (d, d, 1H), 5.78 (d, d J_{AB} = 5.5, J_{AX} = 0.8, J_{BX} = 1.1), 1.24 (d, 3H, J = 7), 1.18 (s, 3H)].

3a,7-Dimethyl-$\Delta^{1,7:2,3}$-perhydroindane

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (0.050 g, 0.33 mmole) was dissolved in ether-isopentane (4:1, 15 ml), placed in a Pyrex tube, capped with a rubber septum and purged with argon for five minutes. The solution was cooled in liquid nitrogen to form a rigid glass. A quartz window in the Dewar permitted direct irradiation of the sample. After six hours, the irradiation was discontinued, the sample warmed to room temperature and analyzed by glpc and tlc. Only one new product was observed. This preparation was repeated twice. The combined solutions were concentrated to give a pale yellow oil (145 mg). The two components were readily separated by column chromatography on silica gel (3 g) packed in pentane. The sample was loaded onto the column and eluted with pentane (100 ml) which separated all of the new product from the starting material. The combined fractions were concentrated with the aid of a rotatory evaporator to give 3a,7-dimethyl-$\Delta^{1,7:2,3}$-perhydroindane (95 mg). Preparative glpc through 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 130°, gave an analytical sample of 3a,7-dimethyl-$\Delta^{1,7a:2,3}$-perhydroindane: ir (film) 1640, 1600 (diene), 851, 796 (RHC=CRR′), 728 (cis RHC=CHR′); uv (CH_3OH) 256 nm (ϵ 3,850); nmr (CCl_4) δ 5.70-6.20 (3H), 3.0 (m), 2.2-0.8 (6H), 1.15 (s, 3H), 1.18 (d, 3H); mass spectrum (70 ev) (Figure 25) m/e 148 (46), 133 (100), 105 (70), 91 (51), 77 (18), 65 (12), 51 (11).

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.16; H, 10.73.

Ozonolysis of 3a,7-dimethyl-$\Delta^{1,7a:2,3}$-perhydroindane

3a,7-Dimethyl-$\Delta^{1,7a:2,3}$-perhydroindane (0.100 g, 0.67 mmole) was dissolved in methanol (10 ml), placed in an ozonolysis tube which had been previously attached to a potassium iodide trap, cooled in an acetone-Dry Ice trap and ozonized for fifteen minutes (Welsbach Ozonizer). To the cold solution was added sodium iodide (0.100 g) and glacial acetic acid (1 ml). Effervescence was observed upon warming to room temperature. To this iodine-colored solution was added a few drops of aqueous sodium thiosulfite solution until discoloration was complete. The solvent was removed with the aid of a rotatory evaporator followed by addition of water (1 ml). This solution was extracted three times with ether (3 ml). The ether extracts were combined, dried over magnesium sulfate and concentrated. This solution contained one major product. Preparative glpc through 12 ft. by 3/8 in. 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 150°, gave a mixture of <u>cis</u> and <u>trans</u>-2,6-dimethylcyclohexanone: ir (film) 1709; nmr (CCl_4) δ 2.70-1.15 (μ, 8H), 0.96 (d, J = 6.0 Hz). This sample was compared to a sample of 90% <u>cis</u>, 10% <u>trans</u>-2,6-dimethylcyclohexanone. The glpc retention times, ir spectra and nmr spectra were identical for the two samples.

Irradiation of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone in furan at -80°

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (0.100 g, 0.57 mmole) was placed in a Pyrex tube, dissolved in furan-ether (1:4, 5 ml), capped with a rubber septum and degassed with argon for two minutes. The solution was cooled in ethanol-Dry Ice contained in a quartz Dewar with a transparent window and then irradiated (4.5 hours). Tlc analysis showed complete destruction of starting material. The solvent was removed with the aid of a rotatory evaporator to give a light yellow oil which was chromatographed on silica gel (15 g) packed in hexane. The column was eluted with benzene (100 ml, 20 mg of unidentified material) and ether-benzene (1:10, 100 ml, 88 mg (150)). Recrystallization of (150) gave an analytical sample of 4,8-dimethyl-15-oxa-tetracyclo [7.4.1.1.^{10,13}0^{3,8}]pentadeca-2,11-dien-14-one: mp 131-2°; ir (CCl_4) 1729 cm^{-1}; nmr ($CDCl_3$) δ 6.30 (d, d, 1H, $J_{11,12}$ = 6.0 Hz), 6.20 (d, d, 1H, $J_{10,11}$ = 1.5 Hz), 5.62 (1H, J_{12} = 6.0 Hz), 5.00 (1H, $J_{9,10}$ = 1.5 Hz), 4.62 (1H, J = 2 Hz), 2.75 (1H, $J_{1,9}$ = 1.5 Hz), 2.57 (m), 1.99 (1H), 2.4-0.8 (m, 6H), 1.23 (s, 3H), 1.18 (d, 3H); mass spectrum (70 ev), 244 (100), 229 (17), 187 (30), 163 (26), 147 (17), 133 (16), 121 (15), 108 (12), 105 (12), 90 (19), 81 (15), 65 (8), 54 (13).

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: 78.55; H, 8.11.

Irradiation of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone in furan-ether (1:4) at 0°

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (0.040 g, 0.23 mmole) was dissolved in furan-ether (1:4, 5 ml), placed in a Pyrex tube, capped with a rubber septum and purged with argon for three minutes. The solution was cooled in an ice water bath and irradiated at 0° in a Rayonet reactor (300 nm) for twenty four hours. Tlc analysis showed nearly complete destruction of starting material. The solvent was removed to give a light yellow oil which was chromatographed on silica gel (4 g) packed in hexane. Elution with ether-benzene (1:10, 100 ml) gave 4,8-dimethyl-15-oxa-tetracyclo$[7.4.1.1^{10,13}0^{3,8}]$pentadeca-2,11-dien-14-one: mp 131-2°. The nmr spectrum of this adduct was identical to the nmr spectrum of the furan adduct (**150**) obtained at -80°.

Irradiation of 5α,8aα-dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone in 45% aqueous acetic acid

5α,8aα-Dimethyl-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (0.250 g, 1.66 mmole) was dissolved in aqueous acetic acid (45%, 20 ml), placed in a Pyrex tube, degassed with argon for ten minutes and irradiated in a

Rayonet reactor (300 nm) for twelve hours. Toluene (20 ml) was added followed by removal of all the solvent on a rotatory evaporator. The residue was dissolved in carbon tetrachloride, dried over magnesium sulfate, concentrated and chromatographed on silica gel (25 g) packed in hexane. Elution with benzene-hexane (1:1, 250 ml) gave a phenol not reported by Kroop and Ermann and further elution with benzene-hexane (3:1, 250 ml) gave 4,8-Dimethyl-5,6,7,8,-tetrahydro-2-naphthol (161 mg): mp 95-95° [lit. (40) mp 95.5-96.5]. The new phenolic product not previously reported was not completely characterized but the spectral data suggested that it was a product derived from a diene-ketene derivative: ir (CCl_4) 3600, 2910, 1615, 1575, 1450, 1340, 1285, 1260, 1225, 1026, 861; nmr (CCl_4) δ 6.45-6.15, (~2H), 4.3 (~1H), 3.25-2.25 (m), 2.18 (s, ~3H), 2.0-1.65 (4H, m), 1.22 (d, 3H).

Investigation of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)-naphthalenone

Low temperature irradiation of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone

8aα-Carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone (5 mg) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then mounted in the Air Products low temperature infrared spectroscopy unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of the experimental section for the Air Products low temperature unit. A Pyrex filter was used throughout the irradiation. The sample was irradiated eighty five minutes. The results of these irradiations are shown in Figures 29, 30 and 31 and Tables 10 and 11.

Table 10. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-(cyclo)-2(4aH)-naphthalenone

Duration of Irradiation (min)	Absorbances 2138 cm^{-1}	2116 cm^{-1}	1825 cm^{-1}	1810 cm^{-1}	1710 cm^{-1}
0	0.000	0.000	0.000	0.000	1.130
5	0.013	0.048	0.060	0.054	1.030
10	0.028	0.090	0.064	0.064	0.964
15	0.045	0.140	0.064	0.064	0.894
25	0.077	0.202	0.062	0.064	0.854
45	0.110	0.292	0.050	0.050	0.768
65	0.139	0.366	0.050	0.050	0.650
85	0.172	0.422	0.044	0.050	0.592
105	0.176	0.432	0.044	0.036	0.523

Table 11. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 8aα-carbethoxy-1,5,6,7,8,8a-hexahydro-1β,4a-cyclo-2-(4aH)naphthalenone

Temperature (^{o}C)	Absorbances 2138 cm^{-1}	 2116 cm^{-1}
-165	0.169	0.427
-155	0.161	0.439
-143	0.156	0.439
-129	0.146	0.450
-122	0.137	0.439
-112	0.124	0.427
-104	0.107	0.380
- 96	0.097	0.338
- 85	0.080	0.303
- 74	0.064	0.267
- 69	0.042	0.204
- 61	0.012	0.068

2-Carbethoxycyclohexanone

Diethylcarbonate (~700 ml) was distilled from a few grams of sodium hydride directly into a 3l flask which had previously been swept dry with argon and charged with sodium hydride (50%) oil dispersion (0.8 mole). Cyclohexanone (39.2 g, 0.4 mole) was dissolved in a small amount of dry diethyl carbonate and added dropwise to the stirred sodium hydride diethyl carbonate mixture over a period of two to three hours. Absolute ethanol (1 ml) was added to initiate the reaction. The reaction was complete after four hours. During this time, a thick slurry of sodium enolate formed. This mixture was poured into an ice cold mixture of ether, water, and a slight excess of acetic acid. The organic layer was separated, washed with ice cold 10% sodium carbonate solution to neutrality and dried over sodium sulfate. The solvent was removed on a rotatory evaporator followed by short path distillation to give 2-carbethoxycyclohexanone (63 g, 0.37 mole): bp 106-108 (12 mm) [lit. (92) bp 107-109 (14 mm)].

2-Keto-10-carbethoxy-$\Delta^{1,9}$-octahydronaphthalene

Sodium methoxide (0.438 g, 8.1 mmole) was added to absolute methanol (84 ml) which had been previously purged with argon. The solution was cooled in an ice bath followed by the dropwise addition with continous stirring of 2-carbethoxycyclohexanone (13 g, 0.37 mole). The addition took twenty minutes. Methyl vinyl ketone (34.8 g, 0.498 mole) was added dropwise over a period of thirty minutes followed by warming to room temperature and stirring for another thirty minutes. The solution was neutralized with glacial acetic acid, concentrated, dissolved in water, extracted with ether, washed with brine and dried over magnesium sulfate. The crude condensation product was used for the cyclization step without further purification. This diketone (101 g, 0.421 mole) was dissolved in a small amount of methanol and added dropwise to sodium methoxide (1 mole) in methanol (600 ml) with rapid stirring. The mixture was kept under argon during the addition. After twenty minutes, glacial acetic acid was added dropwise until the mixture was slightly acidic. The color of the solution turned from red to gold. The methanol was removed followed by addition of enough water to dissolve the sodium acetate. The aqueous phase was extracted twice with ether. The combined extracts were dried over magnesium sulfate, concentrated and distilled to give 2-keto-10-carbethoxy-$\Delta^{1,9}$-octahydronaphthalene (62 g): bp 138-142° (2 mm) [lit. (93) bp 140-143 (2.5 mm)].

3-Keto-9-carbethoxy-$\Delta^{1:4}$-hexahydronaphthalene

2-Keto-10-carbethoxy-$\Delta^{1,9}$-octahydronaphthalene (35.5 g, 0.16 mole), selenium dioxide (20 g, 0.18 mole) and acetic acid (5 ml) were dissolved in _t_-butyl alcohol (2000 ml) and refluxed for forty eight hours. This solution was continuously purged with argon throughout this period. The mixture was cooled to room temperature, filtered through Celite, concentrated and diluted with ether (200 ml) and filtered to remove residual selenium. The ethereal solution was washed with dilute sodium hydroxide solution, water and dried over magnesium sulfate. Distillation of this material gave 3-keto-9-carbethoxy-$\Delta^{1,4}$-hexahydronaphthalene (12.4 g): bp 141-146° (3 mm) [lit. (93) bp 145-147° (4 mm)].

Investigation of 2,4,6-Cyclooctatrienone

Low temperature irradiation of neat 2,4,6-cyclooctatrienone

2,4,6-Cyclooctatrienone (5 µl) was placed between two sodium chloride plates (25 mm by 4 mm) which were then mounted in the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A Corning 0-51 filter was used throughout the irradiation. The sample was irradiated for twenty minutes. The results of the irradiations are shown in Figures 33, 34, 35 and 36 and Tables 12 and 13.

Room temperature irradiation of neat 2,4,6-cyclooctatrienone

2,4,6-Cyclooctatrienone (5 µl) was placed between two polished sodium chloride plates (25 mm by 4 mm) which were then mounted in the Air Products low temperature infrared unit. The room temperature spectrum of the starting

Table 12. Absorbances of selected absorption bands obtained from the infrared spectra of a cold, irradiated sample of 2,4,6-cyclooctatrienone

Duration of Irradiation (min)	Absorbances			
	2113 cm^{-1}	1731 cm^{-1}	1668 cm^{-1}	1620 cm^{-1}
0	0.000	0	0.630	0.305
5	0.180	0.217	0.481	0.230
10	0.301	0.330	0.393	0.179
15	0.367	0.377	0.338	0.158
20	0.382	0.387	0.274	0.127

Table 13. Absorbances of selected absorption bands which were calculated from the infrared spectra obtained while warming a cold, irradiated sample of 2,4,6-cyclooctatrienone

Temperature (°C)	Absorbances			
	2113 cm^{-1}	1731 cm^{-1}	1709 cm^{-1}	1668 cm^{-1}
-151	0.428	0.418	0.000	0.301
-127	0.424	0.334	0.143	0.305
-107	0.419	0.181	0.228	0.300
- 99	0.405	0.060	0.248	0.300
- 85	0.403	0.0	0.265	0.350
- 82	0.398	0.0	0.260	0.346
- 75	0.363	0.0	0.276	0.346

Table 13 (Cont.)

Temperature (°C)	Absorbances			
	2113 cm^{-1}	1731 cm^{-1}	1709 cm^{-1}	1668 cm^{-1}
- 64	0.305	0.0	0.276	0.373
- 51	0.100	0.0	0.276	0.040

material was recorded on a Beckman IR-9 spectrometer. The sample was then irradiated for six, one minute intervals. A Corning 0-51 filter was used throughout the irradiation. Absorption bands at 1709 cm^{-1}, 1760 cm^{-1} and 1825 cm^{-1} were clearly observable after these irradiations. After the cell was demounted, glpc analysis of this crude mixture on 4 ft by 1/4 in 20% SF-96 on 60-80 mesh Chromosorb W, 90°, showed that 2,4,6-cyclooctatrienone was the only volatile component under these conditions. No bicyclo[4.2.0]octa-4,7-dien-2-one could be detected.

Irradiation of 2,4,6-cyclooctatrienone in a rigid, methanol glass at -190°

2,4,6-Cyclooctatrienone (15 µl) was mixed with methanol (5 µl) until a homogenous solution was obtained. A sample of this solution was placed between two polished sodium chloride plates (25 mm by 4 mm) which were separated by a metal spacer (0.025 mm). The plates were then mounted in the Air Products low temperature infrared unit. The spectra at room temperature and at low temperature, the irradiation procedure and warmup procedure were all carried out as described in the general procedure of this experimental section for the Air Products low temperature unit. A Corning 0-51 filter was used throughout the irradiation. The carbonyl absorptions were clearly observable for the triene-ketene and *trans,cis,cis*-2,4,6-cyclooctatrienone. The warmup procedure was carried out as previously described for 2,4,6-cyclooctatrienone. The *trans* isomer underwent its transformations as observed for neat 2,4,6-cyclooctatrienone at about -120°. The triene-ketene had nearly completely disappeared when the cell reached -82°. During this period, a new carbonyl absorption appeared at 1739 cm^{-1} which is the absorption expected for 1,2-addition of methanol to the ketene.

Preparative scale irradiation of 2,4,6-cyclooctatrienone at -190° in an ether-methanol glass

2,4,6-Cyclooctatrienone (200 mg, 1.66 mmole) was placed in a Pyrex tube with ether-methanol (4:1, 10 ml), capped with a rubber septum and purged with argon for ten minutes. The sample was placed in a Dewar flask designed with a Pyrex window and then cooled with liquid nitrogen. The sample was irradiated for eight hours and then allowed to warm to room temperature and concentrated. Preparative glpc through 12 ft by 3/8 in 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 150°, gave a methyl ester whose spectra were identical to the spectra obtained from one of the esters isolated by irradiation of 2,4,6-cyclooctatrienone in methanol at room temperature.

Irradiation of 2,4,6-cyclooctatrienone in a rigid, furan containing glass at -190°

2,4,6-Cyclooctatrienone (15 µl) was mixed with a solution of ether-isopentane-furan (10:5:1, 10 µl) until a homogenous solution was obtained. A sample of this solution was placed between two sodium chloride plates (25 mm by 4 mm) which were separated by a metal spacer (0.012 mm). The two salt plates were mounted in the Air Products low temperature infrared unit, cooled to -190° and irradiated ten minutes through Pyrex. The carbonyl absorption bands for the triene-ketene and _trans,cis,cis_-2,4,6-cyclooctatrienone were both formed as usual. No products were observed with carbonyl absorptions at 1715 cm^{-1}. This is the expected position for the absorption bands of the Diels-Alder adducts of furan and _trans,cis,cis_-2,4,6-cyclooctatrienone. The cell was then allowed to warm gradually while the region between 1550 cm^{-1} and 1800 cm^{-1} was repeatedly scanned. After the carbonyl absorption of the trans-isomer disappeared, the cell was cooled to -190° for comparison spectra. A new absorption band was observed at 1715 cm^{-1}. This crude mixture was warmed to room temperature. Analysis of this mixture by tlc showed that two adducts were present with R_F values identical to the R_F values of the Diels-Alder adducts obtained at room temperature.

Preparative irradiation of 2,4,6-cyclooctatrienone in a rigid, furan containing glass at -190°

2,4,6-Cyclooctatrienone (50 mg, 0.42 mmole) was dissolved in ether-isopentane-furan (2:1:0.3, 5 ml), placed in a Pyrex tube, capped with a rubber septum and degassed with argon for two minutes. The solution was cooled with liquid nitrogen in a Dewar flask with a Pyrex window and then irradiated through a Corning 0-51 filter. After two hours, the solution was removed from the irradiation unit and allowed to warm to room temperature. A comparison of this irradiated sample to an identical sample which had not been irradiated and to a sample that had been irradiated at room temperature was made by tlc. No detectable change occurred to the sample that remained at room temperature and was not irradiated. The solution which was irradiated at room temperature contained bicyclo[4.2.0]octa-4,7-dien-2-one and the two Diels-Alder adducts (157) and (158). The solution which had been irradiated at low temperature contained only starting material and the two Diels-Alder adducts (157) and (158). The bicyclic isomer (91) was not detected in this sample. Analysis of this sample by glpc on 4 ft by 1/4 in 20% SF-96 on 60-80 mesh Chromosorb W, 90°, showed only 2,4,6-cyclooctatrienone in the mixture. No bicyclic isomer (91) was detected.

Irradiation of 2,4,6-cyclooctatrienone in methanol at room temperature

2,4,6-Cyclooctatrienone (0.30 g, 2.5 mmole) was dissolved in methanol (100 ml), placed in a Pyrex tube, capped with a rubber septum and purged with argon for ten minutes. The solution was then irradiated for three hours in a Rayonet reactor (350 nm). Tlc analysis showed nearly complete destruction of starting material. Preparative glpc on 12 ft by 3/8 in 10% Carbowax 20 M on 60-80 mesh Chromosorb W, 165°, gave pure samples of two isomeric esters reported by Buchi (54): ester (163): ir (CCl_4) 870, 968, 1000, 1140, 1175, 1260, 1430, 1620, 1715 [lit. (54) ir (CCl_4) 870, 1000, 1140, 1175, 1260, 1430, 1620, 1715 cm^{-1}]: nmr (CCl_4) δ 7.90-5.40 (m, 6H), 3.68 (s, 3H), 1.81 (d, J = 6 Hz, 2H): ester (164): ir (CCl_4) 860, 880, 1000, 1040, 1140, 1185, 1225, 1265, 1435, 1620, 1715; nmr (CCl_4) δ 7.50-5.50 (m, 6H), 3.69 (s, 3H), 1.86 (d, J = 6 Hz, 3H). Ester (**164**) did not exhibit the strong absorption at 968 cm^{-1} which appeared in ester (**163**). Ester (**164**) may therefore be the all *cis* isomer.

Irradiation of 2,4,6-cyclooctatrienone in ether at room temperature

2,4,6-Cyclooctatrienone (0.40 g, 3.3 mmole) was dissolved in ether (100 ml), placed in a Pyrex tube, capped with a rubber septum and purged with argon for ten minutes. The solution was then irradiated for fourteen hours in a Rayonet reactor (350 nm). Tlc analysis of this irradiated solution showed only a trace of starting material. Preparative glpc of this crude photomixture through 8 ft by 1/4 in 10% SF 96 on 60-80 mesh Chromosorb W, 100°, gave bicyclo[4.2.0]octa-4,7-dien-2-one: ir (film) 703, 758, 1234, 1265, 1310, 1709, 2110 and 3040 cm^{-1}; [lit. (54) ir (CS_2) 700, 755 cm^{-1} (CCl_4) 1235, 1265, 1310, 1710, 2920 and 3050 cm^{-1}]; nmr (CCl_4) δ 6.32-5.90 (m, 2H), 5.90-5.48 (m, 2H), 3.86-3.32 (m, 2H), 3.00-2.78 (m, 2H).

Irradiation of 2,4,6-cyclooctatrienone in furan at room temperature

2,4,6-Cyclooctatrienone (1.0 g, 8.3 mmole) was placed in a Pyrex tube and dissolved in freshly distilled furan. The tube was degassed with argon for five minutes and irradiated in a Rayonet reactor (350 nm) for thirty six hours. Analysis of this solution by tlc and ir showed complete destruction of starting material with formation of three new products. The solution was concentrated on a rotatory evaporator to give a pale yellow oil (1.14 g). Addition of hexane (2 ml) followed by cooling gave a nearly complete separation of adducts (**157**) and (**158**) from the third component, bicyclo[4.2.0]octa-4,7-dien-2-one. The nearly crystalline adducts (0.28 g) were dissolved in a small amount of benzene and chromatographed on silica gel packed in hexane. Elution was begun with benzene (1000 ml), ether-benzene (5%, 500 ml) and ether benzene (10%, 500 ml). Only a trace of 2,4,6-cyclooctatrienone was obtained. Further elution with ether-benzene (15%, 500 ml) gave adduct (**157**) (88 mg) and with ether-benzene (20%, 500 ml) gave adduct (**158**) (84 mg). Recrystallization from hexane gave analytical samples of both adducts. Physcial and spectral properties of adduct (**157**) follow: mp 101-102°; ir (CCl_4) 1715 cm^{-1}; nmr ($CDCl_3$) δ 6.41 (2H), 6.29-5.45 (m, 4H), 5.01 (d, J = 4 Hz, 1H), 4.73 (s, 1H), 3.37 (d, d, J = 4 Hz, J^1 = 7.5 Hz, 1H), 3.11 (2H), 2.54 (d, d, 1H, J = 7.5 Hz, J'' = 4 Hz); mass spectrum (70 ev) (Figure 41) m/e 188 (5), 121 (7), 120 (42), 119 (14), 107 (23), 94 (41), 92 (45), 91 (100), 81 (67), 77 (19), 65 (21), 51 (22), 41 (17).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57, H, 6.43. Found:

C, 76.56; H, 6.50.

Adduct (158): mp 112-114°; ir (CCl_4) 1715 cm^{-1}; nmr ($CDCl_3$) δ 6.57 (d, d, J = 5.7, J′ = 1.93, 1H), 6.31 (d, d, 1H, J = 5.7 Hz, J″ = 1.9 Hz), 6.21-5.47 (m, 4H), 5.20 (s, 1H), 4.95 (d, 1H, J = 4 Hz), 3.59-2.97 (m, 3H), 2.77 (d, 1H, J = 8 Hz); mass spectrum (70 ev) (Figure 45) m/e 188 (9), 170 (8), 160 (15), 132 (18), 121 (33), 120 (100), 119 (45), 118 (21), 117 (25), 108 (18), 107 (59), 105 (17), 92 (91), 91 (99), 82 (17), 81 (99), 78 (89), 68 (81), 55 (27).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.67; H, 6.55.

Irradiation of 2-cyclooctenone in furan at room temperature

2-Cyclooctenone (3.0 g, 25.2 mmole) was placed in a Pyrex tube, dissolved in freshly distilled furan (100 ml), capped with a rubber septum and purged with argon for five minutes. The solution was then irradiated in a Rayonet reactor (300 nm) until all starting material was destroyed. The solution was concentratad to give a light yellow oil (3.11 g) which was chromtographed on silica gel (180 g) packed in hexane. The oil was dissolved in s small amount of benzene and loaded onto the column. Elution was begun with benzene (500 ml) and ether-benzene (5%, 500 ml). Adduct (159) (1.48 g) was obtained. Further elution with ether-benzene (10%, 500 ml- gave adduct (160) (1.40 g). Short path distillation gave analytical samples of each adduct. Adduct (159): bp 103-105° (0.2 mm); ir (film) 1690 cm^{-1}; nmr (CCl_4) δ 6.28 (2H), 4.88 (d, 1H), 4,38 (s, 1H), 2.88-2.62 (m, 1H), 2.55-1.20 (m, 11 H).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.29.

Adduct (160): bp 101-103° (0.16 mm); ir (film) 1690 cm^{-1}; nmr (CCl_4) δ 6.30 (d, d, J = 5.8, J^1 = 1.8, 2H), 5.04 (s, 1H), 4.69 (d, 1H, J = 4 Hz), 2.95-0.51 (μ, 12H).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.09; H, 8.37.

General procedure for catalytic hydrogenation of adducts (157), (158), (159) and (160)

Each adduct (150 mg, $\sim$0.77 mmole) was dissolved in methanol (1 ml) and added to a mixture of palladium on charcoal (5%, 10 mg) in methanol (10 ml) which had been previously purged with hydrogen. The hydrogenation was stopped upon uptake of the requisite number of moles of hydrogen. The catalyst was then removed by filtration through Celite, followed by concentration with the aid of a rotatory evaporator. Preparative glpc of reduced adducts (157) and (159) and reduced adducts (158) and (160) through 12 ft. by 3/8 in. 10% SE-30 on 60-80 mesh Chromosorb W, 170°, gave analytical samples of perhydro adducts (161) and (162). Adduct (161): ir (film) 1690 cm^{-1}; nmr (CCl_4) δ

4.53 (t, 1H), 4.03 (d, 1H, J = 4 Hz), 2.73-2.21 (m, 3H), 2.11-1.05 (m, 13H); mass spectrum (70 ev) (Figure 42) m/e 194 (32), 153 (53), 152 (61), 139 (28), 124 (28), 110 (32), 109 (22), 108 (56), 107 (41), 140 (23), 99 (26), 96 (61), 82 (81), 80 (76), 68 (84), 56 (100), 42 (101).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.15; H, 9.29.

Adduct (162): ir (film) 1696 cm^{-1}; nmr (CCl_4) δ 4.74 (d, J = 4 Hz, 1H), 4.28 (m, 1H), 3.02-1.00 (m, 16H); mass spectrum (70 ev) (Figure 46) m/e 194 (31), 150 (55), 118 (51), 107 (54), 95 (56), 81 (80), 67 (89), 55 (94), 41 (100).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.25; H, 9.26.

Base catalyzed isomerization of adduct (159)

Adduct (159) (400 mg, 2.08 mmole) was dissolved in methanolic potassium hydroxide (4%, 10 ml). Water (1 ml) was added followed by refluxing this solution for two hours in an argon atmosphere. The solution was cooled to room temperature, poured into water (10 ml), extracted with ether (15 ml) and dried over magnesium sulfate. Evaporation of the solvent gave a nearly pure sample of the isomerized ketone (165): ir (CCl_4) 1690 cm^{-1}; nmr (CCl_4) δ 6.42 collapsed AB, 2H), 5.03 (s, 1H), 4.55 (s, 1H), 2.88-0.90 (m, 12H).

Competition experiment between the addition of furan to *trans,cis,cis*-2,4,6-cyclooctatrienone and electrocyclic closure to bicyclo[4.2.0]octa-4,7-dien-2-one

Nine samples were prepared each containing 2,4,6-cyclooctatrienone (150 mg, 1.25 mmole), freshly distilled furan and anhydrous ether. The furan concentrations were varied from zero to thirteen moles per liter with the total volume of each sample adjusted to a constant volume (3 ml). Each sample was contained in a Pyrex tube (13 by 100 mm), purged with argon, sealed and irradiated (48 hours) in a Rayonet reactor (350 nm) rotating wheel. The relative yield of bicyclo[4.2.0]octa-4,7-dien-2-one and the furan adducts (**157**) and (**158**) were obtained by integration of selected absorptions of the nmr spectra of the reaction mixtures. The absorptions between δ 3.44 and 3.86 (2H) were chosen for bicyclo[4.2.0]octa-4,7-dien-2-one and the absorptions at δ 3.58-3.68 (1H) for adduct (**157**) and at δ 4.99-5.09 (1H) for adduct (**158**). There were no other significant nmr absorptions at these positions.

A second series of samples was prepared to study the effect of varying irradiation times on product formation and the effect of changing furan concentrations on the yield of bicyclo[4.2.0]octa-4,7-dien-2-one. Each sample contained 2,4,6-cyclooctatrienone (0.050 g, 4.16 x 10^{-4}

mole), toluene (0.0133 g, 1.45×10^{-4} mole and furan as shown in Table 14. The volume of each sample was increased to a total volume of 0.360 ml with benzene. Each sample was irradiated in a sealed nmr tube until approximately 90% of the starting material had been destroyed. The yield of bicyclo[4.2.0]octa-4,7-dien-2-one was obtained by integrating a two proton absorption of bicyclo[4.2.0]octa-4,7-dien-2-one at δ 3.5 relative to benzene at δ 7.2 and is shown in Figure 49 and Table 14. Sample one was followed periodically throughout the irradiation. The moles bicyclo[4.2.0]octa-4,7-dien-2-one formed throughout the irradiation are shown in Table 15 and Figure 50.

Table 14. Furan concentration effects on 2,4,6-cyclooctatrienone photochemistry

Sample	[furan]	$\frac{1}{[\text{furan}]}$	moles ($\underset{\sim}{91}$)	[$\underset{\sim}{91}$]
1	1.93	0.518	2.32×10^{-4}	0.645
2	5.79	0.173	1.76×10^{-4}	0.490
3	11.6	0.086	1.57×10^{-4}	0.433

Table 15. Formation of bicyclo[4.2.0]octa-4,7-dien-2-one as a function of irradiation time

Irradiation time	moles **91**	[**91**]
0	0	0
5.6	0.47×10^{-4}	0.130
9.5	0.81×10^{-4}	0.225
15.5	1.28×10^{-4}	0.356
27.5	2.32×10^{-4}	0.645

Cyclooctatetraene oxide

Cyclooctatetraene (104 g, 1.00 mole) was placed in a two-liter, three-necked flask fitted with a mechanical stirrer, thermometer and dropping funnel. The solution was degassed with argon and cooled with an ice bath. The sulfuric acid (1%) in commercial peracetic acid (45%) was neutralized by adding sodium acetate (5.0 g) to the peracetic acid (100 ml) immediately before it was used. The stirrer was started and the peracetic acid solution (10 ml) was added. When the temperature of the reaction mixture reached 29°, the flask was cooled to 15° with the ice bath. The addition of peracetic acid was continued at a rate such that the reaction temperature was kept in the range of 29-31° by raising or lowering the cooling bath. Constant attenuation was required to control the temperature of the exothermic reaction. After peracetic acid (200 ml) was added, the solution was allowed to stand (1.5 hrs). The reaction was then poured into cold water (1000 ml). The yellow oil which separated was extracted into pentane (600 ml) and washed with two portions of water (150 ml) and five portions of sodium hydroxide (10%, 50 ml) and dried over magnesium sulfate at 5°. Concentration followed by distillation through a twenty centimeter spinning band column gave pure cyclooctatetraene oxide (27 g): bp 75-76 (13 mm) [lit. (94) bp 75-76 (12 mm)]; nmr (CCl_4) δ 6.26-5.68 (m, 6H), 3.31 (s, 2H).

2,4,6-Cyclooctatrienone

A two-liter, three-necked flask was fitted with a mechanical stirrer, reflux condensor and dropping funnel. The system was completely degassed with argon and kept under a positive pressure of argon at all times. Anhydrous ether (120 ml) was then added to the flask followed by lithium wire (8.4 g, 1.2 mole) which had been cut into small pieces. A solution of bromobenzene (104 g, 0.66 mole) in dry ether (240 ml) was added at a rate sufficient to maintain reflux. The mixture was refluxed and then cooled to -15° in a Dry-Ice-Acetone bath. The phenyl lithium was converted to lithium diethylamide by addition of a solution of diethylamine (43.8 g, 0.6 mole) in dry ether (120 ml) during a period of thirty minutes. A solution of cycloctatetraene oxide (27 g, 0.225 mole) in dry ether (120 ml) was added to the lithium diethylamide solution during a period of ten minutes. The reaction mixture was maintained at -8 to -12°. A deep orange color followed and there was an appreciable heat of reaction. The reaction was stirred at -10° for fifteen minutes after the addition was complete. Sulfuric acid (3N, 400 ml) was added, slowly at first and then at a rate which kept the internal temperature at 0° to 5° with continued cooling and stirring. The two orange layers were separated and the aqueous layer was extracted with ether (600 ml). The combined ether solutions were then washed with saturated sodium bicarbonate solution (25 ml) and water (50 ml). The ether layer was dried over sodium sulfate and concentrated. The crude oil was distilled through a six inch spinning band column to give pure 2,4,6-cyclooctatrienone (20 g): bp 96° (17 mm) [lit. (93) bp 107° (23 mm)]; nmr (CCl_4) δ 6.97-5.50 (m, 6H), 2.95 (d, J = 8 Hz, 2H).

3-Cyclooctenyl acetate

Cyclooctene (187 g, 1.7 mole), mercuric acetate (575, 1.8 mole) and acetic acid (850 ml) were placed in a two-liter, three-necked flask fitted with a mechanical stirrer and reflux condensor. The mixture was then stirred at room temperature (45 min) while a yellow precipitate formed and then refluxed ten hours. The dark brown solution was cooled to room temperature and filtered to remove metallic mercury (317.5 g). The solution was concentrated and then poured into cold water (1500 ml). This mixture was extracted with four portions of ether (300 ml). The combined ether extracts were washed with sodium bicarbonate solution (5%), water, and dried over magnesium sulfate. After filtration of this solution, distillation gave 3-cyclooctenyl acetate (110 g): bp 55-59 (1.2 mm) [lit. (95) bp 55-59 (1 mm)].

2-Cyclooctenol

3-Cyclooctenyl acetate (110 g, 0.66 mole) was added dropwise with ice water cooling to a solution of potassium hydroxide (90 g, 1.5 mole) in water (80 ml) and ethanol (150 ml). The solution turned yellow and was stirred at room temperature for three hours. The solution was poured into cold water (1000 ml) and extracted with ether (700 ml). These extracts were washed with dilute hydrochloric acid, water, dried over magnesium sulfate and concentrated to give crude 2-cyclooctenol which upon distillation gave pure 2-cyclooctenol: bp 74° (1.8 mm) [lit. (95) bp 74° (2 mm)].

2-Cyclooctenone

A solution of chromium trioxide (42 g, 0.42 mole), water (210 ml) and concentrated sulfuric acid (34 ml) was slowly added to a solution of 2-cyclooctenol (78 g, 0.62 mole) in acetone (210 ml). The solution was cooled in an ice bath and stirred slowly with a magnetic stirrer. The addition required two hours. The acetone layer was separated from the aqueous layer, followed by addition of water (1000 ml) to the aqueous layer. This aqueous mixture was extracted with two portions of ether (250 ml). The ether-acetone extracts were washed with water and dried over magnesium sulfate to give crude 2-cyclooctenone. Distillation through a Vigreux column (12 in) gave 2-cyclooctenone: bp 91-95° (14 mm) [lit. (95) bp 89° (14 mm)].

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