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Photochemical synthesis of β-lactones and β-lactams

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PHOTOCHEMICAL SYNTHESIS
OF β-LACTONES AND β-LACTAMS

by

William Raymond Adams

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967

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VITA

The author was born in Niagara Falls, New York to Mr. and Mrs. William Adams. He graduated from LaSalle High School in June, 1954 and was employed from 1954 to 1957 by Oldbury Electrochemical Company as a laboratory and pilot plant technician. In September, 1957 he enrolled at Rochester Institute of Technology, Rochester, New York. He was granted an Associates of Applied Science degree in June, 1960 and a Bachelor of Science degree in June, 1962. The author was employed in the Control Laboratories at Rochester Gas and Electric Company during his cooperative employment with Rochester Institute of Technology.

In July, 1962 the author enrolled at Iowa State University of Science and Technology as a graduate student with a teaching assistantship. He carried out his research in the field of organic chemistry under the direction of Dr. O. L. Chapman. The author was awarded the DuPont Teaching Award in September, 1964 and received the Master of Science degree in August, 1965. The author was graduated with the Ph.D. degree from Iowa State University of Science and Technology in August, 1967.

INTRODUCTION

In the past ten years there has been a growing interest in light-induced transformations of organic molecules in general and conjugated ketones in particular. α,β-Unsaturated ketones are known to undergo a variety of photoreactions including valence tautomerization, dimerization, cleavage, structural rearrangement and photocycloaddition. These photocycloadditions have proved to be a versatile synthetic tool and have been utilized in the synthesis of cubane, caryophyllene, tropolones, oxetanes and cyclobutanes.

The photocyclization processes have quite recently been extended to include α,β-unsaturated acids, esters, nitriles and nitro compounds, thus increasing the synthetic potential of these reactions.

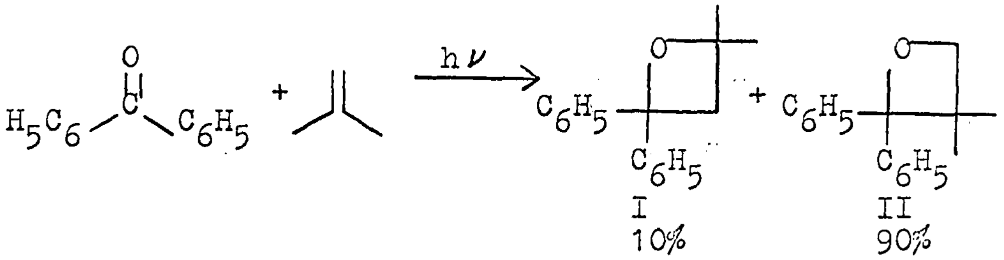
This thesis describes a study of the photochemistry of several α,β-unsaturated acids and amides in an effort to extend the synthetic versatility of photochemistry.

HISTORICAL

Photocycloaddition Reactions

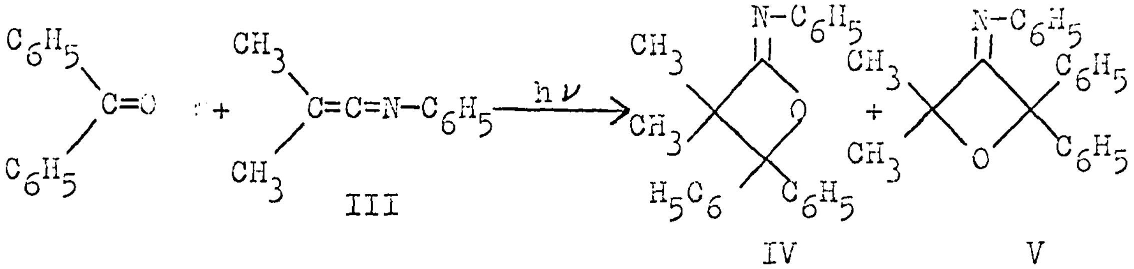
Paterno-Büchi Reaction

Formation of oxetanes by photocycloaddition of aldehydes and ketones to olefins provide an attractive entry into small ring heterocyclic systems. Irradiation of benzophenone in the presence of excess isobutylene gives only two oxetanes (I and II) in high yield (1,2,3,4).



The reactions involve the n,Pi* triplet state of the carbonyl system and the predominant isomer is correctly predicted from consideration of the more stable biradical (ground state) intermediate. A large number of such reactions are known and have been recently reviewed (5,6,7).

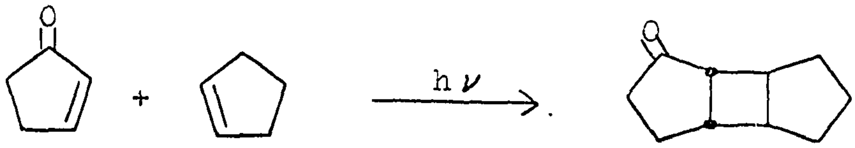
Photoinduced cycloaddition of aldehydes and ketones to ketenimines to give imino-oxetanes is an extension of the Paterno-Büchi reaction. Irradiation of benzophenone in the presence of dimethyl-N-(phenyl)ketenimine (III) gives α-IV and β-V adducts (8). The reaction appears to be very versatile and it was found that the photocyclization of fluorenone to seven ketenimines of alkyl and aryl substitution results in exclusive α-adduct formation (9).



The α-adducts can be isomerized on Florisil to β-lactams, thus providing a convenient synthetic route to various substituted β-lactams.

Intermolecular Photocycloaddition

The first instance of photocyclization of an olefin to an α,β-unsaturated carbonyl system was reported in 1962 (10). Irradiation of 2-cyclopentenone in a ten-fold excess of cyclopentene gives cis-anti-cis-tricyclo[5.3.0]decan-2-one (VI).

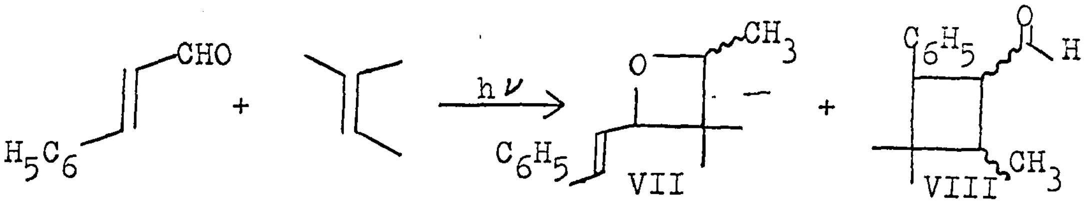


VI

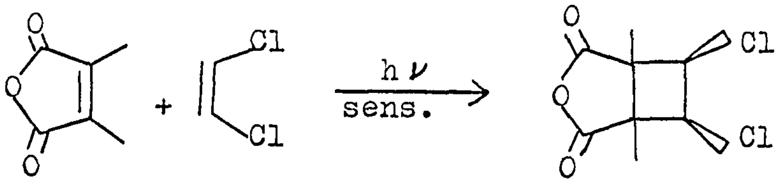
The reactions of α,β-unsaturated ketones appear to be limited in that only 2-cyclopentenones, 3-cyclohexenones enolizable 1,3-diketones (11) and a variety of quinones (12) undergo intermolecular photocyclizations with olefins (13). A series of rules concerning photochemical additions between α,β-unsaturated carbonyl compounds and olefins has been formulated (14).

The choice of the addend molecules appears to be vast since photocyclizations have been accomplished with cyclic, acyclic, negative and positive substituted olefins (15), acetylenes (13,16), and allenes (13).

Recently the scope of the photocycloaddition reactions have been extended to other α,β-unsaturated carbonyl systems. Crotonaldehyde and cinnamaldehyde have been shown to undergo photocyclizations with olefins (17). This is exemplified by the reaction of cinnamaldehyde with 2-methyl-2-butene to form an oxetane VII and a cyclobutane VIII.



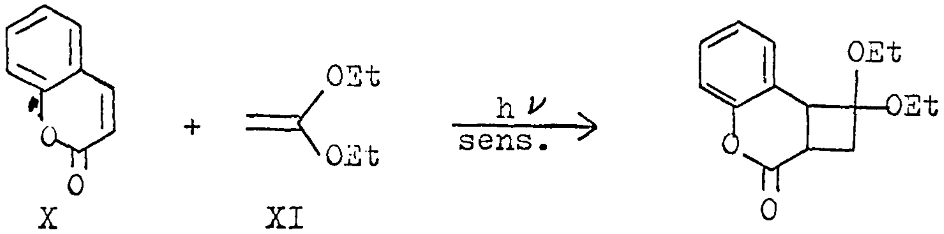
Dimethylmaleic anhydride will add to various olefins in the presence of benzophenone as sensitizer to give a series of photoadducts (18). For example, irradiation of dimethylmaleic anhydride in the presence of cis-1,2-dichloroethylene proceeds with retension of olefin configuration to give photoproduct IX.



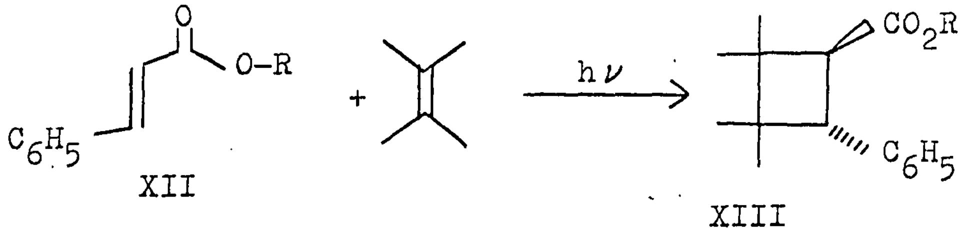
IX

Photocycloaddition of maleic anhydride and its derivatives to acetylenes provides a facile synthetic route to substituted cyclobutenes (19,20).

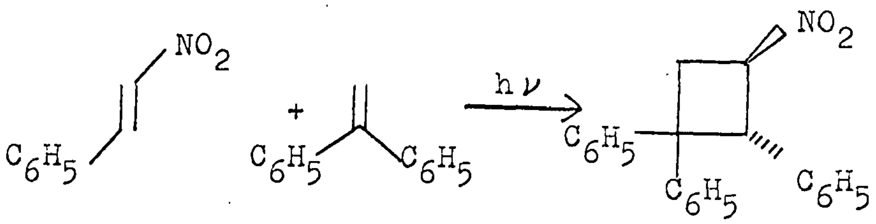
Coumarin (X), which is known to undergo photodimerization (21,22,23), has recently been reported (24) to undergo sensitized photocycloaddition reactions with tetramethylethylene, cyclopentene and ketene diethylacetal (XI).



Irradiation of a solution of trans-methylcinnamate (XII, R=CH_3) or trans-cinnamic acid (XII, R=H) in the presence of tetramethylethylene results in an exclusive yield (25) of the trans-photoadduct XIII.



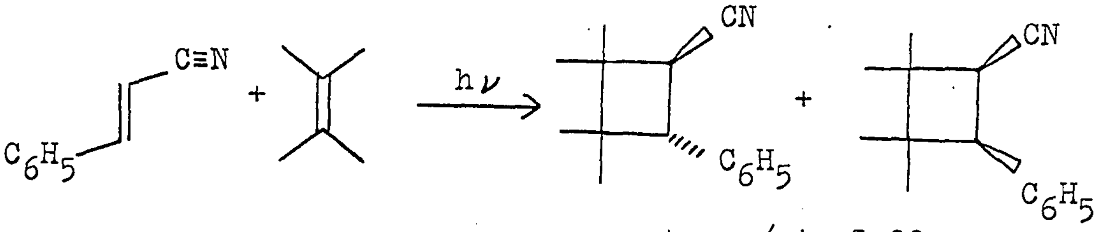
Recent investigations have shown that α,β-unsaturated nitro and cyano-compounds also will add to olefins to form cyclobutanes in a manner analogous to unsaturated carbonyl moieties. Irradiation of trans-β-nitrostyrene (XIV) in the presence of excess 1,1-diphenylethylene affords a single photoadduct XV in which the nitro and phenyl groups are oriented trans to each other (26).



XIV XV

Similar irradiations of XIV in cyclopentene, cyclohexene, styrene, and tetramethylethylene gives analogous cyclobutane derivatives in each case (26).

trans-Cinnamonitrile (XVI) undergoes photocycloaddition in the presence of tetramethylethylene to give a mixture of cis and trans-cyanocyclobutanes (XVII and XVIII) respectively.[1]



trans/cis=5.00

XVI XVII XVIII

Photochemical Decarboxylations

The photochemical decarboxylation of pyruvic acid has been observed in the gas phase and in solution (27,28). In solution the reaction path is highly dependent on the medium. In aqueous solution pyruvic acid (XIX) is photodecarboxylated to give acetoin (XX), whereas in hydrogen donating organic solvents

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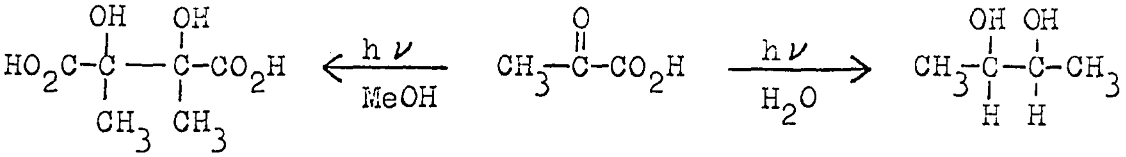
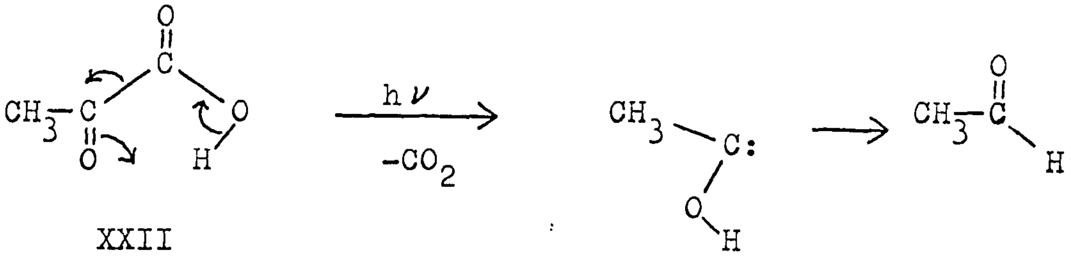
[1] W. R. Adams, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Data from research notebook. 1967.

photoreduction occurs to yield dimethyltartaric acid (XXI).



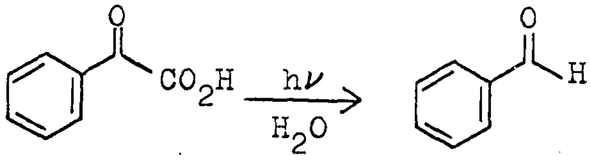
XXI XIX XX

Pyruvic acid in the gas phase undergoes decarboxylation to yield acetaldehyde. It was concluded (28) that the primary photochemical process (vapor phase) is a concerted decarboxylation from a cyclic transition state XXII.



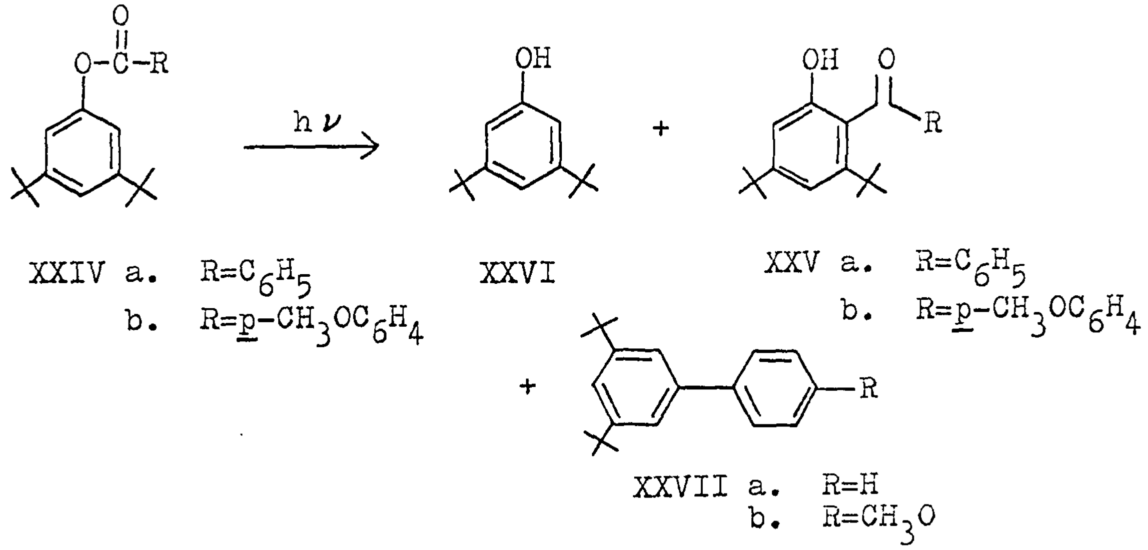
XXII

Photolysis of benzoylformic acid (XXIII) in aqueous solution exhibits a different photochemical process, the main product being benzaldehyde (27).



XXIII

The photo-Fries rearrangement (29) of aryl esters is accompanied in several cases by decarboxylation products (30, 31). Irradiation of 3,5-di-t-butylphenylbenzoate (XXIVa) gives 3,5-di-t-butylphenol (XXVI), a hydroxyketone XXVa, a product which has lost the elements of carbon dioxide XXVIIa, benzoic acid and a trace of biphenyl (32).



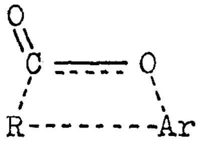
XXIV a. $R=C_6H_5$
b. $R=$*p*$-CH_3OC_6H_4$

XXVI

XXV a. $R=C_6H_5$
b. $R=$*p*$-CH_3OC_6H_4$

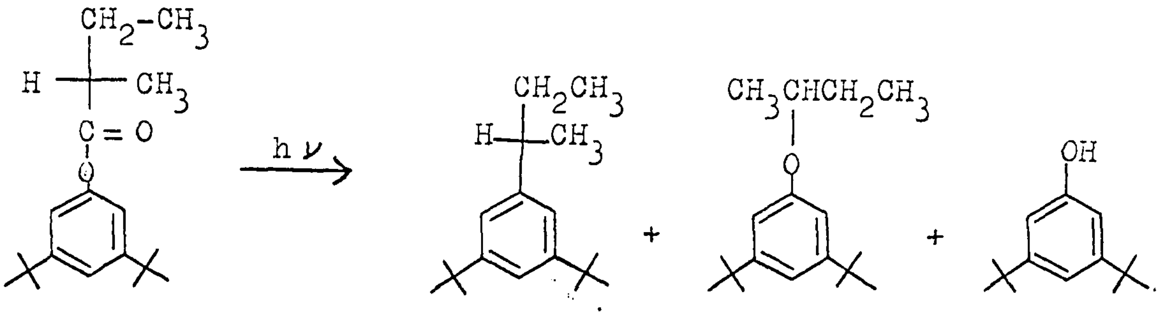
XXVII a. $R=H$
b. $R=CH_3O$

Finnegan and Knudson (32) suggested that this photoexpulsion of carbon dioxide proceeds in a concerted fashion via a transition state XXVIII which requires that the configuration



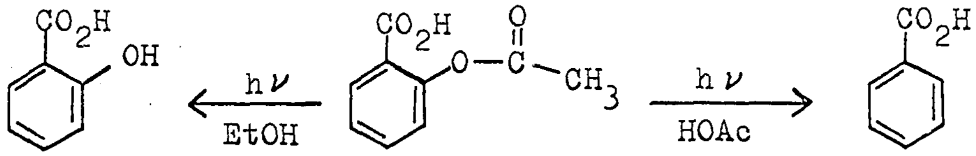
XXVIII

of the α-carbon in the R group be retained during the transformation. In support of this mechanism, photodecarboxylation with predominant retention of configuration has been recently reported (33). Irradiation of S-(+)-XXIX yielded S-(+)-2-(3,5-di-*t*-butylphenyl)butane (XXX), racemic 3,5-di-*t*-butylphenyl-*sec*-butylether (XXXI) and 3,5-di-*t*-butylphenol (XXXII).



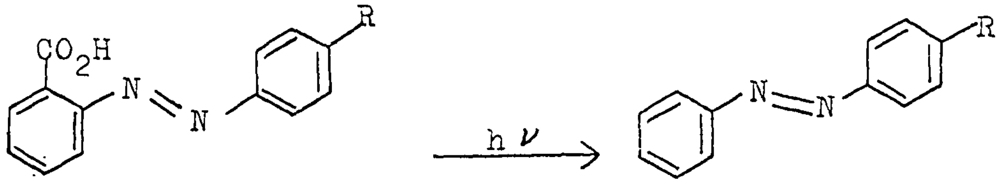
XXIX XXX XXXI XXXII

Acetylsalicylic acid (XXXIII) is photodecomposed to benzoic acid in acetic acid solution (34). The presence of the o-carboxy substituent appears to be necessary for de-acetoxylation as m and p-acetoxybenzoic acids under the same conditions yield m and p-hydroxybenzoic acids, respectively.



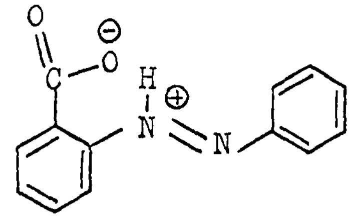
XXXIII

Irradiation of azobenzene-2-carboxylic acid (XXXIV, R=H) and its 4'-methyl, 4'-chloro and 4'-dimethylamino (XXXIV, R= CH_3, Cl and $N(CH_3)_2$) in benzene solution yields the corresponding decarboxylated azo compounds (35). The position of the carboxylic acid moiety appears crucial since neither azobenzene-3-carboxylic acid nor azobenzene-4-carboxylic acid undergoes photochemical decarboxylation under identical conditions.



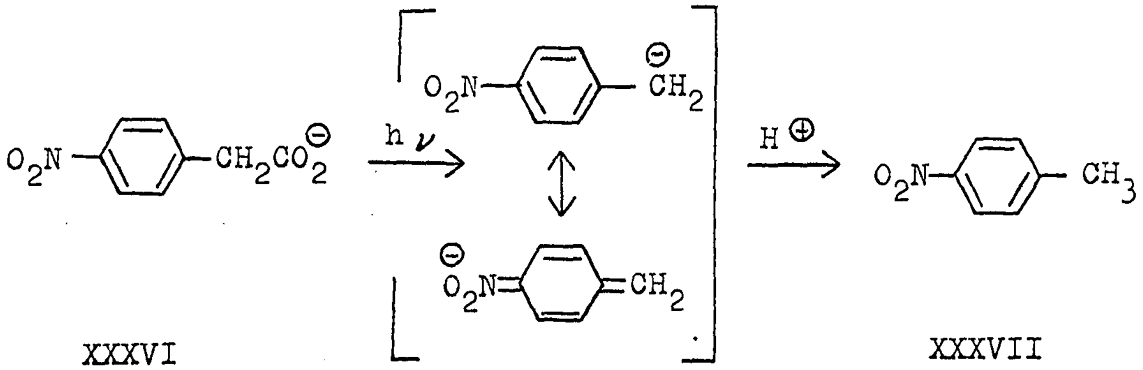
XXXIV

The zwitterionic form XXXV is proposed as playing an essential role in the decarboxylation.



XXV

Photolytic decarboxylation is observed when 2,3, or 4-nitrophenylactic acids are irradiated in basic solution (36). The following reaction shown for the 4-nitrophenylacetate ion (XXXVI) occurs to give 4-nitrotoluene (XXXVII).

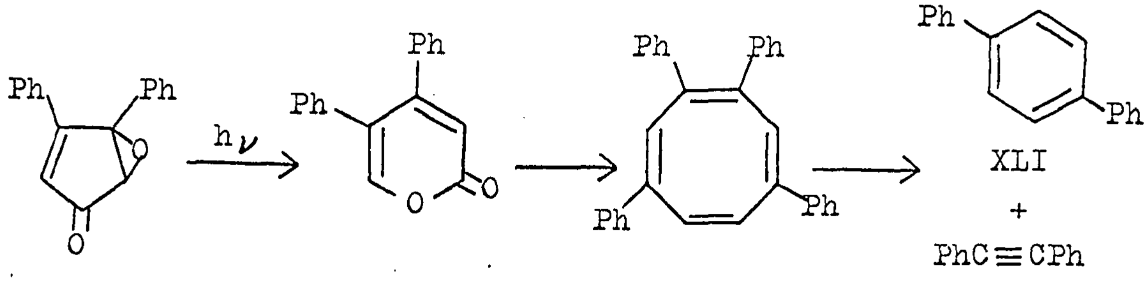


XXXVI

XXXVII

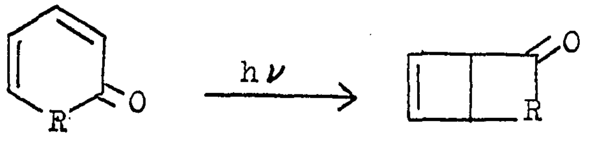
Under similar conditions the unsubstituted phenylacetate anion and undissociated nitrophenylacetic acids did not undergo appreciable photodecarboxylation.

The light-induced rearrangement of 3,4-diphenyl-4,5-epoxy-2-cyclopentenone (XXXVIII) represents a complex photochemical transformation (37). Photolysis of XXXVIII in anhydrous ether for 18 hours afforded a mixture of products. The two major components were p-terphenyl (XLI) and diphenylacetylene (XLII). Irradiation of XXXVIII for shorter periods of time gave in addition to XLI and XLII, 4,5-diphenyl-3-pyrone (XXXIX) and 1,2,4,7-tetraphenylcyclooctatetraene (XL).



XXXVIII XXXIX XL XLII

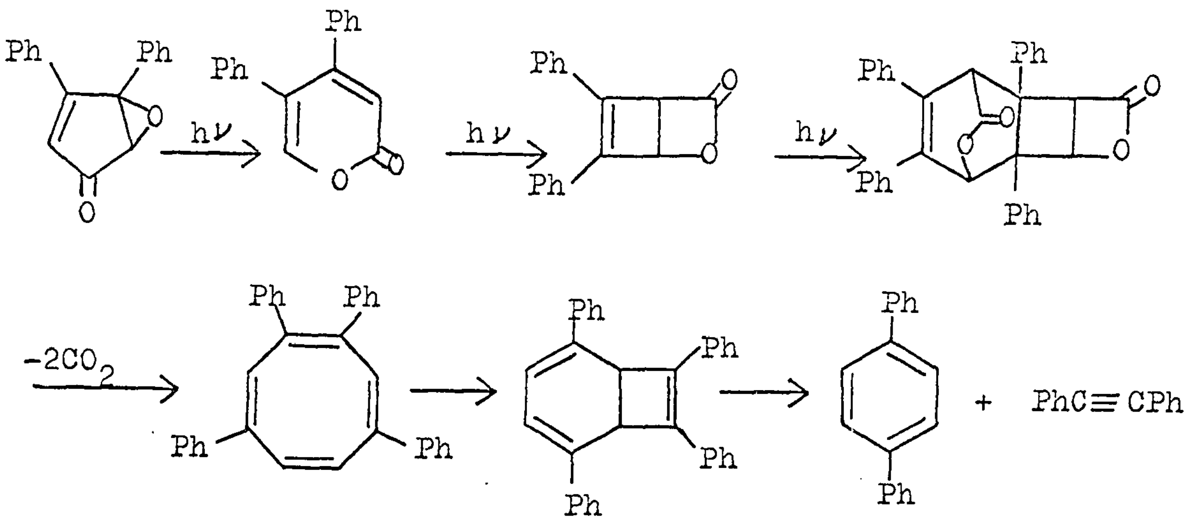
Corey (38) found that the low temperature ultraviolet irradiation of 2-pyrone (XLIIIa) in ether afforded in almost quantitative yield a photoisomer to which a bicyclic β-lactone structure XLIVa was assigned. Isolation of this



XLIIIa. R=O
b. R=NCH_3

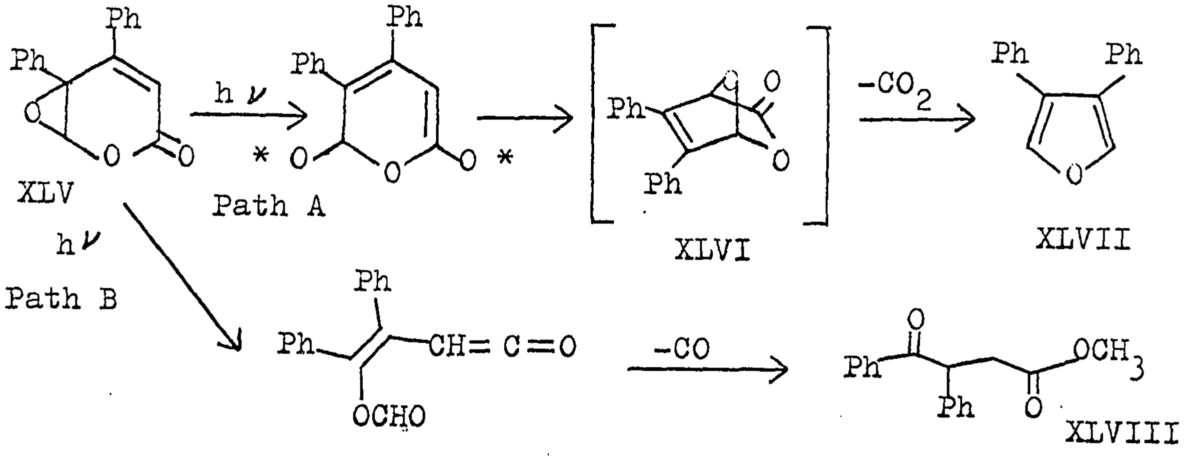
XLIVa. R=O
b. R=NCH_3

intermediate suggests the reaction scheme shown below.



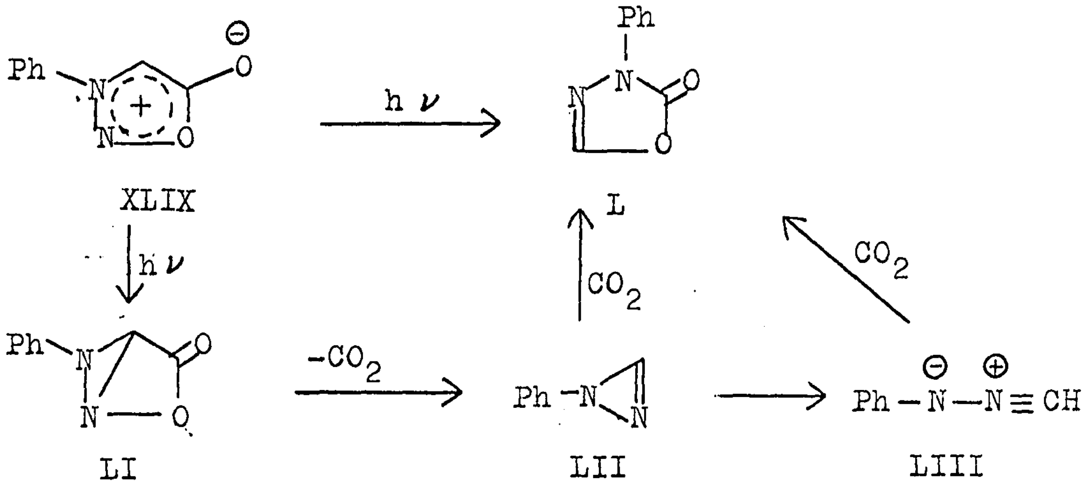
The final step in the sequence involves a known (39) photochemical decomposition of 1,2,4,7-tetraphenylcyclooctatetraene (XL).

A closely related transformation of 5,6-epoxy-4,5-diphenyl-2-pyrone (XLV) has been disclosed (40). Irradiation of XLV in methanol gave 3,4-diphenylfuran (XLVII) and methyl decylacetate (XLVIII).

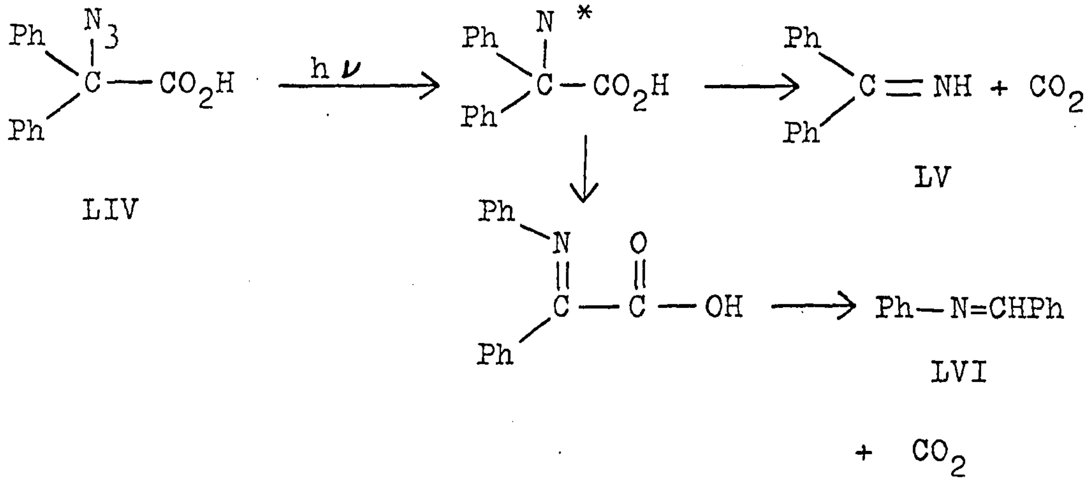


The products were explained by two different photochemical paths. Path A involves a highly reactive lactone intermediate XLVI which subsequently undergoes decarboxylation, while Path B involves a ring fission giving a ketene intermediate which reacts with solvent to give XLVIII.

Irradiation of N-phenylsydnone (XLIX) in benzene or dioxane solutions gives CO_2 (98%) and a mixture of ten photoproducts from which 4-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (L) was isolated (41). XLIX irradiated in dioxane with introduction of ^{14}C-labeled CO_2 produced active L containing 80% of the activity of the photoproducts. It was postulated that irradiation caused decarboxylation of LI to form 1H-diazirine (LII) and subsequent addition of CO_2 to LII or LIII gives L.

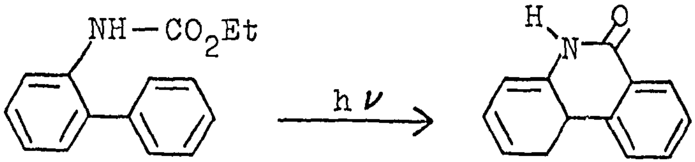


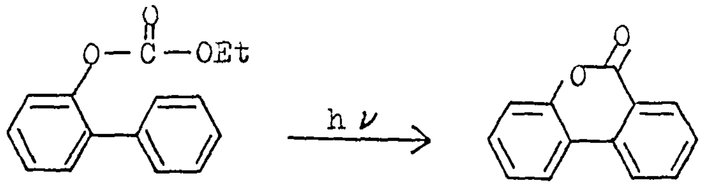
Ultraviolet irradiation of α-azidoacids causes efficient decarboxylation and formation of the lower aldimine or ketimine (42). Photolysis of azidodiphenylacetic acid (LIV) in methanol or in benzene solution yielded benzaldehyde phenylimine (LVI) and benzophenoneimine (LV). The photodecarboxylation probably involves both direct loss of carbon dioxide and also phenyl group migration followed by decarboxylation (42).


LIV LV LVI

Photochemical Transformations of Acids and Related Compounds

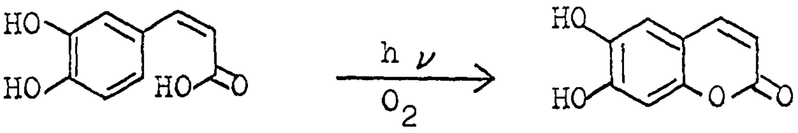
Irradiation of ethyl-N-o-biphenylylcarbamate (LVII) in methanol yields phenanthridone (LVIII) in 85% yield. Under similar conditions, ethyl-o-biphenylylcarbonate (LIX) undergoes photoacylation to afford dibenz-α-pyrone (LX) in 85% yield (43).


LVII LVIII



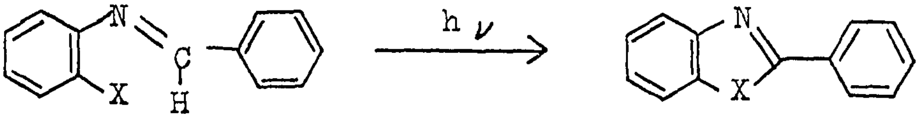
LIX LX

Irradiation of caffeic acid (LXI) in methanol or acetic acid in presence of oxygen gives esculetin (LXII) in 10% yield. The photochemical induced oxidative cyclization does not occur in the absence of oxygen (44).



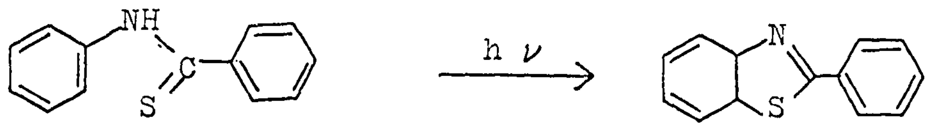
LXI LXII

The photolysis of several o-substituted Schiff bases has recently been reported (45). Irradiation of LXIII a-c in hexane gives LXIV a-c. The versatility of the photochemical oxidation is demonstrated by the irradiation of thiobenzanalide (LXV) in hexane to give LXIV c.



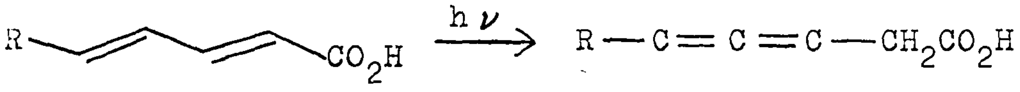
LXIII a. X=OH
b. $X=NH_2$
c. X=SH

LXIV a. X=O
b. X=NH
c. X=S



LXV LXIV c

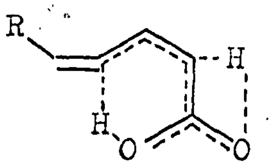
Sorbic acid (LXVI a) and the homologous acid LXVI b in dilute ethereal solution are isomerized by light to the corresponding allenes LXVII a and LXVII b (46).



LXVI a. $R=CH_3$
b. $R=H$

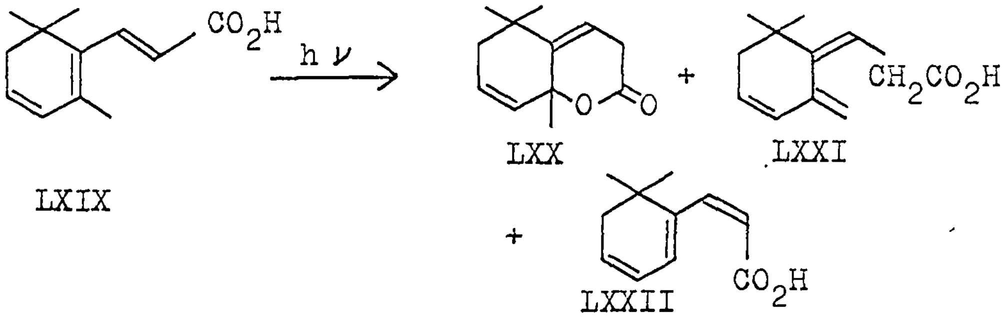
LXVII a. $R=CH_3$
b. $R=H$

The photoisomerization is postulated as proceeding through LXVIII after preliminary conversion to the 2,3-cis-isomer (46). No allene-type product was detected from the irradiation of a 5% aqueous potassium sorbate solution whereas irradiation of a 10% solution of methyl sorbate in ether containing 10% formic acid resulted in a 8% yield of the methyl ester of LXVII a.



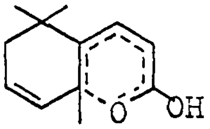
LXVIII

Dehydro-β-cyclocitrylideneacetic acid (LXIX) when irradiated in hexane yields a δ-lactone LXX and a mixture of acids LXXI and LXXII (47,48).



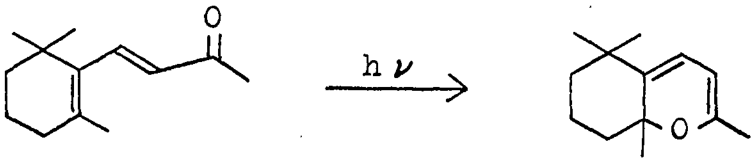
LXIX LXX LXXI LXXII

The lactonization is viewed as proceeding through LXXIII.



LXXIII

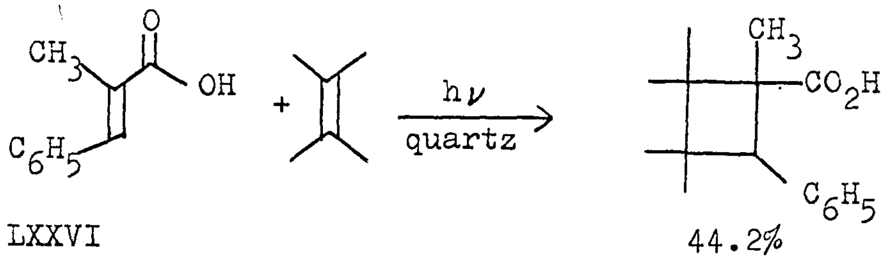
It is interesting that β-ionone (LXXIV) undergoes photocyclization in a similar manner to form the pyran LXXV (49).



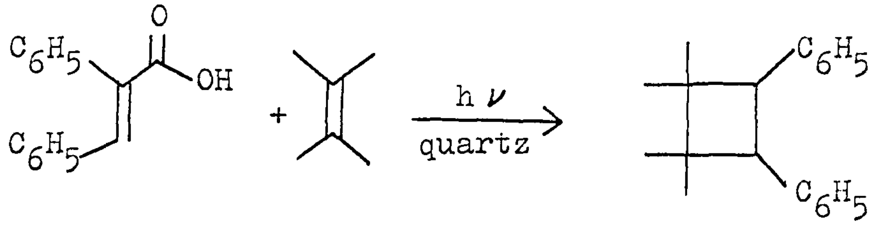
LXXIV LXXV

RESULTS

Recent investigations (25), prompted by successful photocycloadditions of olefins to α,β-unsaturated ketones, confirmed that α,β-unsaturated acids are capable of undergoing similar photocyclizations with olefins. Ultraviolet irradiation of trans-cinnamic acid and α-methylcinnamic acid in neat tetramethylethylene (conditions chosen to facilitate photocycloaddition) afforded cyclobutane carboxylic acid adducts in good yield. The photo-induced cycloaddition of α-methylcinnamic acid (LXXVI) to tetramethylethylene is shown below.



In an attempt to extend the scope of this reaction, irradiation of cis-α-phenylcinnamic acid (LXXVII) in the presence of tetramethylethylene afforded 1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 66.5%) as the only product. Elemental analysis gave $C_{20}H_{24}$ showing the product had lost the elements of carbon dioxide. The infrared spectrum in potassium bromide (Figure 1, page 23) confirmed the loss of the carboxylic acid moiety giving absorption bands typical of a hydrocarbon. The nmr spectrum (Figure 2, page 25) is in excellent agreement with the structure of the photoproduct LXXVIII. There is a ten proton singlet at δ 7.07, a two proton singlet at δ 3.55 and two six proton singlets at δ 1.12 and δ 0.77. The mass spectrum exhibited a very weak parent ion at m/e 264 and fragment ions at m/e 181 (14.5%), 180 (100%).

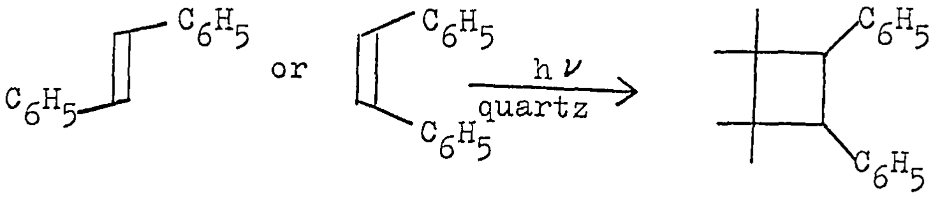


LXXVII LXXVIII

The stereochemistry of the photo-adduct could not be ascertained directly from the spectroscopic data. The *trans*-isomer possesses a two-fold axis of symmetry and the *cis*-isomer has a plane of symmetry which are indistinguishable in the nmr spectrum.

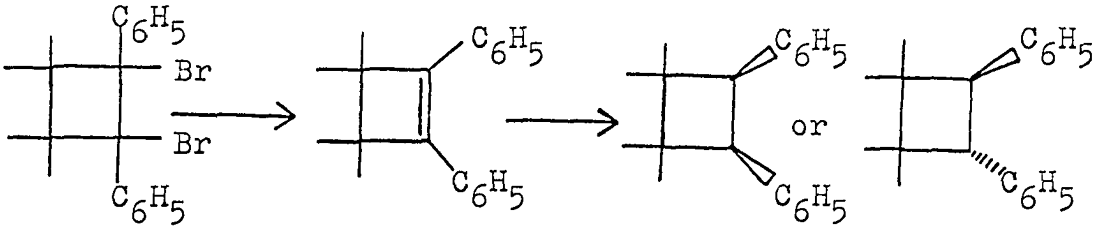
Inspection of the photoproduct LXXVIII leads to the realization that irradiation of *trans* or *cis*-stilbene in the presence of tetramethylethylene should produce analogous adducts, and if the photoreaction is stereoselective, the product struc- as well as the stereochemistry would be realized.

The ultraviolet irradiation of either *cis* or *trans*-stilbene in the presence of tetramethylethylene yielded 1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) which was identical to the photo-adduct obtained from the photocyclization of *cis*-α-phenylcinnamic acid to tetramethylethylene. Under identical conditions the photocyclization of *cis*-stilbene to tetramethylethylene was observed to be slower (44 hr) than for the trans-isomer (19 hr).



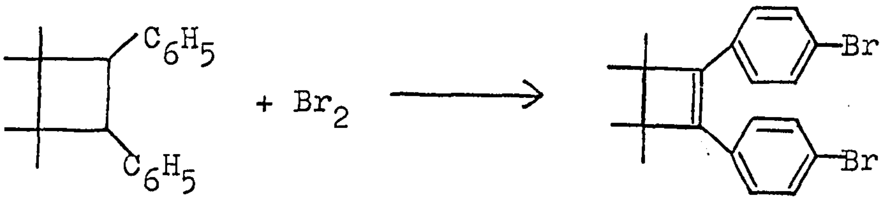
LXXVIII

An alternate attempt to circumvent the stereochemistry of the photo-adduct is outlined below. Synthesis of the cyclobutene (LXXIX) from the photoproduct followed by a stereospecific reduction would hopefully afford either cis or trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane.



LXXIX

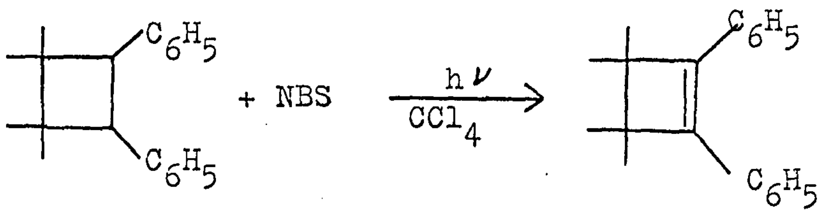
Conversion of LXXVIII by excess bromine gave a novel crystalline compound which was shown to be 1,2-(di-p-bromophenyl)-3,3,4,4-tetramethylcyclobutene (LXXX) in 32% yield. The infrared spectrum in potassium bromide showed a strong absorption band at 12.25μ which is typical for 1,4-disubstituted



LXXVIII LXXX

benzenes (50). The nmr spectrum (carbon tetrachloride) showed an eight proton aromatic A_2B_2 pattern $\gamma_A = \delta\ 7.14$, $\gamma_B = \delta\ 7.39$, (J=8.5 cps) and a twelve proton singlet at $\delta\ 1.26$. The magnetic equivalence of the methyl groups is in accord with the proposed structure LXXX. The presence of the stilbene chromophor is shown in the ultraviolet spectrum (95% ethanol) giving λ max 289 mμ (ϵ 10,100) and 240 mμ (ϵ 15,600). The mass spectrum exhibited an intense parent ion at m/e 418 and a P + 2 ion (m/e 420, 206% of parent ion). Elemental analysis gave $C_{20}H_{20}Br_2$ in support of the proposed structure.

Utilization of this novel reaction under milder oxidation conditions would conceivably produce the desired cyclobutene LXXIX. This was indeed the case. Oxidation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) with N-bromosuccinimide gave 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) in 80% yield. The infrared spectrum in potassium bromide (Figure 1, page 23) showed strong absorption bands at 13.45μ and 14.39μ attributed to C-H out-of-plane bending of



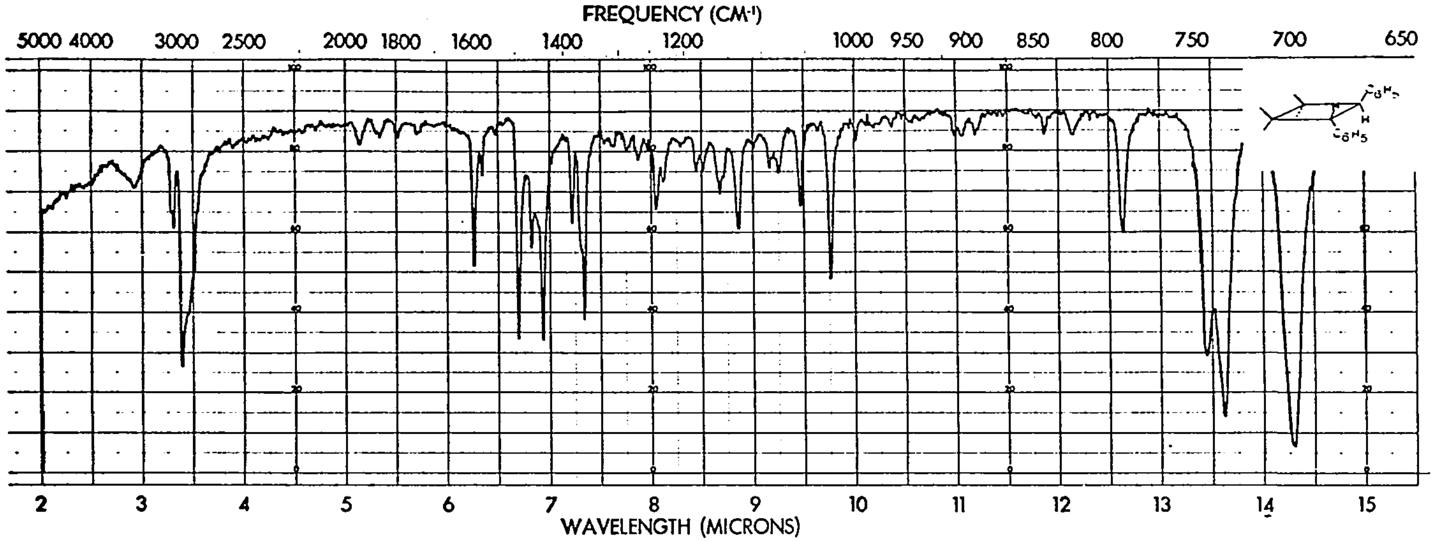
LXXVIII LXXIX

monosubstituted benzenes (50). The intense ultraviolet absorption at λ max (95% ethanol) 278 mμ (ϵ 6,300) and 225 mμ (ϵ 10,000) confirms the presence of the cis-stilbene chromophor

Figure 1. Infrared spectra

Top - *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) in potassium bromide

Bottom - 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) in potassium bromide


FREQUENCY (CM-1)
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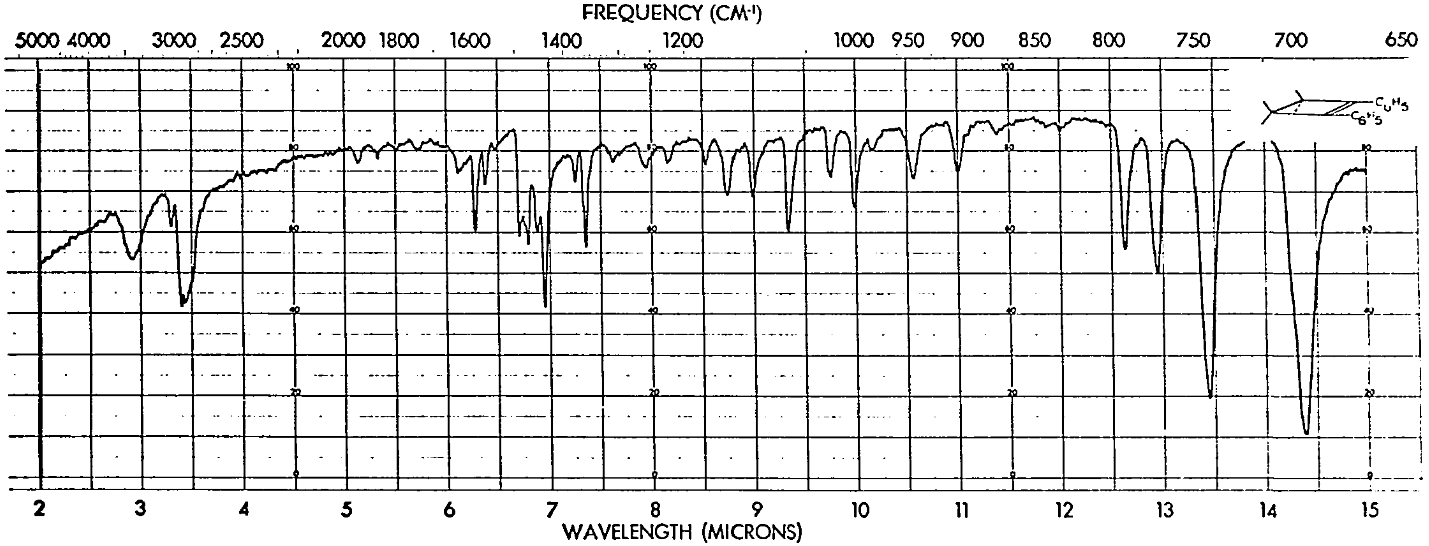
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
C6H5
H
C6H5


FREQUENCY (CM-1)
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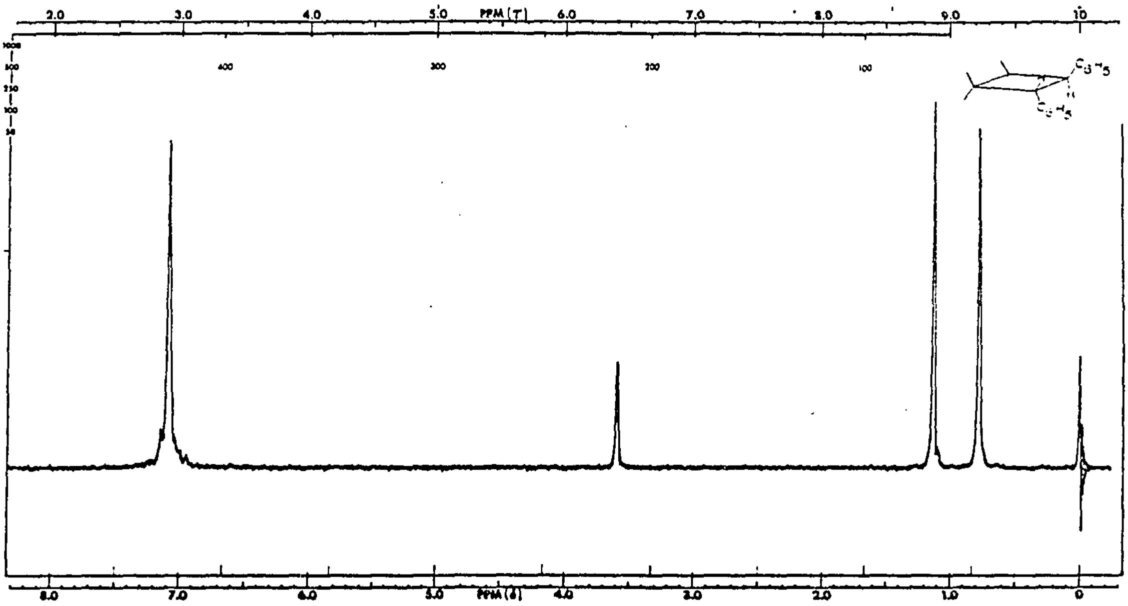
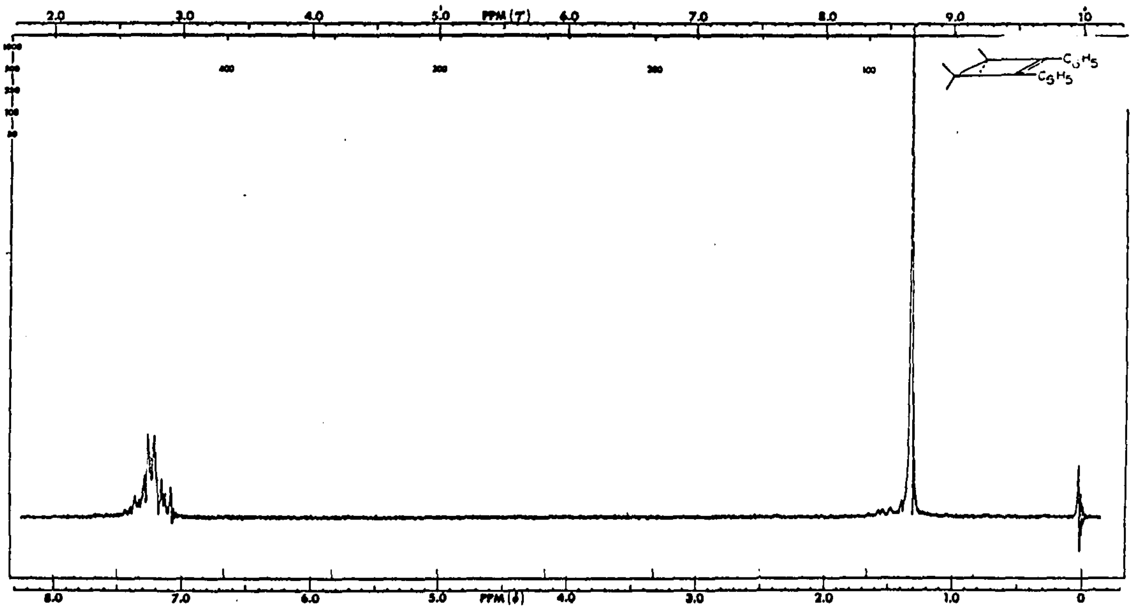
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
C6H5
C6H5

Figure 2. Nuclear magnetic resonance spectra

Top - trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) in carbon tetrachloride

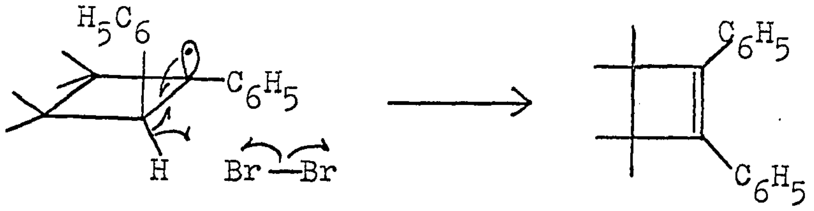
Bottom - 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) in carbon tetrachloride


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
400
300
200
100
C6H5
C6H5
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
C6H5
C6H5
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

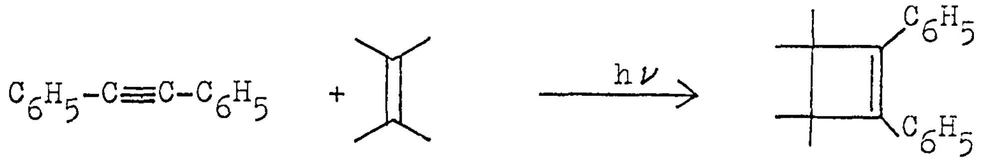
(51). The nmr spectrum is shown in Figure 2, page 25. There is a multiplet centered at δ 7.25 and a singlet at δ 1.32. The peak areas are in the ratio of 5:6 respectively. The structure was also confirmed by the mass spectrum which gave an intense molecular ion at m/e 262 and by the elemental analysis.

This unprecedented oxidation merits further comment concerning the mechanism. Recent studies (52) indicate that benzylic brominations with N-bromosuccinimide, the bromine radical is the hydrogen-abstracting reagent. Thus a hydrogen atom abstraction followed by hydrogen atom transfer from the cyclobutane radical to bromine could proceed in the following manner.



An alternate mechanism involving bromine substitution followed by elimination of hydrogen bromide is less likely due to steric requirements imposed by the bulky cyclobutane molecule.

An authentic sample of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) was prepared by photocycloaddition of diphenylacetylene to tetramethylethylene in 30% yield. The infrared spectrum in a potassium bromide pellet was identical in every detail to that of the oxidized compound LXXIX.

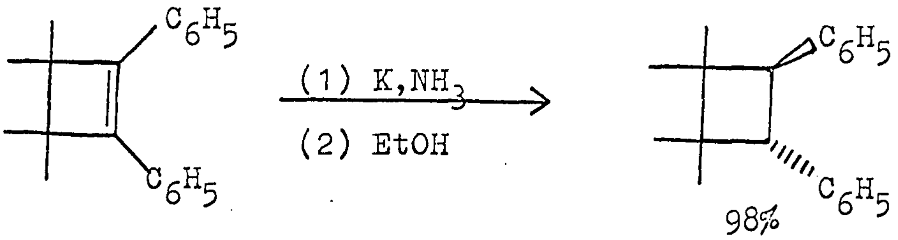


LXXIX

Attempted reduction of the cyclobutene LXXIX by catalytic hydrogenation over platinum oxide or palladium on charcoal at various hydrogen pressures failed, presumably due to the steric hindrance of the gem-dimethyl groups. Diimide reduction (53,54) using hydrazine and hydrogen peroxide or *p*-toluenesulfonyl hydrazine also failed.

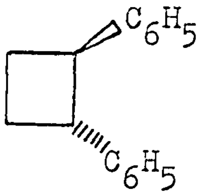
Olefinic bonds which are conjugated with aromatic nuclei are readily hydrogenated by alkali metals in liquid ammonia. The reduction of the stilbenoid bond results in the formation of two asymmetric centers and the more stable of two possible stereochemical arrangements is usually produced (55,56).

Reduction of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) using potassium in liquid ammonia gave the original cyclobutane LXXVIII obtained from the photoaddition of the *cis*-acid to tetramethylethylene, which is thus assigned *trans* stereochemistry.



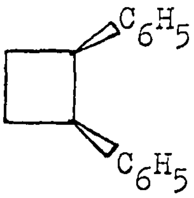
LXXIX LXXVIII

The *trans* stereochemical assignment is supported by the recent synthesis of *cis* and *trans*-1,2-diphenylcyclobutane (57). The configurations of the *cis* and *trans* isomers were assigned from the nmr spectra. The absorption band of the α-protons of *trans*-1,2-diphenylcyclobutane (LXXXI) was centered at δ 3.55, while that of *cis*-1,2-diphenylcyclobutane (LXXXII) was centered at δ 3.94. The *cis* isomer was readily isomerized to the *trans* isomer by treatment with potassium *t*-butoxide in dimethyl sulfoxide which indicates that the more stable isomer is isolated from basic conditions. The chemical shift of the benzylic protons of the *trans*-cyclobutane LXXXI is in excellent agreement with that of *trans*-1,2-diphenyl-3,3,4,4-cyclobutane (LXXVIII) which also absorbs at δ 3.55.



δ 3.55

LXXXI

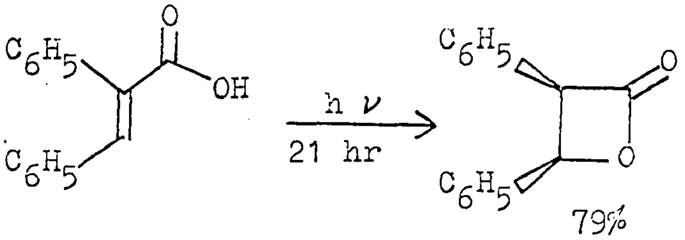


δ 3.94

LXXXII

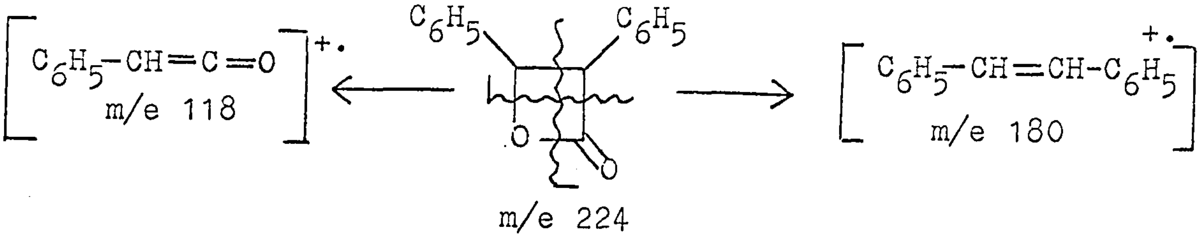
The aromatic proton resonance in the nmr spectrum of *trans*-1,2-diphenyl-3,3,4,4-cyclobutane (LXXVIII) appeared as a sharp singlet which lends additional support to the stereochemical assignment. Curtin (58) has shown that the aromatic proton resonance of *trans*-1,2-diphenylcyclopentane appeared as a sharp singlet while a multiplet was observed for *cis*-1,2-diphenylcyclopentane.

In an effort to gain insight to the mechanism of the photodecarboxylation, a benzene solution of <u>cis</u>-α-phenylcinnamic acid (LXXVII) was irradiated using a Pyrex filter. The reaction was monitored in the infrared spectrum (Figure 3, page 32). The carboxylic acid band (5.95μ) gradually diminished during the course of the reaction and was replaced by an intense band at 5.45μ. At the end of the irradiation the acid band was completely removed. The nmr of the crude residue showed two AB proton patterns at $\gamma_A = \delta\, 5.12$, $\gamma_B = \delta\, 5.68$ (J= 7.0 cps); $\gamma_A{}' = \delta\, 4.59$, $\gamma_B{}' = \delta\, 5.37$ (J= 4.5 cps), which were assigned to <u>cis</u> and <u>trans</u>-α,β-diphenyl-β-propiolactone respectively. The assignment of configuration was made on the basis of the nmr spectra. The benzylic protons of the <u>trans</u>-β-lactone experience significant shielding by the adjacent aromatic ring (57,58). The <u>cis</u> and <u>trans</u>-α,β-diphenyl-β-propiolactone ratio was about 3:1 respectively and longer irradiation time failed to change this ratio. Crystallization of the residue gave only <u>cis</u>-α,β-diphenyl-β-propiolactone (LXXXIII) in 79% yield. The structural assignment was confirmed by the strong absorption band at 5.45μ in the infrared spectrum (Figure 3, page 32) which is typical for β-lactones (59). The nmr (Figure 5, page 47) showed a ten proton multiplet centered



LXXVII LXXXIII

at δ 7.10 and an AB proton pattern $\gamma_A = \delta\, 5.30$, $\gamma_B = \delta\, 5.84$ (J= 7.0 cps). Elemental analysis and the mass spectrum also support the β-lactone structure LXXXIII. The mass spectrum shows a base peak at m/e 118 which is assigned to the phenyl ketene radical cation. The stilbene ion molecule (m/e 180, 16.4% of base) results from the alternate cleavage of the parent ion (m/e 224).



The β-lactone structure LXXXIII is also supported by pyrolysis giving cis-stilbene (76%) and carbon dioxide (92%). The isolation of cis-stilbene suggests that decarboxylation of the β-lactone undergoes a stereospecific cis expulsion of carbon dioxide. This interpretation is in accord only with a cis-diphenyl configuration of the β-lactone.

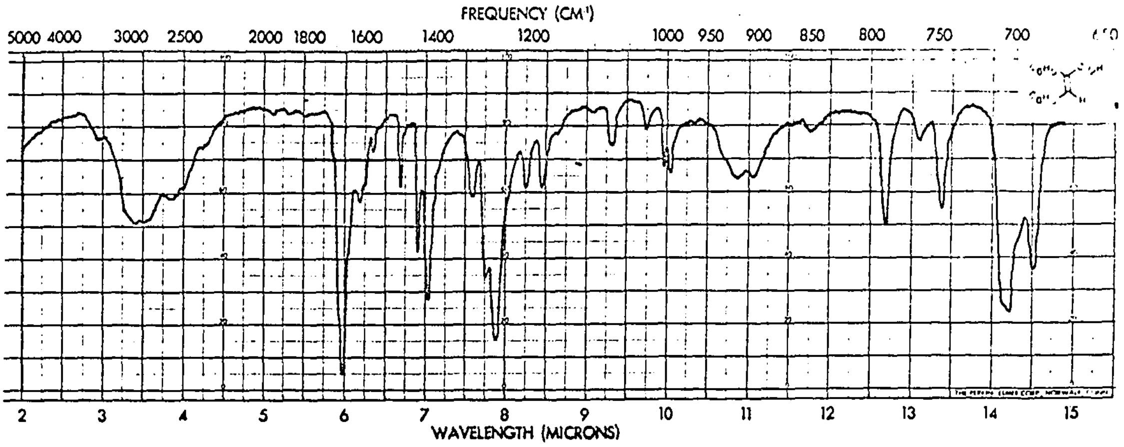
Noyce and Banitt (60) have recently shown that decarboxylation of β-lactones in aqueous solution occur by a stereospecific cis elimination. Decarboxylation of cis-α-methyl-β-(p-chlorophenyl)-β-propiolactone (LXXXIV) in a buffer solution (pH 6.2) at 25 or 100° affords pure cis-propene LXXXV. Similarly, the trans-β-lactone LXXXVI under identical conditions gave pure trans-propene LXXXVII.

Figure 3. Infrared spectra

Top - *cis*-α-phenylcinnamic acid (LXXVII) in potassium bromide

Middle - photochemical isomerization of *cis*-α-phenylcinnamic acid (LXXVII) to *cis*-α, β-diphenyl-β-propiolactone (LXXXIII) in chloroform

Bottom - *cis*-α, β-diphenyl-β-propiolactone (LXXXIII) in potassium bromide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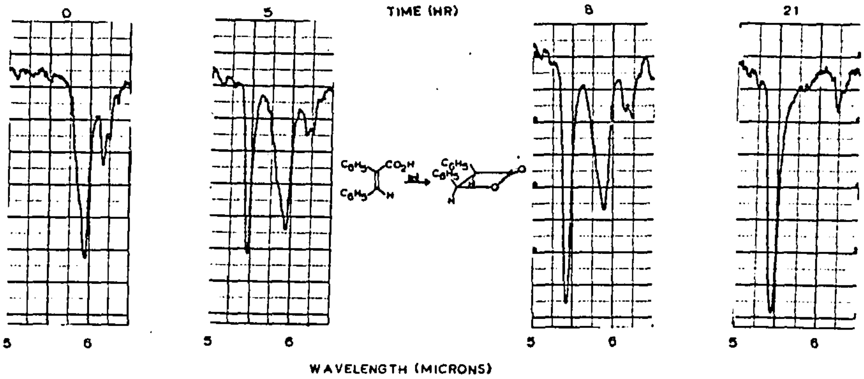
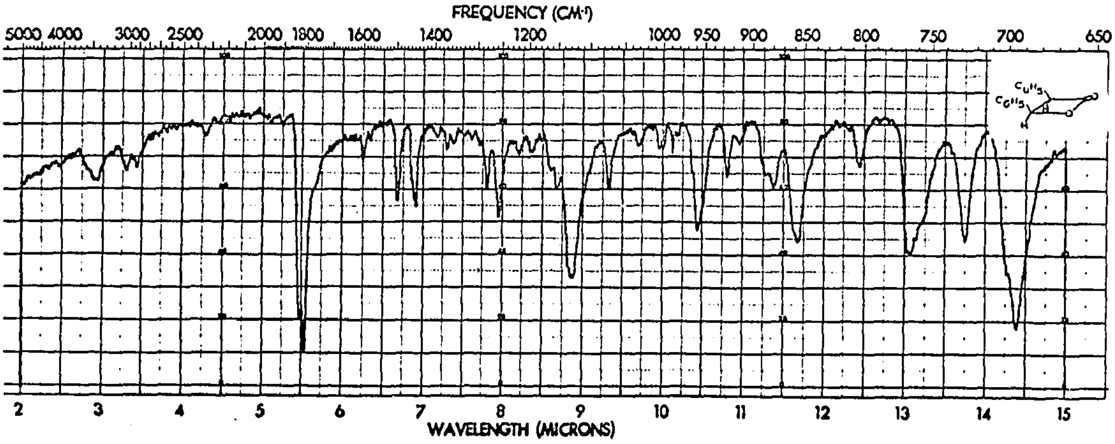
WAVELENGTH (MICRONS)


TIME (HR)
0
5
8
21
5 6
WAVELENGTH (MICRONS)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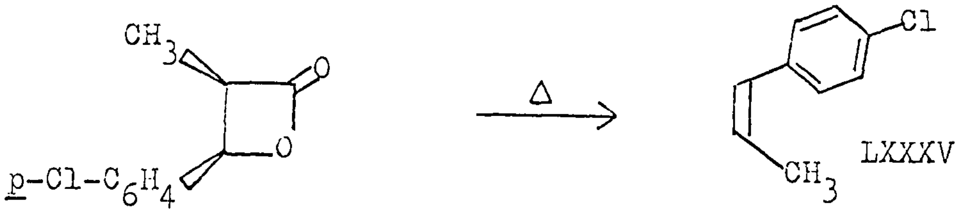
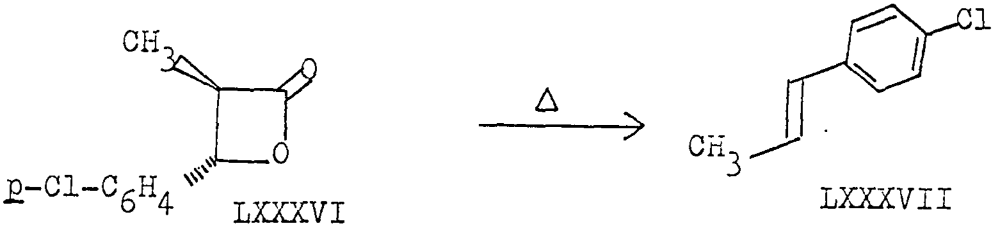
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

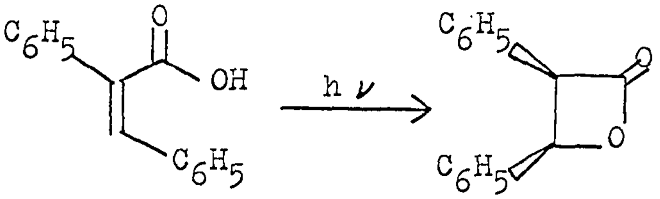


LXXXIV LXXXV



LXXXVI LXXXVII

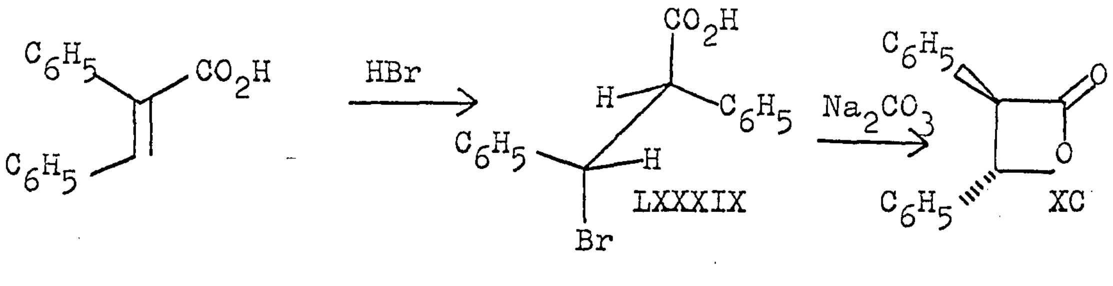
Photolysis of trans-α-phenylcinnamic acid (LXXXVIII) using conditions identical to that of cis-α-phenylcinnamic acid required a longer irradiation period (46 hr) for conversion to the cis-β-lactone LXXXIII. The low yield of the



LXXXVIII LXXXIII

β-lactone (12.5%) presumably resulted from the prolonged irradiation period.

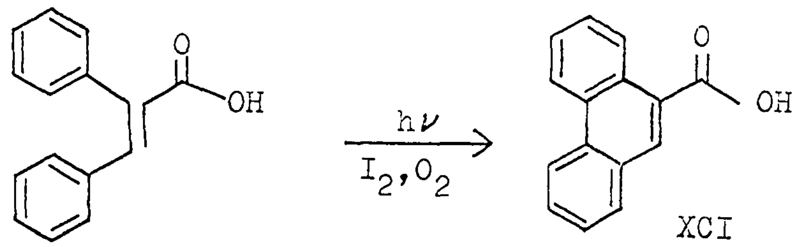
Independent synthesis of trans-β-lactone was attempted following the scheme below.



trans-Addition of hydrogen bromide gave erythro-3-bromo-2,3-diphenylpropanoic acid LXXXIX which upon treatment of sodium carbonate gave a mixture of trans-stilbene and a small quantity of trans-β-lactone XC. The infrared spectrum of the mixture in potassium bromide gave an intense β-lactone band at 5.46μ. The nmr spectrum confirmed the presence of the β-lactone which gave a AB proton pattern $\gamma_A = \delta 4.62$, $\gamma_B = \delta 5.39$ ($J_{AB} = 4.5$ cps). The smaller coupling constant for the trans benzylic protons of the β-lactone is consonant with the structural assignment (see Table 2).

The photochemistry of cis-α-phenylcinnamic acid has been previously investigated by other workers. Stoemer and Voht (61) obtained the less stable trans-α-phenylcinnamic acid by irradiating an aqueous solution of sodium cis-α-phenylcinnamate for 3-4 days using a quartz filter. Somewhat higher yields of the trans-acid (about 50%) were obtained when the free acid was irradiated in water, benzene, ethanol or acetone solutions. No other products were reported by these workers.

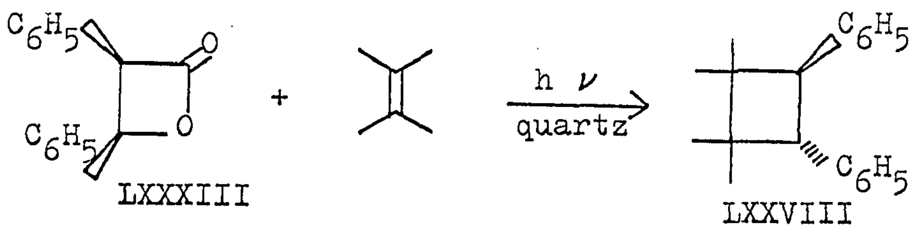
In conjunction with their investigations on the photocyclization of cis-stilbene, Mallory and Wood (62) irradiated with an unfiltered mercury arc lamp, a 0.1 molar solution of cis-α-phenylcinnamic acid containing 0.0005 molar solution of iodine in one liter of cyclohexane or benzene open to the air. The only product isolated was 9-anthranoic acid (XCI, mp 255-256°) in 72% yield.



XCI

It is significant that in our investigations we found no evidence for the presence of the phenanthrene derivative. We have verified this oxidation and observed only a small amount of β-lactone in the infrared spectrum during the irradiation. Since our irradiations were run under non-oxidative conditions (e.g., solution was degassed with nitrogen and sealed) an alternate photochemical path is apparently favored. Most recent results (63) indicate that the phenanthrene formation does not occur in solution if oxygen is rigorously excluded. Addition of iodine to the reaction appears to enhance the rate of cyclization and its function has been suggested (63) to be that of a hydrogen acceptor.

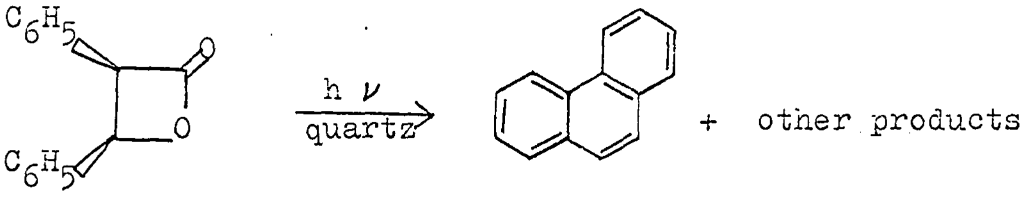
Evidence that cis-α,β-diphenyl-β-propiolactone (LXXXIII) was the intermediate responsible for the formation of trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane was confirmed by the finding that the photolysis of LXXXIII in the presence of tetramethylethylene afforded the identical trans-cyclobutane LXXVIII in 85% yield.



LXXXIII

LXXVIII

Irradiation of the β-lactone LXXXIII in the absence of tetramethylethylene gave a complex mixture from which phenanthrene (XCII) was isolated in 37% yield. Phenanthrene has been shown to be produced from the photocyclization of cis-stilbene (64).



Linnell and Noyes (65) have shown that the photodegradation of liquid β-propiolactone at 2537 Å gave an equally complex mixture. In addition to a large amount of polymer, ethylene, acetaldehyde, and acrylic acid were isolated.

A summary of the interrelated photochemical reactions is shown in Figure 4.

Irradiation of several α-p-phenyl and β-p-phenyl substituted acids XCIII a-l were attempted to observe the effects of electron donating or withdrawing substituents on the β-lactone formation. The results are compiled in Tables 1 and 2.

β-Lactones XCIV a-d were isolated in the pure form and all possessed the cis-diphenyl configuration (see Experimental). The trans-β-lactones although present (vide infra) were never isolated. The isolation of the pure β-lactones were hampered by the presence of both cis and trans isomers in the crude products and in several cases olefins resulting from the

Figure 4. Reaction scheme

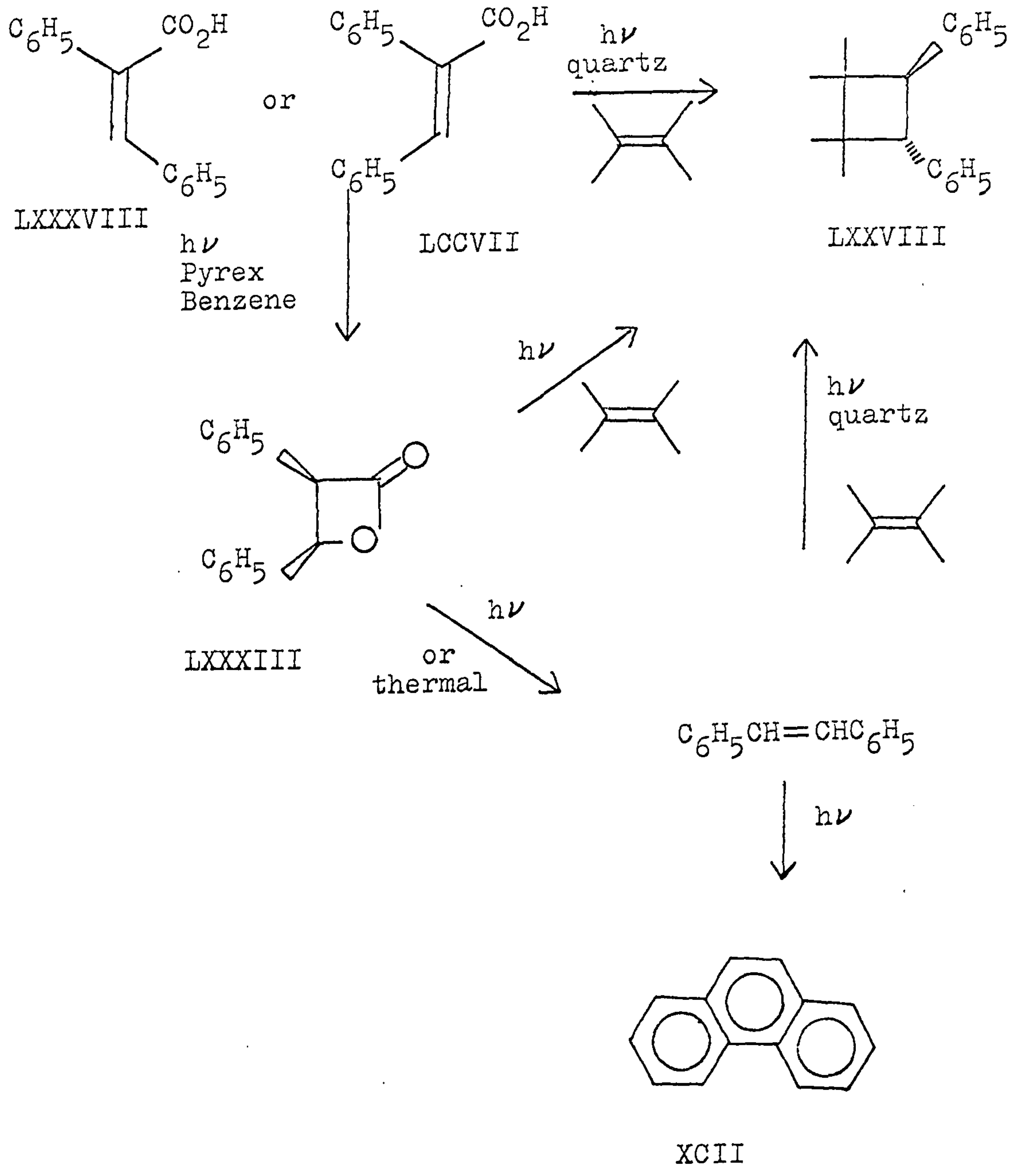
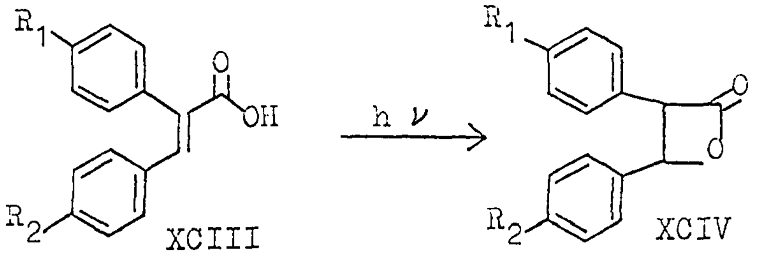

C_6H_5
CO_2H
C_6H_5
LXXXVIII
or
C_6H_5
CO_2H
C_6H_5
LCCVII
hν
quartz
C_6H_5
C_6H_5
LXXVIII
hν
Pyrex
Benzene
hν
hν
quartz
C_6H_5
C_6H_5
LXXXIII
hν
or
thermal
$C_6H_5CH{=}CHC_6H_5$
hν
XCII

Table 1. Substituent effect on β-lactone formation from *cis*-α-phenylcinnamic acids[a].



	Acid	λ max, mμ[b]	Irradiation time, hr	*trans/cis* ratio[e]
a.	R_1=H, R_2=H	286(16,000)	21	0.4
b.	R_1=CH_3, R_2=H	284(18,000)	23.5	0.9
c.	R_1=H, R_2=CH_3	297(20,000)	28.5	0.3
d.	R_1=Cl, R_2=H	290(17,000)	72[c]	0.6
e.	R_1=H, R_2=Cl	296(20,000)	26	0.8
f.	R_1=F, R_2=H	288(17,000)	41	1.0
g.	R_1=CN, R_2=H	293(16,000)	72[c]	0.0
h.	R_1=H, R_2=CN	289(20,000)	5	0.7
i.	R_1=NO_2, R_2=H	293(16,000)[d]	72	no lactone
j.	R_1=H, R_2=NO_2	310(12,000)[d]	36[c]	1.0
k.	R_1=OCH_3, R_2=H	323(sh) (15,000)	10.5	1.0
l.	R_1=H, R_2=OCH_3	313(22,000)	96	no lactone

[a] The acids (2.0 g) in benzene were irradiated in a Pyrex vessel with a Hanovia Type A 550-watt lamp. The solutions were degassed with nitrogen throughout the irradiation.

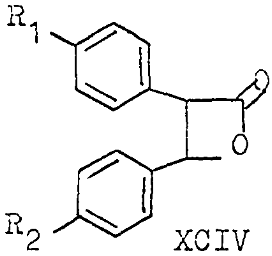
[b] The ultraviolet spectra were taken in spectral grade cyclohexane (Fischer Scientific Company).

[c] Reaction did not go to completion.

[d] The extinction coefficient is a minimum value due to the insolubility of the acids in cyclohexane.

[e] Calculated from the nmr spectra of the crude product.

Table 2. Nuclear magnetic resonance of p-substituted α, β-diphenyl-β-propiolactone[a,b].



XCIV

	Lactone		cis	J,cps		trans	J,cps
		A	B		A	B	
a.	R_1=H,R_2=H	5.12	5.68	7.0	4.59	5.37	4.5
b.	R_1=CH_3,R_2=H	5.03	5.60	7.0	4.50	5.30	4.5
c.	R_1=H,R_2=CH_3	5.05	5.62	7.0	4.53	5.34	4.5
d.	R_1=Cl,R_2=H	5.09	5.67	7.0	4.55	5.32	4.5
e.	R_1=H,R_2=Cl	5.16	5.69	7.0	4.59	5.33	4.5
f.	R_1=F,R_2=H	5.15	5.72	7.0	4.60	5.35	4.5
g.	R_1=CN,R_2=H	5.37	5.89	7.0		nil	
h.	R_1=H,R_2=CN	5.37	5.87	7.0	4.66	5.50	4.5
i.	R_1=NO_2,R_2=H		nil			nil	
j.	R_1=H,R_2=NO_2	5.35	5.88	7.0	4.69	5.52	4.5
k.	R_1=OCH_3,R_2=H	5.05	5.62	7.0	4.51	5.28	4.5
l.	R_1=H,R_2=OCH_3		nil			nil	

---

[a] All spectra were run in deuteriochloroform containing tetramethylsilane as internal standard. Resonance positions are given as δ-values relative to internal tetramethylsilane.

[b] Resonance positions were taken from spectra of crude products in which both isomers were present. Spectra of the pure *cis* isomers isolated are described in the experimental section.

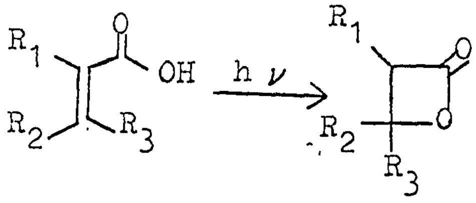
decarboxylation of the β-lactones were isolated.

Several dramatic effects are observed in Table 1. Assuming the parent acid XCIII a as the standard, the β-p-cyano acid XCIII h reacts four times as fast whereas the β-p-methoxy substituted acid XCIII l does not react at all. It appears that electron withdrawing substituents on the β-phenyl ring enhance the isomerization while electron donating substituents impair it. Substitution of the α-phenyl ring appears to reverse the substituent effect on the β-lactone formation but not as effectively. The generality does not seem to apply to the nitro substituted acids. Aromatic nitro compounds are known to absorb at wavelengths longer than 290 mμ thus making the excitation of the conjugated acid moiety less efficient. In addition both nitro acids had only a limited solubility in benzene and only after 12-13 hours of irradiation was the solution homogeneous. In any case, the β-p-nitro substituted acid XCIII j appears to isomerize to the lactone faster than the α-p-nitro XCIII i compound.

Careful examination of the crude β-lactones prior to recrystallization revealed mixtures of cis and trans-β-lactones were present in every case except lactone XCIV g. The nuclear magnetic resonance absorption of the β-lactones are shown in Table 2. The structural assignments were based on the coupling constants of the benzylic protons as well as their resonance positions although reservations must be made when dealing with mixtures.

The ranges of vicinal *cis* (4.6-11.38 cps) and *trans* (2.24-10.72 cps) coupling constants are considerable. The *cis* coupling constants are usually larger than the *trans* coupling constants, but the assignment of *cis* and *trans* stereochemistry to adjacent groups in cyclobutane rings, on the basis of coupling constants alone, cannot be made with any assurance (66). Assignments in the present case were based on the coupling constants of *cis* and *trans*-α,β-diphenyl-β-propiolactone.

The formation of β-lactones from photolysis of α,β-unsaturated acids appears to have some generality. A variety of α-substituted cinnamic and crotonic acids (XCV a-f) gave β-lactones. The isomerization was always slower than observed for α-phenylcinnamic acid (LXVIII) and no lactones were isolated from this series. The β-lactones were always obtained as mixtures with the unsaturated acid and separation was not achieved. The formation of the β-lactones was confirmed by nuclear magnetic resonance and infrared spectroscopy.



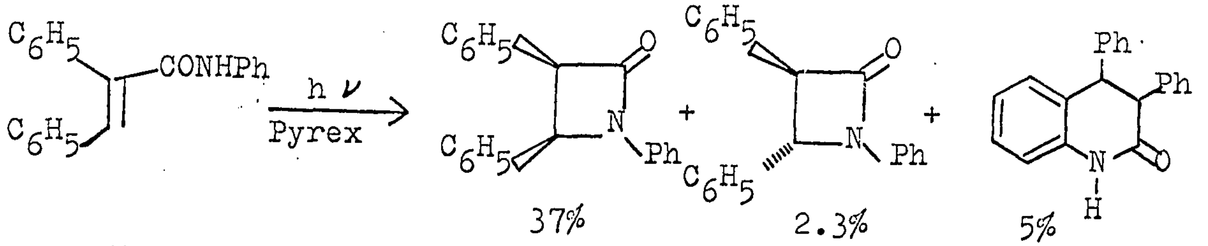
XCV

	R_1	R_2	R_3
a.	C_6H_5	C_6H_5	H
b.	CH_3	C_6H_5	H
c.	C_6H_5	CH_3	H
d.	C_6H_5	C_6H_5	C_6H_5
e.	C_6H_5	H	H
f.	CH_3	CH_3	H (67)

It is significant that crotonic acid (XCV, R_2=CH_3, R_1=R_3=H trans-cinnamic acid (XCV, R_2=C_6H_5, R_1=R_3=H), β,β-diphenylacrylic acid (XCV, R_2=R_3=C_6H_5,R_1=H), and biphenyleneacrylic acid failed to give detectable yields of β-lactones. Only cis trans-isomerization was observed with crotonic and trans-cinnamic acids whereas the latter two acids failed to undergo any photochemical transformation.

The ability of the unsaturated acid to undergo photochemical isomerization to the β-lactone depends on substitution of the acrylic acid. Substitution of the α-position appears to be a prerequisite to the success of the photochemical isomerization. If both α and β positions are substituted, the β-lactone formation appears to be facile while substitution only at the β-position failed to give β-lactones.

Amides XCVI and CIII undergo a similar photochemical isomerization to β-lactams. Photolysis of cis-α-phenylcinnamanilide (XCVI) in benzene for 23 hours with ultraviolet light above 290 mμ afforded a mixture of products. Separation by Silica Gel chromatography and fractional recrystallization gave cis and trans-1,3,4-triphenyl-2-azetidinone (XCVII, XCVIII) respectively, together with other products.

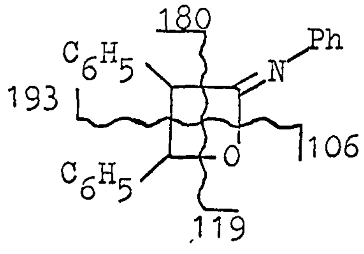


37% 2.3% 5%

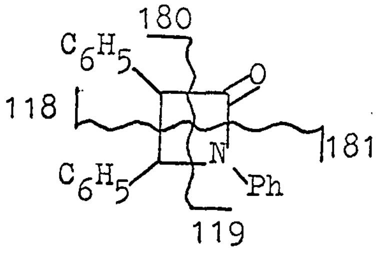
XCVI XCVII XCVIII XCIX

The infrared spectrum of trans-1,3,4-triphenyl-2-azetidinone (XCVIII) in potassium bromide is shown in Figure 6, page 49. There is a strong carbonyl band at 5.73 μ which is consistent with a β-lactam structure (59). The nmr spectrum (Figure 5, page 47) shows a fifteen proton multiplet centered at δ 7.30 and an AB proton pattern $\gamma_A = \delta\ 4.25$, $\gamma_B = \delta\ 4.94$ (J_{AB}=3.0 cps). The structure assignment is also confirmed by the mass spectrum and elemental analysis.

The isomerized product was assigned the β-lactam structure rather than the α-iminooxetane structure C on the basis of the mass spectral cleavage patterns. The α-iminooxetane structure would be expected to show olefin (m/e 180) and ketenimine (m/e 193) fragments while fragmentation of the β-lactam would give olefin (m/e 180) and benzaldehyde anil (m/e 181) radical cations (9). The mass spectrum shows a base peak at m/e 180 and a benzaldehyd anil radical cation at m/e 181 (33.7% of base) which is consonant only with the β-lactam structure.

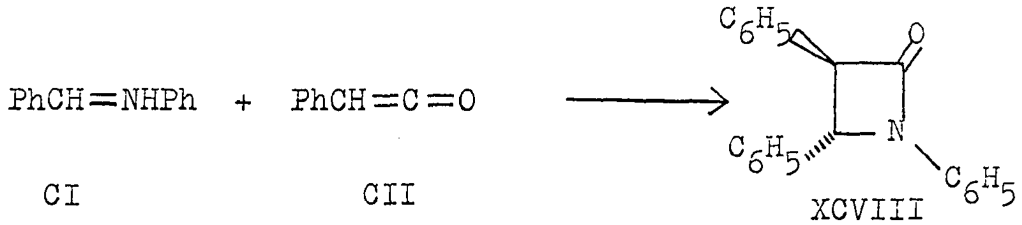


C



The infrared analysis fails to distinguish between α-iminooxetane and β-lactam structures since the imino group of the former and the carbonyl group of the latter have almost identical stretching frequencies (9).

An authenic sample of trans-1,3,4-triphenyl-2-azetidinone (XCVIII) was prepared from the condensation of benzal aniline (CI) and phenylketene (CII). The infrared spectrum in potassium bromide of trans-1,3,4-triphenyl-2-azetidinone (XCVIII) was identical in all respects to that of the trans-β-lactam isolated from the photolysis of cis-α-phenylcinnamanilide (XCVI).



The stereochemical assignment of the trans-β-lactam was based on the smaller coupling constant of the benzylic protons compared to that of the cis-β-lactam (vide infra). Also, in the preparation of the authentic β-lactam it is clear that the cis form in which the 3 and 4 phenyl groups are eclipsed, would be of much higher energy than the trans isomer and it is highly probable that the latter is formed exclusively in reactions such as the cycloaddition of phenylketene and benzaldehyde anils.

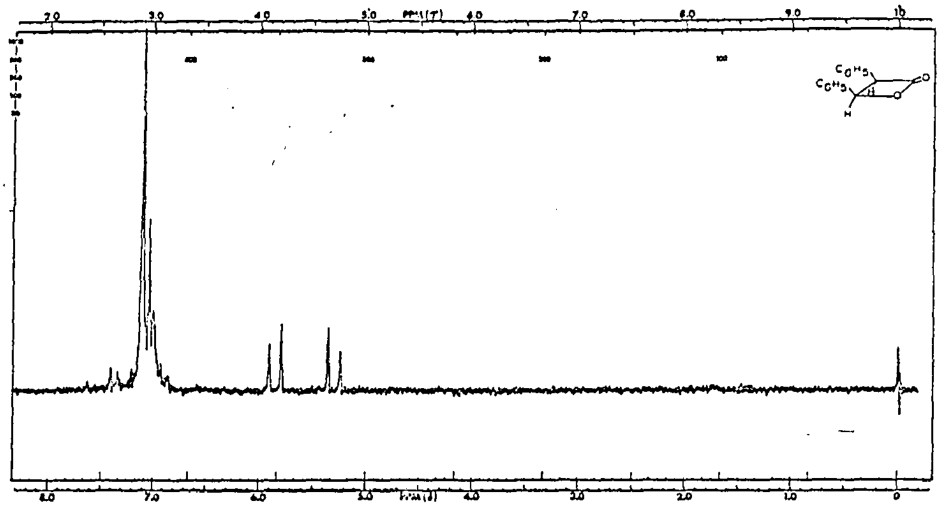
cis-1,3,4-Triphenyl-2-azetidinone (XCVII) also gave a strong carbonyl band at 5.75μ in the infrared spectrum (Figure 6, page 49). The nmr spectrum (Figure 5, page 47) is in excellent agreement with the structure. A fifteen proton multiplet was centered at δ 7.20 and an AB proton pattern $\gamma_A = \delta\,4.96$,

Figure 5. Nuclear magnetic resonance spectra

Top - *cis*-α,β-diphenyl-β-propiolactone (LXXXIII) in deuteriochloroform

Middle - *trans*-1,3,4-triphenyl-2-azetidinone (XCVIII) in deuteriochloroform

Bottom - *cis*-1,3,4-triphenyl-2-azetidinone (XCVII) in deuteriochloroform


PPM (τ)
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3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
C6H5
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H
O
PPM (δ)
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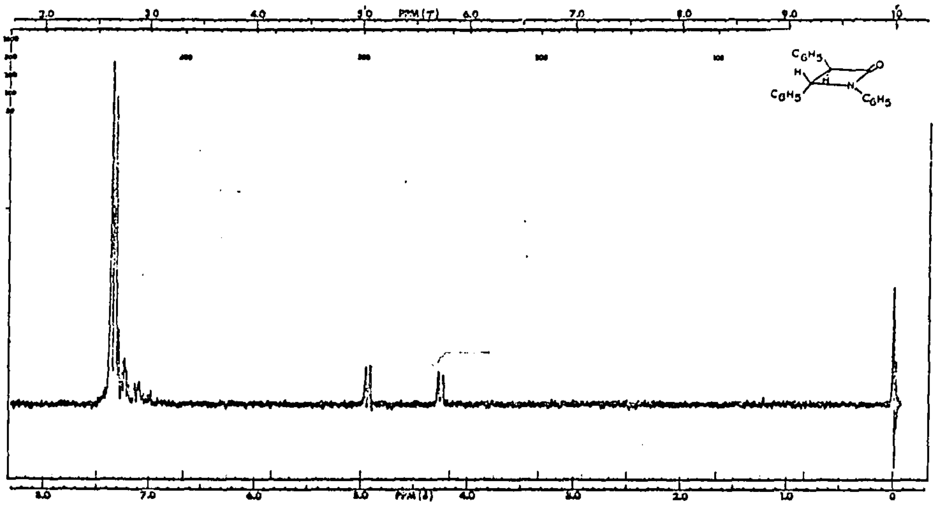
6.0
5.0
4.0
3.0
2.0
1.0
0


PPM (τ)
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3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
C6H5
H
C6H5
N
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PPM (δ)
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6.0
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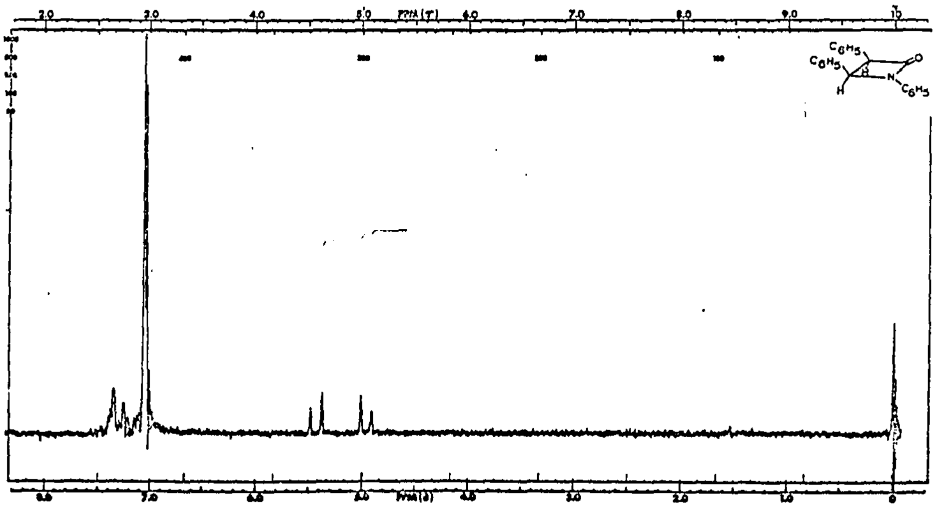
3.0
2.0
1.0
0


PPM (τ)
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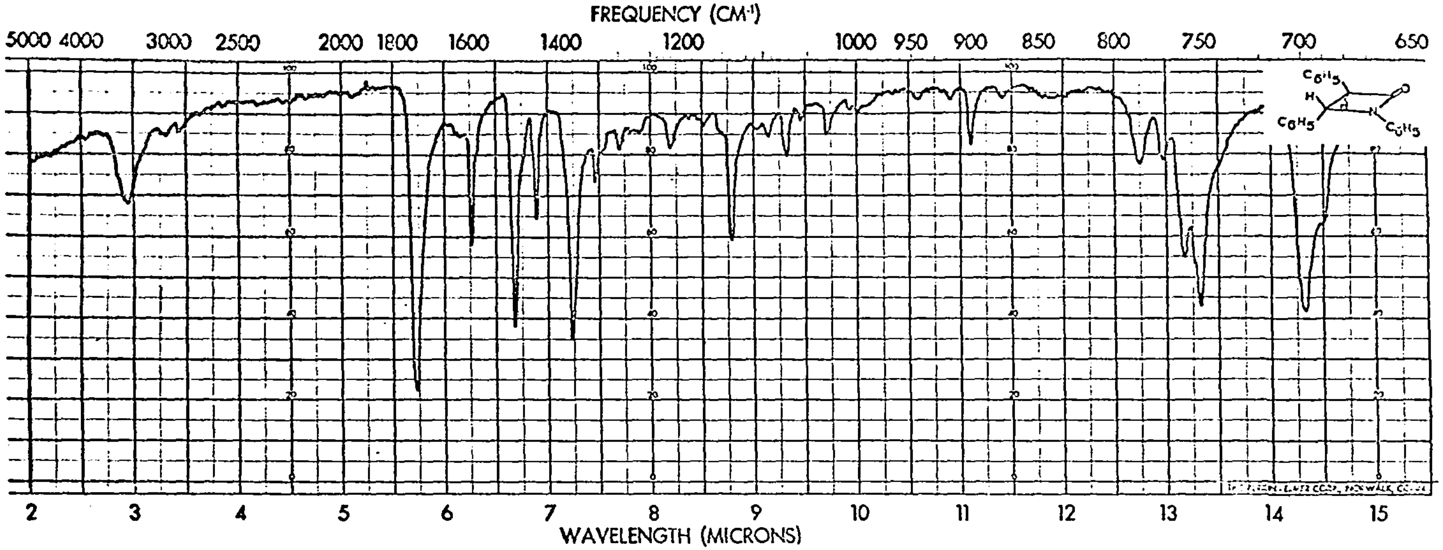
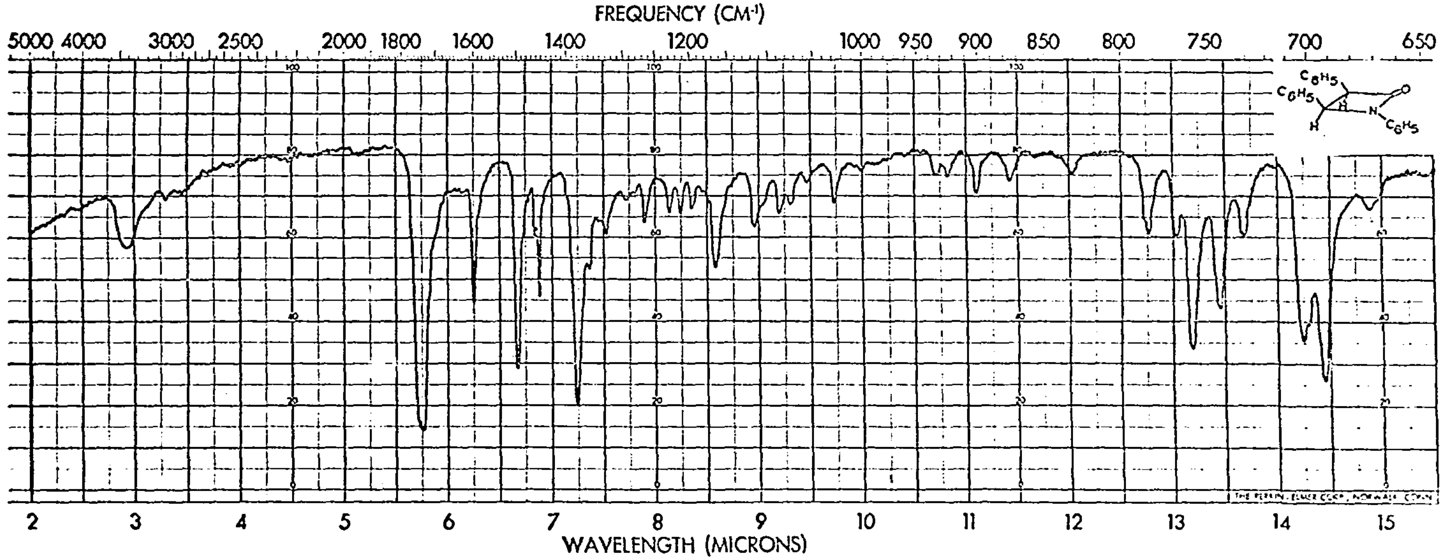
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
C6H5
C6H5
H
N
C6H5
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

Figure 6. Infrared spectra

Top - trans-1,3,4-triphenyl-2-azetidinone (XCVIII) in potassium bromide

Bottom - cis-1,3,4-triphenyl-2-azetidinone (XCVII) in potassium bromide


FREQUENCY (CM-1)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
C6H5
H
C6H5
O
N
C6H5
H
100
80
60
40
20
0
THE PERKIN-ELMER CORP., NORWALK, CONN.
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM-1)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
C6H5
C6H5
H
O
N
C6H5
H
100
80
60
40
20
0
THE PERKIN-ELMER CORP., NORWALK, CONN.
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

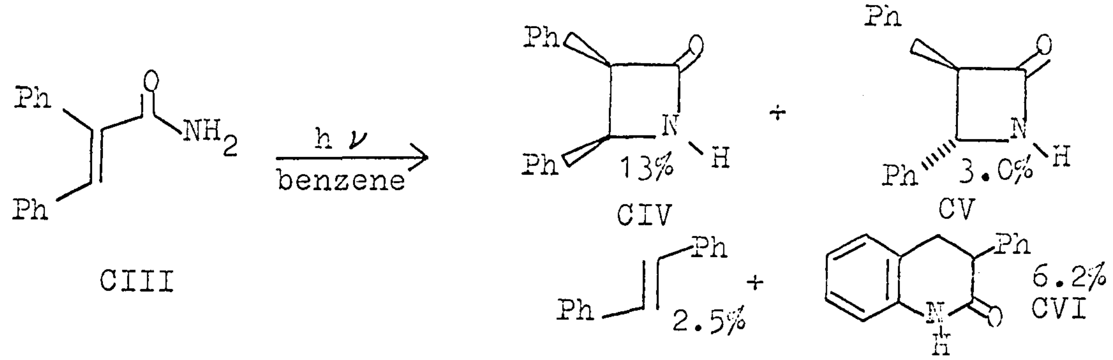
$\gamma_B = \delta\, 5.44$ (J_{AB}=7.0 cps). The structure is also supported by elemental analysis and the mass spectrum exhibited a strong parent ion at m/e 299 (30%) and fragment ions at m/e 181 (100%) and 180 (86%).

Attempted pyrolysis of cis and trans-β-lactams on an Aerograph Model 512 vapor phase chromatograph packed with 20% SE-30 on Chromosorb P at temperatures ranging from 200-350^o were not successful.

A third compound whose structure was tentatively assigned as cis-3,4-diphenylhydrocarbostyril (XCIX) gave a strong carbonyl band at 5.98μ in the infrared spectrum (KBr). The nmr spectrum gave a N-H proton singlet at $\delta\, 9.35$, an aromatic multiplet centered at $\delta\, 7.10$ and an AB proton pattern $\gamma_A = \delta\, 4.17$, $\gamma_B = \delta\, 4.43$ (J_{AB}=6.0 cps). The mass spectrum exhibited an intense molecular ion at m/e 299. The stereochemistry is assigned cis in view of the small coupling constant of the benzylic protons (68). Cyclization of cis-1,3,4-triphenyl-2-azetidinone to cis-3,4-diphenylhydrocarbostyril is analogous to other non-oxidative photocyclizations of acrylanilides (67).

Ultraviolet irradiation of cis-α-phenylcinnamamide (CIII) in benzene for 70 hours gave a complex mixture which upon separation by chromatography and fractional recrystallization gave trans-stilbene, and cis and trans-3,4-diphenyl-2-azetidinone (CIV, CV) respectively. A fourth photoproduct was isolated and tentatively identified as 3-phenylhydrocarbostyril

(CVI). Unreacted amide CIII was also recovered.



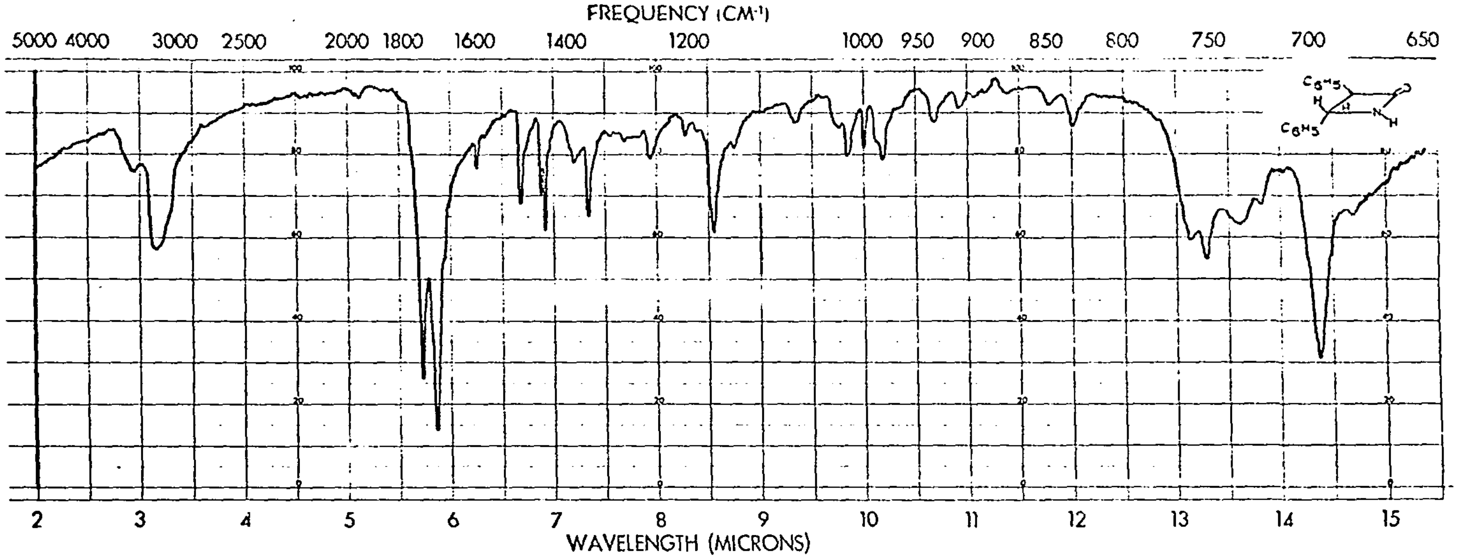
The infrared spectrum (Figure 7, page 53) in potassium bromide of <u>cis</u>-3,4-diphenyl-2-azetidinone (CIV) shows an intense carbonyl band at 5.72 and 5.78μ which collapses to a single band (5.67μ) in chloroform. The nmr spectrum (Figure 8, page 55) shows a ten proton multiplet centered at δ 7.00, one proton multiplet centered at δ 6.80 and an AB proton pattern $\gamma_A = \delta\, 4.87$, $\gamma_B = \delta\, 5.12$ (J_{AB}=6.0 cps). The A proton appears as a doublet of doublets (J=1.8 cps). Spin-spin decoupling by irradiation at 410 cps downfield from tetramethylsilane causes the A proton to collapse to a doublet. The structure was also confirmed by elemental analysis and the mass spectrum exhibited an intense parent ion at m/e 223 (38%) and fragment ions at m/e 180 (25%) and 118 (100%).

The structural assignment of <u>trans</u>-3,4-diphenyl-2-azetidinone (CV) was confirmed by the infrared spectrum (Figure 7, page 53) in potassium bromide. There are two carbonyl bands at 5.72 and 5.86μ which collapsed to a single band at 5.67μ when the spectrum is run in chloroform. The nmr spectrum (Figure 8, page 55) shows a ten proton multiplet centered at

Figure 7. Infrared spectra

Top - *trans*-3,4-diphenyl-2-azetidinone (CV) in potassium bromide

Bottom - *cis*-3,4-diphenyl-2-azetidinone (CIV) in potassium bromide


FREQUENCY (CM⁻¹)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
C6H5
H
H
N
H
O
C6H5
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

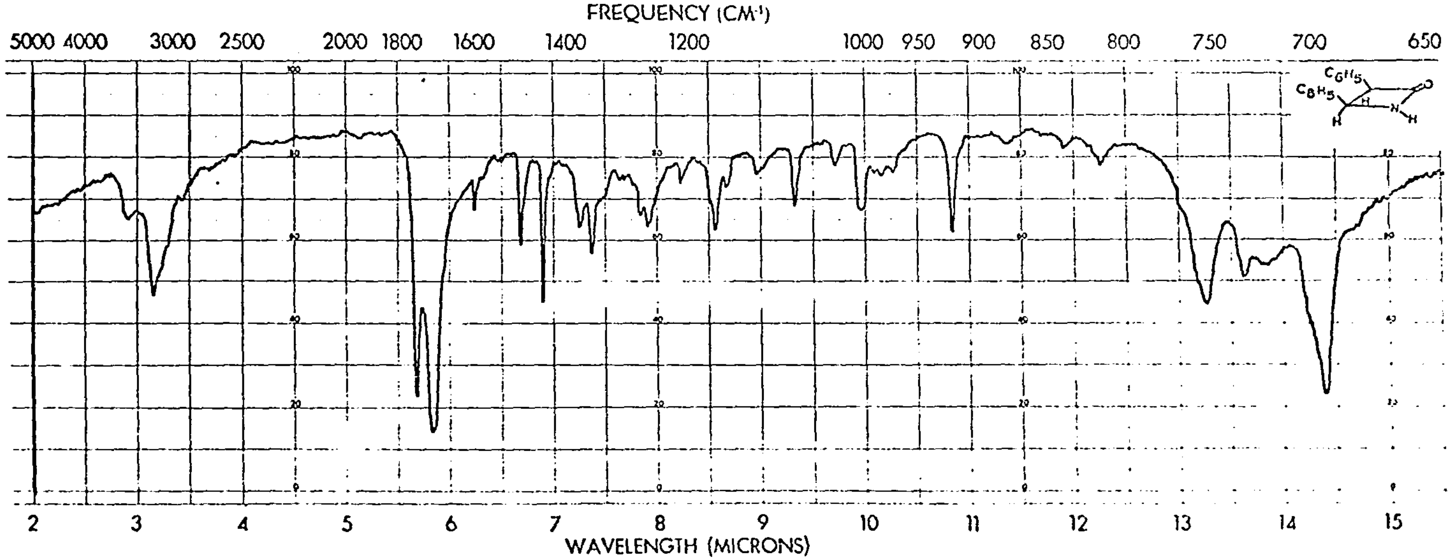
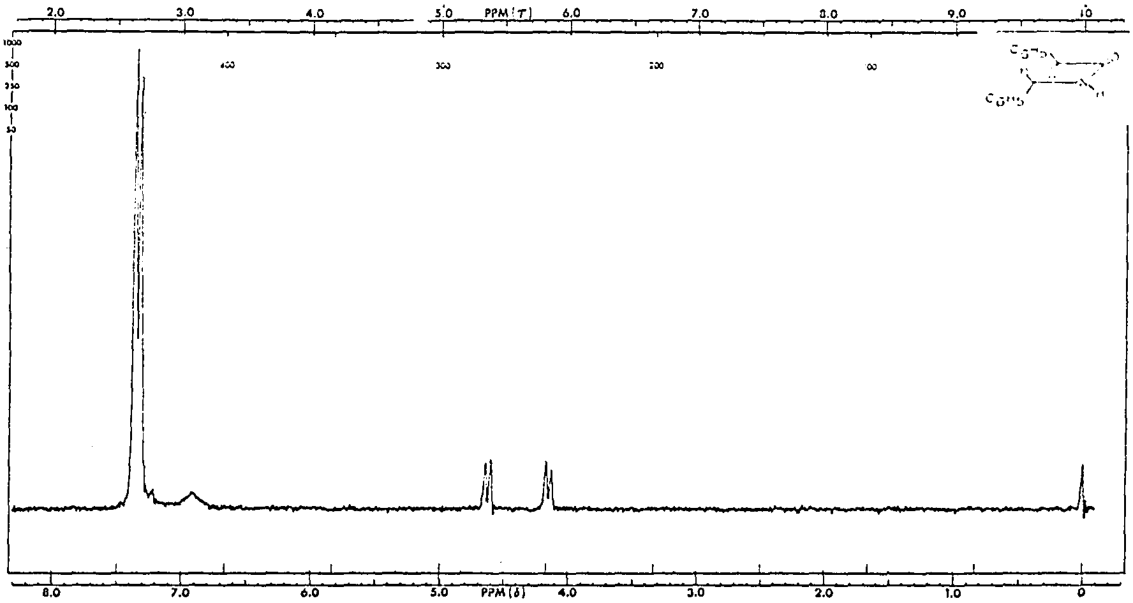

FREQUENCY (CM⁻¹)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
C6H5
C6H5
H
N
H
O
H
2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

Figure 8. Nuclear magnetic resonance spectra

Top - *trans*-3,4-diphenyl-2-azetidinone (CV) in deuteriochloroform

Bottom - *cis*-3,4-diphenyl-2-azetidinone (CIV) in deuteriochloroform


PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
400
300
200
100
C_6H_5
C_6H_5
PPM (δ)
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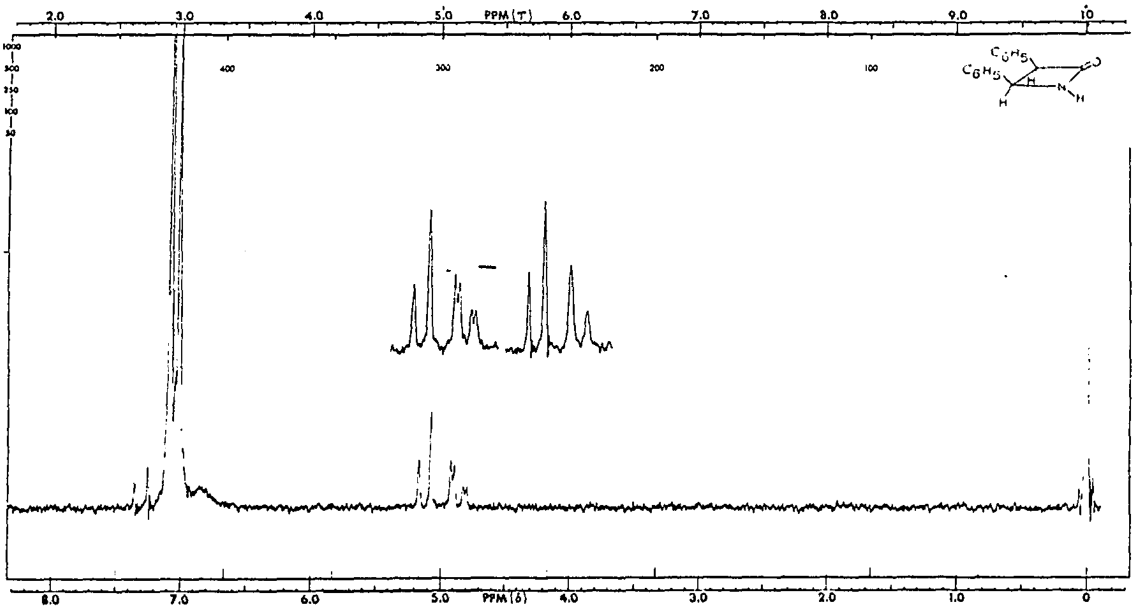
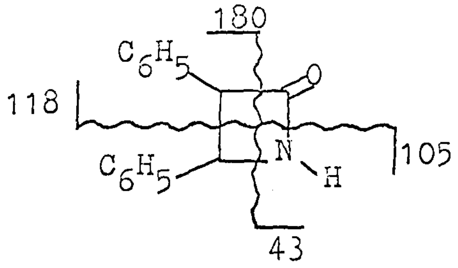
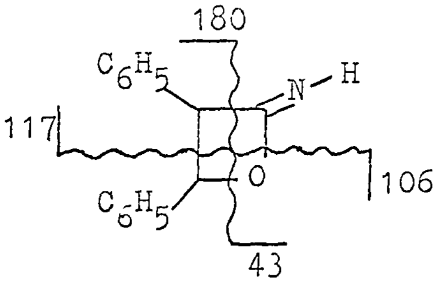
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
400
300
200
100
C_6H_5
C_6H_5
H
H
N
H
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

δ 7.34 and one proton centered at δ 6.90 and an AB proton pattern $\gamma_A = \delta 4.15$, $\gamma_B = \delta 4.62$ (J_{AB}=3.0 cps). The mass spectrum gave an intense molecular ion at m/e 223 (11%) and fragment ions at m/e 180 (100%), 165 (20%), and 118 (69%).

The β-lactam structural assignment is confirmed by the mass spectral cleavage patterns. Both cis and trans-3,4-diphenyl-2-azetidinone gave intense fragment ions at m/e 118 which is assigned to the phenylketene radical ion.



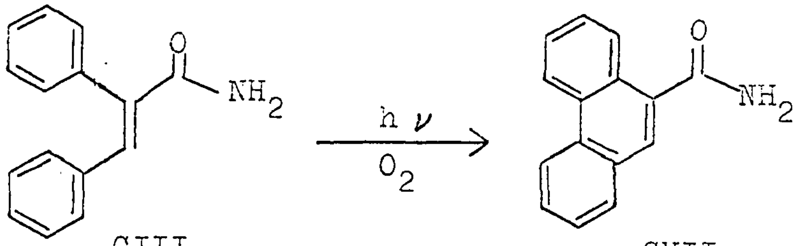


The stereochemical arrangement of the cis and trans-β-lactam CIV and CV were assigned by comparing the coupling constants with those of cis and trans-1,3,4-triphenyl-2-azetidinone (XCVII, XCVIII) respectively.

3-Phenylhydrocarbostyril (CVI) showed an intense carbonyl band at 5.96μ in the infrared spectrum. The nmr spectrum gave a one proton multiplet centered at δ 9.15, an aromatic proton multiplet centered at δ 7.20 and an A_2B proton pattern $\gamma_A = \delta 3.18$, $\gamma_B = \delta 3.80$ (J_{AB}=8.2 cps). The structure was supported by the elemental analysis and the mass spectrum which showed an intense parent ion at m/e 223 (100%).

Sargent and Timmons have reported (69) the photocyclization of cis-α-phenylcinnamamide (CIII) to 9-carbamoylphenanthrene

(CVII, mp 226°, 41%) by irradiation in ethanol in the presence of air. The authors also isolated a residue from the irradiation but further separation was not attained.



CIII CVII

In contrast to the conditions employed by Sargent and Timmons our irradiations were degassed with prepurified nitrogen for 30 minutes and sealed. We have no evidence that the phenanthrene derivative (CVII) was a product in our irradiation. Our results emphasize the need for oxygen in the oxidative cyclizations.

The photochemical isomerization to produce β-lactones and β-lactams has distinct advantages over other methods of preparation (70,71) due to the simplicity of the reaction and the production of the cis-isomer as the major product. The ability to form both diastereomeric β-lactams simultaneously is unprecedented in β-lactam synthesis. Until now, both cis and trans-isomers had never been observed in the preparation of monocyclic β-lactams.

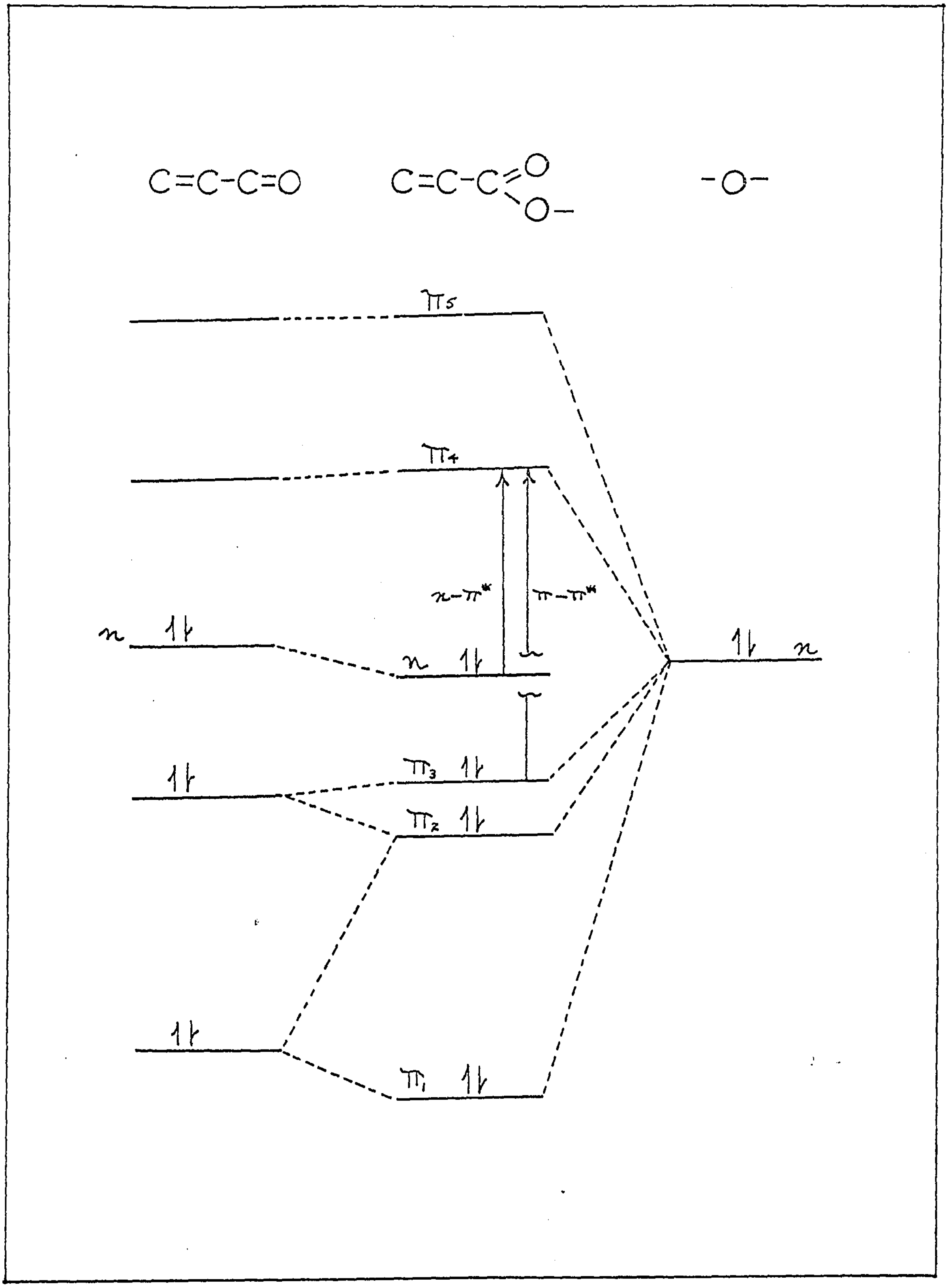
DISCUSSION

Spectral Considerations

By analogy with α,β-unsaturated ketones and aldehydes (72), one should expect to observe two different transitions in the ultraviolet spectrum, namely n,Pi* and Pi,Pi* as indicated in Figure 9, page 60. Compared with the corresponding ketones and aldehydes, all electronic levels will be modified by the presence of the hydroxyl oxygen directly attached to the carbonyl group. In unsaturated acids this effect results in a hypsochromic shift of the n,Pi* transition of about 80 mμ relative to corresponding transition of methyl vinyl ketone (73). It has been amply verified that the effect of the hydroxyl group on the Pi,Pi* band of α,β-unsaturated acids is relatively minor (73). Recently Weiss and Ziffer (74) have shown that the vapor phase spectrum of β,β-dimethylacrylic acid exhibits a distinct maximum at 245 mμ which they have tentatively ascribed to the n,Pi* transition on the basis of its low intensity. However, careful investigation of the solution spectra of several α,β-unsaturated acids in water, hexane and cyclohexane failed to indicate the presence of any band above 220 mμ which could be attributed to the n,Pi* transition. We have also failed to observe n,Pi* bands of the acids investigated in ethanol and cyclohexane solutions.

The most likely cause of this anomalous behavior is the ability of the free acids to dimerize. In polar solvents such

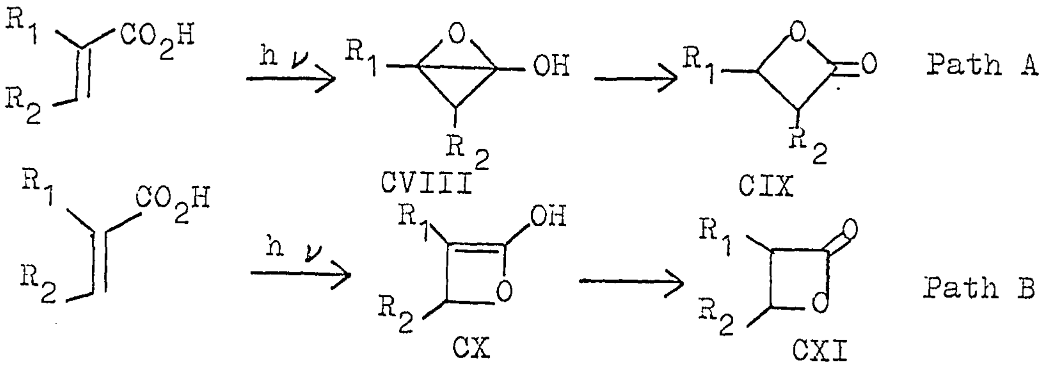
Figure 9. Energy level scheme for the α,β-unsaturated acid system (adapted from Closson, Brady, and Orenski (69)).


C=C-C=O
C=C-C(=O)O-
-O-
π5
π4
n-π*
π-π*
n
n
π3
π2
π1
n

as water and methanol the acid probably exists predominantly as the dissociated species while in non-polar solvents the dimer is probably the favored form (75). This dimerization phenomenon indicates that benzene or cyclohexane is as polar a medium for the acids as is water and it is easily demonstrated (76) that a polar solvent results in a shift of the n,Pi* band to shorter wave length (blue shift) and the Pi,Pi* band to longer wavelengths (red shift). This effect could result in complete masking of the n,Pi* transition by the Pi,Pi* transition. An alternative explanation concerning the anomalous ultraviolet absorption behavior of acids has been recently reported (77).

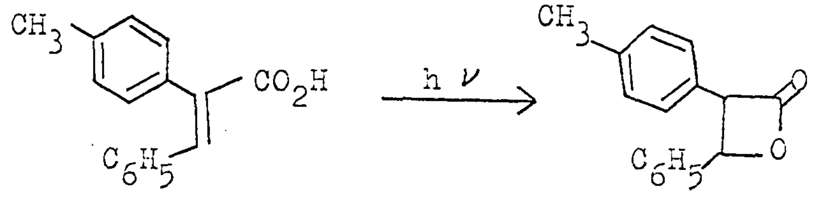
Mechanism

Two structurally different paths could explain the formation of the β-lactone LXXXIII from <u>cis</u> or <u>trans</u>-α-phenylcinnamic acid. Path A involves a photochemical cyclization to

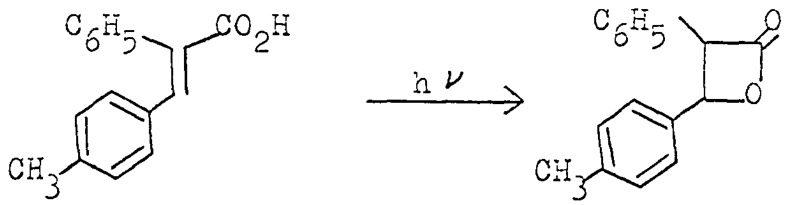


an oxabicyclobutane CVIII followed by subsequent isomerization to the β-lactone CIX. The isomerization to the oxabicyclobutane is analogous to the isomerization of transoid-1,3-butadiene.

(78). Path B involves a valence isomerization to a hydroxy oxetene CX which could ketonize to a β-lactone CXI. Irradiation of *cis*-α-(*p*-tolyl)-cinnamic acid (CXII) affords only α-*p*-tolyl-β-phenyl-β-propiolactone (CXIII) which was identified by the fragmentation of the parent ion (m/e 238) to *p*-tolylketene radical cation (m/e 132, 100% of base). No fragment attributable to phenylketene (m/e 118) was observed. Irradiation of the other isomer, *cis*-α-phenyl-*p*-methylcinnamic acid (CXIV) gave only α-phenyl-β-*p*-tolyl-β-propiolactone (CXV). The lactone gave a weak parent ion at m/e 238 and a phenylketene radical cation at m/e 118 (40.6% of base). These results are consistent only with Path B.

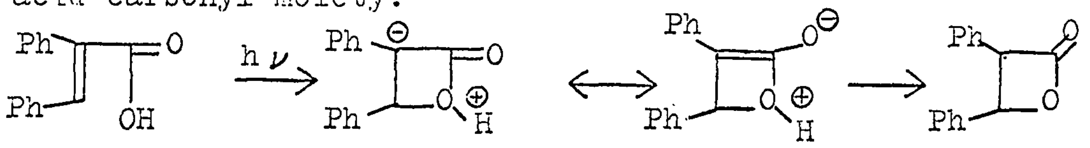


CXII CXIII

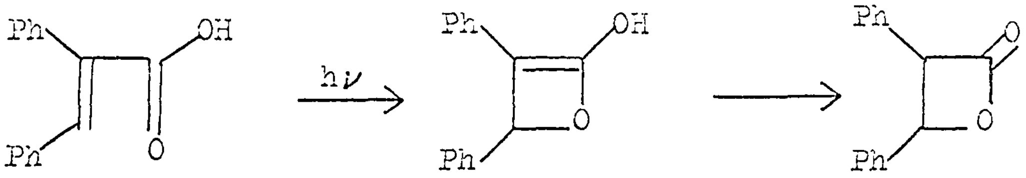


CXIV CXV

Formation of the hydroxy oxetene could occur by the following mechanisms. Mechanism A involves the acid hydroxyl attacking the olefinic bond while Mechanism B involves an attack by the acid carbonyl moiety.

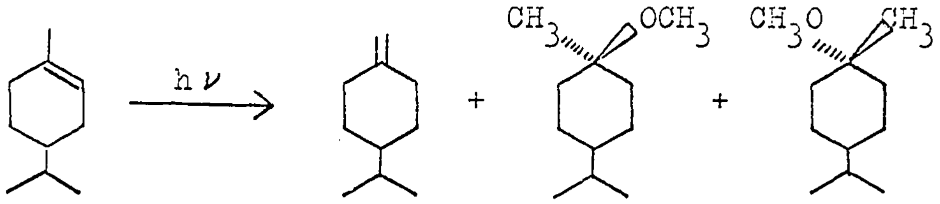


Mechanism A



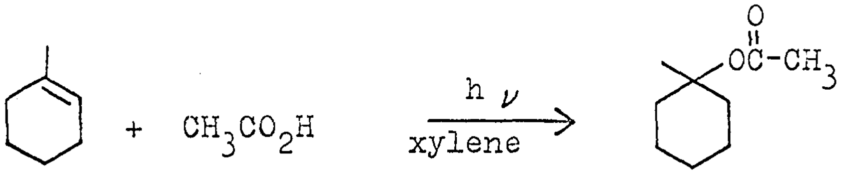
Mechanism B

Independent investigations by Kropp (79) and Marshall and Carroll (80) have revealed the ability of olefinic bonds to undergo photochemical addition with alcohols and acids. Irradiation of 1-methene (CXVI) in methanol-benzene afforded the ethers CXVIII and CXIX in addition to the exocyclic isomer CXVII. 1-Methylcyclohexene (CXX) affords 1-methylcyclohexyl



CXVI CXVII CXVIII CXIX

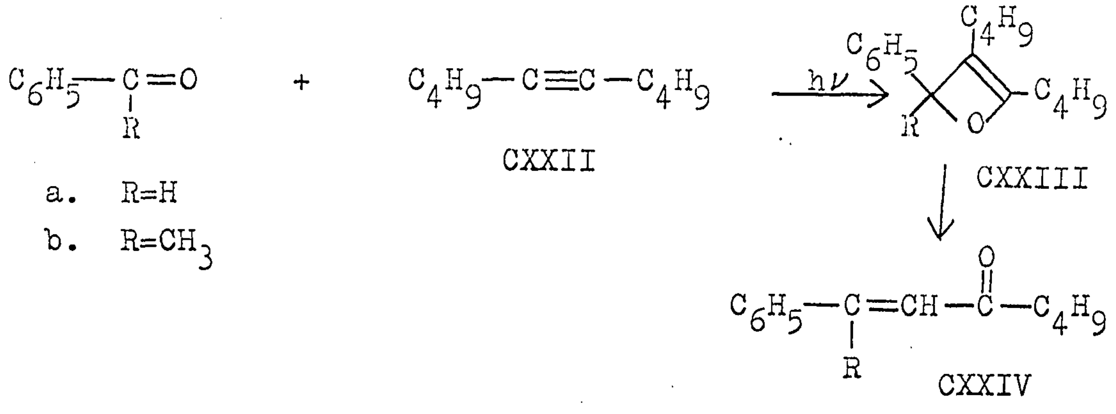
acetate (CXXI) upon irradiation in acetic acid (80). These additions are typical of ionic processes and one could envision



CXX CXXI

the β-lactone formation as an intramolecular addition of the acid moiety to the stilbene double bond (e.g., mechanism A). However, Kropp believes these solvent addition processes involve a highly strained <u>trans</u>-olefin which seeks relief by protonation and subsequent elemination or ether formation. This view is supported by the fact that acyclic olefins do not add methanol. Since the <u>cis</u> <u>trans</u> isomerization of α-phenylcinnamic acid is not sterically impeded, the mechanism is probably not operative in the cyclization to the β-lactone.

There is as yet, no established case of a compound with an unsaturated four-membered cyclic ether (oxetene) reported in the literature (70). Several recent attempts to prepare oxetenes have been unsuccessful. Büchi and coworkers (81) have described a reaction between 5-decyne (CXXII) and aldehydes and ketones on irradiation, but unfortunately the oxetenes that would be expected could not be isolated. Instead an α,β-unsaturated ketone CXXIV, which could conceivably arise from an unstable intermediate oxetene CXXIII, was obtained in low yield.

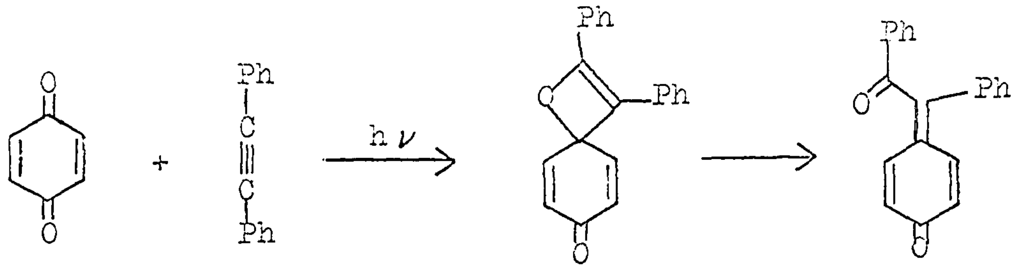


CXXII

CXXIII

CXXIV

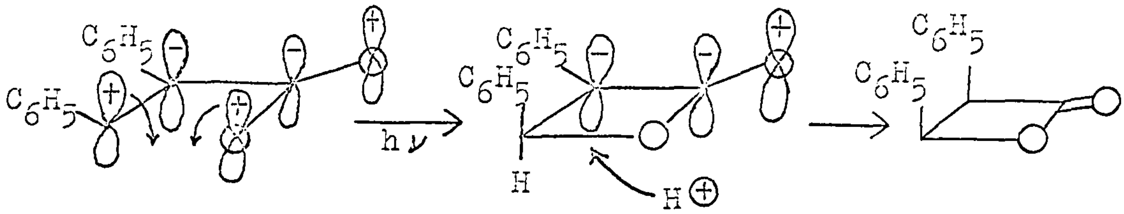
An oxetene intermediate has also been postulated (82,83) in the photocyclization of benzoquinone (CXXV) with diphenylacetylene which is reminiscent of the reaction described by Büchi.



CXXV

In the hope of gaining insight concerning the mechanism of photocyclization, molecular orbitals for ∝-phenylcinnamic and related acids were obtained from simple Hückel molecular orbital calculations using a computor program (84) carried out with the help of Dr. G. Underwood. The parameter values for heteroatoms were taken from Streitwieser (85). The oxygen atoms of the carboxylic acid were assumed to be equivalent and were assigned values of 1.5 and 0.9 for the coulomb and bond integrals respectively.

The ∝, β-unsaturated acid system is basically a modified butadiene structure and the symmetry of the highest occupied molecular orbital (HOMO) in the excited state of ∝-phenylcinnamic acid is shown below. Bond formation can only be achieved by a disrotatory process in agreement with the mechanistic rationale suggested by Hoffman and Woodward (86). The valence isomerization would then be presumably followed by kinetically controlled protonation from the less sterically hindered side of the cyclobutane structure to produce the <u>cis</u>-β-lactone.



The charge densities for the ground, n,Pi* and Pi,Pi* of α and β-p-substituted α-phenylcinnamic acids were calculated using $\zeta = 1 - q_r$ where

ζ = charge density

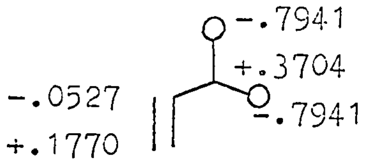
$q_r = {}_j n_j c^2_{jr}$ where q_r is the sum of the electron densities contributed by each electron in each molecular orbital

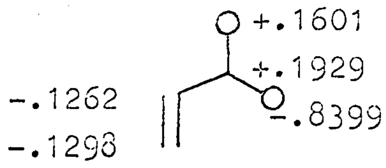
The results are shown in Table 3.

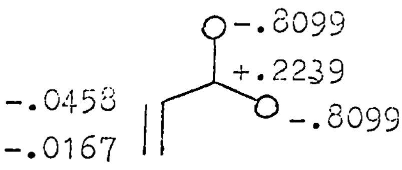
The pronounced characteristics of the n,Pi* and Pi,Pi* excited states are the variation of the charge density at the β-carbon atom. This variation appears to parallel the irradiation times of the substituted acids in a rough way and suggests that an electron deficient β-carbon will facilitate the photoisomerization (see Table 4). This effect can be seen most clearly by comparing the β-<u>p</u>-cyano acid XCIII which bears a formal charge for the Pi,Pi* excitation of +.0520 to that of the β-<u>p</u>-methoxy acid XCIII l with a formal charge of -.0579. Thus, a positive charge density at the β-carbon appears to enhance the reaction while an increasing negative charge

Table 3. Charge densities of Ground, n,Pi* and Pi,Pi* states.

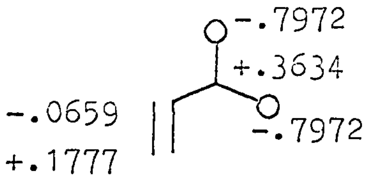
Ground | n,Pi* | Pi,Pi*

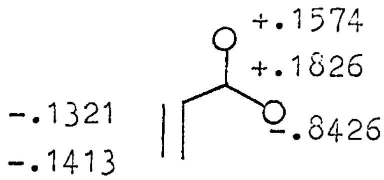


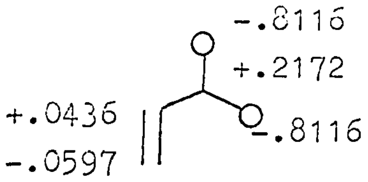




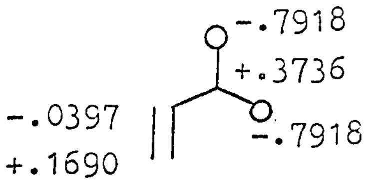
α-phenylcinnamic acid

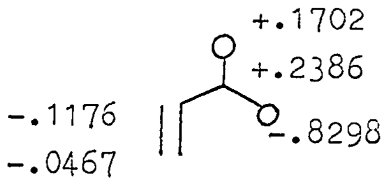


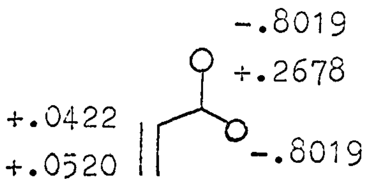




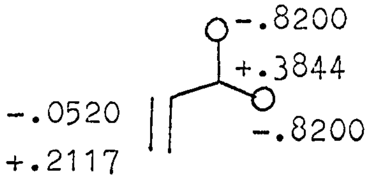
α-phenyl-p-methoxycinnamic acid

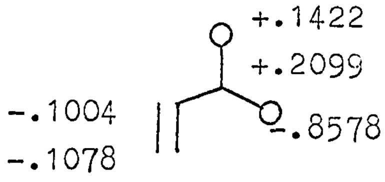


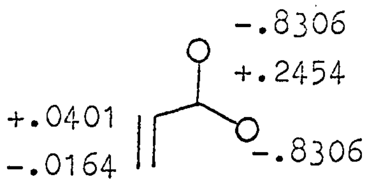




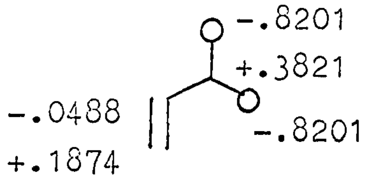
α-phenyl-p-cyanocinnamic acid

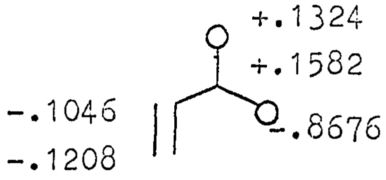


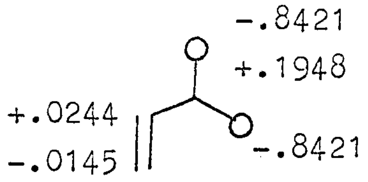




α-(p-cyanophenyl)-cinnamic acid





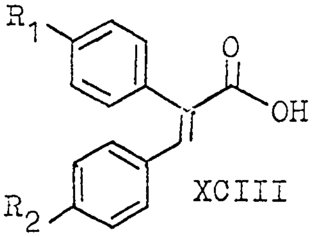


α-(p-methoxyphenyl)-cinnamic acid

density impairs it.

A discrepancy occurs with the unsubstituted XCIII a and the α-p-cyano XCIII g acids. The charge densities predict the irradiation time of XCIII g should be approximately equal to the unsubstituted acid.

Table 4. Correlation of the charge densities of the n,Pi* and Pi,Pi* excited states of the β-carbon with irradiation times.



XCIII

Acid	Charge density at β-carbon n,Pi*	Pi,Pi*	Irradiation time, hr
h. R_1=H,R_2=CN	-.0467	+.0520	5
k. R_1=OCH_3,R_2=H	-.1208	-.0145	10.5
a. R_1=H,R_2=H	-.1298	-.0167	21
g. R_1=CN,R_2=H	-.1078	-.0164	72
l. R_1=H,R_2=OCH_3	-.1413	-.0597	N.R.

The calculated total O-C_4 bond orders of the acids were found to be antibonding in every case and the values did not correlate with the irradiation times of the acids. The O-C_4 bond order for the n,Pi* exerted state varied from -.0557 to -.0888 while the Pi,Pi* state was less antibonding with values ranging from -.0029 to -.0363.

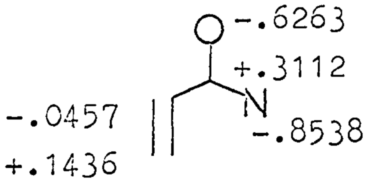
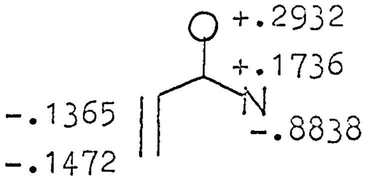
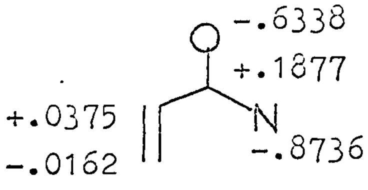
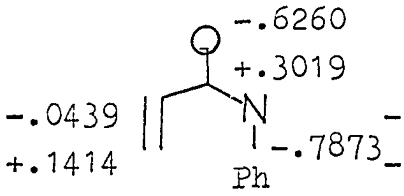
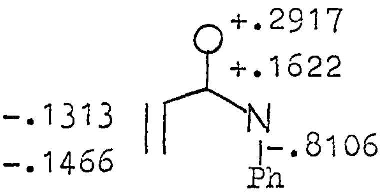
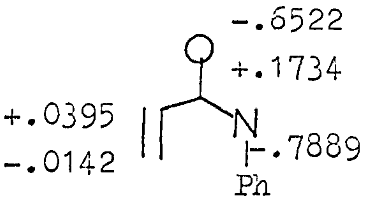
Calculated O-C_4 bond orders of the acid considering only the highest occupied molecular orbital showed an overall bonding tendency. The O-C_4 bond order for the Pi,Pi* excited states varied from +.1431 to +.1769 while the bond orders for the n,Pi* excited states were somewhat less bonding with values ranging from +.0906 to +.1210. The bond orders are in agreement with the supposition that the Pi,Pi* excited state is involved in the photocyclization.

Similar simple Hückel molecular orbital calculations were carried out on the α-phenylcinnamamide and α-phenylcinnamanilide systems. The results are shown in Table 5.

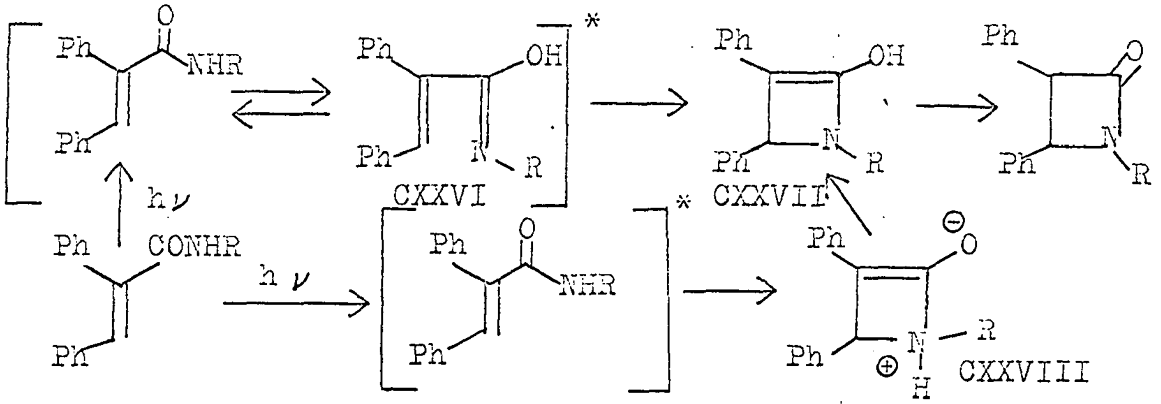
The charge densities suggest as in the case of the acids that an electron deficient β-carbon facilitates the amide isomerization since α-phenylcinnamanilide undergoes a more facile isomerization to the β-lactam than that observed for α-phenylcinnamamide. The irradiation times were 23 and 70 hours respectively.

The total bond calculated for the various electronic states show a decrease in antibonding on excitation with an enhanced C_4-oxygen bond order in the Pi,Pi* excited state of α-phenylcinnamamide. The same general trend is observed with α-phenylcinnamanilide except the nitrogen-C_4 bond order is bonding in the Pi,Pi* excited state. The enhanced nitrogen-C_4 bond order is nicely in accord with the experimental observations since β-lactams rather than α-iminooxetanes are isolated.

Table 5. Charge densities and bond orders of Ground, n,Pi* and Pi,Pi* excited states.

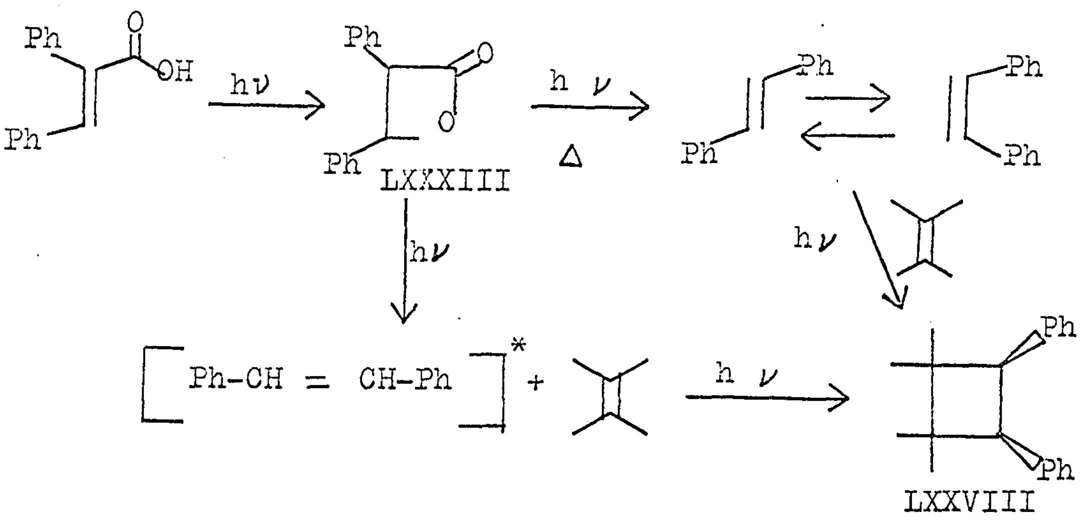
Ground	n,Pi*	n,Pi*
		
O-C$_4$ bond order -.2464 N-C$_4$bond order -.1352	O-C$_4$ bond order -.0934 N-C$_4$bond order -.0466	O-C$_4$ bond order +.0043 N-C$_4$ bond order -.0100
	α-phenylcinnamamide	
		
O-C$_4$ bond order -.2444 N-C$_4$ bond order -.1342	O-C$_4$ bond order -.0904 N-C$_4$ bond order -.0524	O-C$_4$ bond order -.0043 N-C$_4$ bond order +.0012
	α-phenylcinnamanilide	

Several mechanistic routes could explain the photoisomization. An attractive pathway would involve an excited cyclic Schiff base (CXXVI) which could isomerize to the hydroxylazetine (CXXVII) followed by ketonization to the β-lactam.

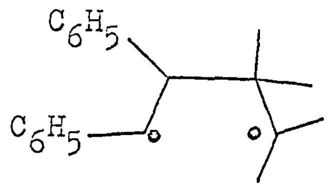


An alternate mechanistic path would involve excitation of the amide followed by a subsequent attack of the β-carbon by the nitrogen atom, to give a resonance stabilized zwitterionic intermediate (CXXVIII). A proton transfer would then give the β-lactam.

The intermediacy of the β-lactone LXXXIII suggests the sequence shown below as a reasonable series of events in the formation of the trans-cyclobutane adduct LXXVIII.



The final step involves the formation of a photoequilibrium mixture of cis and trans-stilbene, either of which could react with tetramethylethylene to form a diradical intermediate CXXIX. Subsequent electron pairing could then afford the more stable trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII).



CXXIX

An alternative concerted cycloaddition mechanism in which only trans-stilbene reacts with the unsaturated addend cannot be unequivocally eliminated. This mechanism is supported by the evidence that trans-stilbene undergoes photocycloaddition to tetramethylethylene faster and cis-trans isomerization of the stilbenes competes effectively with addition.

The mechanism of formation of β-lactams is assumed to be similar to that of the β-lactone isomerization and a more complete and accurate analysis will hopefully provide the answers concerning mechanism of this unprecedented reaction.

EXPERIMENTAL

Instruments

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

The ultraviolet spectra were recorded on a Beckman Model DK-2A or a Cary Model 14 spectrophotometer.

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

The nuclear magnetic resonance spectra were measured on a Varian Associates Model HR-60 or A-60 spectrometer operated at 60 Mc. The spectra were calibrated by the side band technique using tetramethylsilane as an internal standard. Chemical shifts are reported as δ-values.

The mass spectra were recorded on an Atlas CH4 single-focusing mass spectrometer using a solid inlet system at energy of 70 ev.

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Procedure

cis-α-Phenylcinnamic acid (LXXVII):

The procedure is similar to that of Fieser (84). Phenylacetic acid (10.0 g, 0.074 mole), benzaldehyde (12.5 g, 0.118 mole), triethylamine (8 ml), and acetic anhydride (8 ml) were placed in a 250 ml flask and refluxed for 4 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (16 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5% sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from 3:2 ethanol-water yielding LXXVII (12.0 g, 73%, mp 172-173°, reported (88) mp 172-173°); λ max (cyclohexane) 286 mμ (ϵ 15,400), 226 (17,000).

<u>trans-α-Phenylcinnamic acid (LXXXVIII):</u>

The filtrate from the cis-acid described above was acidified to pH 1 with concentrated hydrochloric acid, filtered and recrystallized from 3:2 ethanol-water giving LXXXVIII (1.3 g, 8%, mp 136-137°, lit.(89) mp 136-137°); λ max (cyclohexane) 289 mμ (ϵ 18,300), 222 (11,600).

<u>cis-α-(p-Nitrophenyl)-cinnamic acid (XCIII i):</u>

cis-α-(p-Nitrophenyl)-cinnamic acid was obtained from p-nitrophenylacetic acid and benzaldehyde following the procedure employed for cis-α-phenylcinnamic acid (LXXVII) in 70% yield. Recrystallization from ethanol gave yellow needles, mp 216-217°, reported (88) mp213-214°; λ max (cyclohexane) 293 mμ (ϵ 16,000), 268 (18,000), 225 (sh)(14,000), 216 (sh)(15,000).

<u>cis-α-Phenyl-p-nitrocinnamic acid (XCIII j):</u>

cis-α-Phenyl-p-nitrocinnamic acid was obtained from the condensation of phenylacetic acid and p-nitrobenzaldehyde in 75% yield. Recrystallization from ethanol afforded yellow prisms, mp 227.5-228°, lit (88) mp 224-225°; λ max (cyclohexane) 310 mμ (ε 12,000), 254 (6000), 215 (sh)(13,000).

cis-α-(*p*-Methoxyphenyl)-cinnamic acid (XCIII k):

cis-α-(*p*-Methoxyphenyl)-cinnamic acid was obtained from *p*-methoxyphenylacetic acid and benzaldehyde in 50% yield. Recrystallization from benzene gave colorless crystals, mp 156-157°, lit. (90), mp 157-158°; λ max (cyclohexane) 323 mμ (sh) (ε 15,000), 276 (30,000), 227 (37,000).

cis-α-Phenyl-*p*-methoxycinnamic acid (XCIII l):

cis-α-Phenyl-*p*-methoxycinnamic acid was obtained in 70% yield from the condensation of phenylacetic acid and *p*-anisaldehyde. Recrystallization from ethanol-water gave colorless needles, mp 188-189°, reported (91), mp 188-189°, λ max (cyclohexane) 313 mμ (ε 22,000), 230 (15,000).

cis-α-(*p*-Chlorophenyl)-cinnamic acid (XCIII d):

cis-α-(*p*-Chlorophenyl)-cinnamic acid was prepared from *p*-chlorophenylacetic acid and benzaldehyde in 50% yield. Recrystallization from ethanol yielded colorless needles, mp 180-181.5°, lit. (92) mp 180-181°; λ max (cyclohexane) 290 mμ (ε 17,000), 227 (23,000).

cis-α-Phenyl-*p*-chlorocinnamic acid (XCIII e):

cis-α-Phenyl-*p*-chlorocinnamic acid was obtained from *p*-chlorobenzaldehyde and phenylacetic acid in 30% yield. Recrystallization from ethanol afforded colorless needles, mp 205-206°, lit. (93) mp 202-203°; λ max (cyclohexane) 296 mμ

(ϵ 20,000), 228 (18,000), 222.5 (19,000).

cis-α-(p-Tolyl)-cinnamic acid (XCIII b):

A mixture of p-tolylacetic acid (14.0 g, 0.093 mole), benzaldehyde (14.0 g, 0.132 mole), triethylamine (10 ml) and acetic anhydride (10 ml) was refluxed for 4 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (18 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5% sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from ethanol yielding colorless crystals (13.8 g, 62%, mp 152-153°); infrared (KBr) 2.75-4.50,5.98, 6.20, 6.90, 7.05,8.93, 12.18, 12.90, 13.64, 14.42 μ; nmr ($CDCl_3$), δ 11.15 (1H,m), δ 7.90 (1H,s), δ 7.30-6.95 (9H,m), δ 2.35 (3H,s); λ max (cyclohexane) 284 mμ (ϵ 18,000), 226 (24,000), 222 (23,000).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.67; H, 5.78.

cis-α-Phenyl-p-methylcinnamic acid (XCIII c):

A mixture of phenylacetic acid (7.5 g, 0.055 mole), p-methylbenzaldehyde (8.0 g, 0.067 mole), triethylamine (6 ml), and acetic anhydride (6 ml) was refluxed for 4 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (12 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5%

sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from benzene affording large, colorless needles (7.9 g, 60%, mp 170-171°); infrared (KBr) 2.75-4.50 (broad), 5.97, 6.21, 7.05, 7.78, 7.92, 12.24, 14.04, 14.25 μ; nmr ($CDCl_3$), δ 11.09 (1H,m), δ 7.92 (1H,s), δ 7.30 (5H,m), δ 6.95 (4H,s), δ 2.25 (3H,s); λ max (cyclohexane) 297 mμ (ϵ 20,000), 229 (18,000), 224 (18,000).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.65; H, 5.86.

cis-α-(p-Fluorophenyl)-cinnamic acid (XCIII f):

A mixture of p-fluorophenylacetic acid (12.0 g, 0.078 mole), benzaldehyde (14.0 g, 0.13 mole), triethylamine (10 ml), and acetic anhydride (10 ml) was refluxed for 6 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (20 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5% sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from benzene yielding colorless crystals (10.2 g, 54%, mp 170-171°); infrared (KBr) 2.75-4.00 (broad), 6.00, 6.20, 6.25, 6.62, 6.90, 7.03, 7.88, 8.16, 10.03, 12.00, 12.87, 13.30, 13.52, 14.51 μ; nmr ($CDCl_3$), δ 12.39 (1H, s), δ 7.95 (1H,s), δ 7.40-6.90 (9H,m); λ max (cyclohexane) 288 mμ (ϵ 17,000), 225 (18,000), 221 (18,000).

Anal. Calcd. for $C_{15}H_{11}FO_2$: C, 74.38; H, 4.55; F, 7.85.

Found: C, 74.49; H, 4.62; F, 7.95.

cis-α-(*p*-Cyanophenyl)-cinnamic acid (XCIII g):

A mixture of *p*-cyanophenylacetic acid (9.25 g, 0.057 mole), benzaldehyde (9.0 g, 0.085 mole), triethylamine (6.3 ml), and acetic anhydride (6.3 ml) was reluxed for 4 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (14 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5% sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from ethanol giving light yellow, crystals (7.30 g, 51%, mp 177-179°); infrared (KBr), 2.75-4.00 (broad), 4.50, 5.97, 6.24, 6.92, 7.02, 7.77, 7.87, 11.86, 13.26, 13.39, 14.47μ; nmr ($CDCl_3$), δ 11.29 (1H,m), δ 8.04 (1H, s), A_2B_2 pattern $\gamma_A = \delta\ 7.35$, $\gamma_B = \delta\ 7.67$ (J_{AB}=8.0 cps), δ 7.30-6.95 (5H, m); λ max (cyclohexane) 293 mμ (ε 16,000), 247 (sh) (15,000), 228 (19,000).

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.11; H, 4.42; N, 5.62. Found: C, 76.82; H, 4.47; N, 5.62.

cis-α-Phenyl-*p*-cyanocinnamic acid (XCIII h):

A mixture of *p*-cyanobenzaldehyde (10.0 g, 0.076 mole), phenylacetic acid (6.5 g, 0.049 mole), triethylamine (5.2 ml), and acetic anhydride (5.2 ml) was refluxed for 4 hr. The mixture was cooled, acidified with concentrated hydrochloric acid (14 ml) and extracted with chloroform. The organic solution was washed twice with water and extracted several times with a 5% sodium hydroxide solution. The alkaline extracts were combined and acidified to pH 6 with acetic acid. The precipitate was filtered and recrystallized from ethanol giving light, yellow crystals (3.2 g, 26%, mp 178-180°); infrared (KBr), 2.75-4.00 (broad), 4.50, 4.96, 6.17, 7.07, 7.95, 11.90, 12.00, 14.25 μ ; nmr ($CDCl_3$), δ 11.19 (1H,m), δ 7.89 (1H,s), δ 7.50-7.00 (9H,m); λ max (cyclohexane) 289 mμ (ϵ 20,000), 226 (19,000), 220 (21,000).

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.11; H, 4.42; N, 5.62. Found: C, 77.07; H, 4.46; N, 5.50.

p-Chlorophenylacetic acid :

A solution of p-chlorobenzylcyanide (10.0 g, 0.066 mole), concentrated sulfuric acid (10 ml), water (10 ml) and glacial acetic acid (10 ml) was refluxed for 1 hr. The solution was cooled and poured into water (100 ml). The crude acid was filtered and recrystallized from ethanol-water yielding p-chlorophenylacetic acid (6.3 g, 56%, mp 105-106°, reported (94) mp 105-106°).

p-Cyanophenylacetic acid :

Prepared by the method of Jaejer and Robinson (95). Sodium nitrite (14.0 g) in water (40 ml) was added to an ice-cold solution of p-aminophenylacetic acid (30.0 g, 0.20 mole) and sodium carbonate (21.2 g) in water (150 ml). The mixture was gradually added, with stirring to concentrated hydrochloric acid (84 ml) and water (84 ml) keeping the temperature below 10°. The diazotized solution was slowly added to copper sulfate (48 g) and potassium cyanide (60 g) dissolved in water (250 ml) with vigorous stirring during the addition and 1 hr after. The mixture was heated at 50° for 1 hr, filtered and acidified with concentrated hydrochloric acid. The precipitate was filtered, dissolved in water and decolorized with charcoal. The filtrate was cooled giving large, light, yellow needles (16.0 g, 50%, mp 151-152°, reported (95) mp 152°).

α-Phenylcrotononitrile :

A solution of benzylcyanide (160 g, 1.36 mole), acetaldehyde (88 g, 2.0 mole) and absolute ethanol (250 ml) was cooled in a Dry Ice bath and 15 ml of 20% sodium ethoxide (6.8 g in 100 ml of absolute ethanol) was added, keeping the temperature below 0°. The solution was placed in a refrigerator for 1 day, acetaldehyde (10 g) was added and the solution was replaced in the refrigerator for an additional 16 hr. The solution was was washed twice with water (300 ml). An oil was separated and distilled giving α-phenylcrotononitrile (70 g, 36%, bp 75.5-76° at 0.1 mm, reported (96) bp 100-103° at 1 mm). The infrared spectrum (cap film) gave bands at 3.30, 4.50, 6.77, 6.94, 11.75, 13.20, 14.50 μ.

α-Phenylcrotonic acid :

Using the method of Barltrop (97), hydrogen chloride was bubbled through a solution of α-phenylcrotononitrile

(10 g, 0.07 mole) in methanol (200 ml) for 2 hr. The solution was concentrated under reduced pressure giving a solid which was heated at 100° for 12 hr with concentrated hydrochloric acid (150 ml). The solution was extracted twice with ether. The ethereal solutions were combined and washed several times with water and dried over magnesium sulfate. Concentration under reduced pressure gave a solid. Recrystallization from hexane gave α-phenylcrotonic acid (6.8 g, 60%) mp 136-137°, lit. (98) mp 136-137°; λ max (95% ethanol) 240 mμ (sh) (ϵ 4,700).

β-Phenylcinnamic acid:

1,1-Diphenylethylene (25.0 g, 0.14 mole, Aldrich Chemical Co.) and oxalyl chloride (75.0 g, 0.6 mole, Aldrich Chemical Co.) were refluxed until the evolution of hydrogen chloride ceased (12 hr). Excess oxalyl chloride was removed under reduced pressure and the syrupy residue was stirred into an ice-cold sodium carbonate solution. Water (500 ml) was added, and the solution was boiled for 1 hr. The solution was decolorized with charcoal, filtered and acidified with concentrated hydrochloric acid. The solid was filtered and recrystallized from acetic acid yielding β-phenylcinnamic acid (28.6 g, 91%) mp 167-168°, reported (99) mp 167°; λ max (95% ethanol) 272 mμ (ϵ 12,700), 222 (sh)(16,400).

1,1,2-Triphenylethylene:

A solution of 1,1,2-triphenylethanol (15.0 g, 0.055 mole), prepared in 95% yield by the method of Hell and Wiegandt (100), and acetic acid (250 ml) was refluxed for 2 hr. The solution was extracted with ether, washed with water, neutralized with sodium bicarbonate and washed twice more with water. The ether layer was dried over magnesium sulfate and evaporated under reduced pressure giving a solid (14 g). Recrystallization from 95% ethanol gave the olefin (13.0 g, 93%), mp 68-69°, lit. (100) mp 67-68°.

Triphenylvinyl bromide :

Bromine (20.0 g) was added to a solution of triphenylethylene (31.8 g, 0.124 mole) in glacial acetic acid (200 ml), keeping the temperature of the solution below 40°. Then the solution was refluxed until hydrogen bromide evolution ceased and cooled giving the bromide (40.4 g, 98%) mp 114-115°, reported (101), mp 114-115.5°.

α,β-Diphenylcinnamic acid :

Triphenylvinyl bromide (20.0 g, 0.06 mole) and magnesium (1.6 g) were covered with dry ether (200 ml) and dibromoethylene (2 drops) was added. The mixture was refluxed for 3 hr under a nitrogen atmosphere. The grignard solution was poured into Dry Ice (100 g) and stirred until the Dry Ice disappeared. The solution was acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution was washed with water and extracted several times with a 10% sodium hydroxide solution. The basic extracts were combined, acidified with concentrated hydrochloric acid and filtered. Recrystallization of the residue from acetic acid gave the acid (10.1 g, 56%) mp 219-220°, lit. (101) mp 217-218°; λ max (95% ethanol) 292 mμ (ε 10,200), 235 (19,200), 203 (sh)(40,700).

α-Phenylacrylic acid (XCV e):

α-Phenylacrylic acid was synthesized following a known procedure (102). Recrystallization from methanol-water gave colorless crystals, mp 106-107°, lit. (102) mp 106-107°; λ max (95% ethanol) 245 mμ (ε 5,570), 204 (14,300).

trans-Cinnamic acid:

trans-Cinnamic acid was purchased from Aldrich Chemical Co. Recrystallization from benzene-pentane gave colorless crystals, mp 133-134°, lit. (103) mp 133-134°; λ max (95% ethanol) 272 mμ (ε 25,000), 220 (sh)(22,000), 215 (19,200).

α-Methylcinnamic acid (XCV b):

α-Methylcinnamic acid was purchased from Aldrich Chemical Co. Recrystallization from benzene-pentane yielded colorless needles, mp 91-92°, lit. (104) mp 91-92°; λ max (95% ethanol) 265 mμ (ε 6,650), 204 (5,850).

Crotonic acid:

Crotonic acid was obtained from Aldrich Chemical Co. Recrystallization from hexane gave colorless needles, mp 72-73°, lit. (105) mp 72-73°; λ max (95% ethanol) 205 mμ (ε 12,600).

Biphenyleneacrylic acid:

Biphenyleneacrylic acid was obtained from Aldrich Chemical

Co. and recrystallized from acetic acid, mp 222-223°, lit. (106) mp 222-223°; λ max (95% ethanol) 258 mμ (ε 26,900), 232 (26,900).

cis-α-Phenylcinnamamide (CIII):

The cis-α-phenylcinnamamide was prepared by adding cis-α-phenylcinnamoyl chloride to an ice-cold solution of ammonium hydroxide. Crystallization from acetone-water gave colorless needles, mp 127-128°, reported (107) mp 127°; λ max (95% ethanol) 280 mμ (ε 14,100), 220 (15,500), 205 (20,800).

cis-α-Phenylcinnamanilide (XCVI):

The cis-α-phenylcinnamanilide was prepared by adding cis-α-phenylcinnamoyl chloride to a solution of aniline in benzene. Recrystallization from chloroform-benzene gave colorless prisms, mp 141-142°, lit. (108) mp 140°; λ max (95% ethanol) 292 mμ (ε 21,800), 221 (19,100).

Irradiation of cis-α-phenylcinnamic (LXXVII) acid in the presence of tetramethylethylene

A solution of LXXVII (4.0 g, 0.018 mole), tetramethylethylene (10 g, 0.12 mole) and ether (250 ml) was degassed with nitrogen for 0.5 hr. The solution was irradiated in a quartz immersion irradiation apparatus using a Hanovia Type A 550-watt mercury arc lamp. The progress of the reaction was followed by periodically removing aliquots and measuring their ultraviolet absorption. After 20.5 hr the ultraviolet spectrum showed complete absence of the 282 mμ absorption initially present.

Alternatively, the process was followed by infrared absorption by observing the loss of the acid carbonyl band at 5.96 μ. The solvent was removed under reduced pressure giving a yellow solid (3.51 g). The infrared spectrum (KBr) showed bands at 3.38, 6.25, 6.68, 6.92, 7.33, 9.75, 12.62, 13.43, 13.60, 14.28 μ. The solid was dissolved in Skelly B and poured onto a 2.5" X 20" column prepared with 200 g of Silica Gel. The column was eluted with 500 ml of Skelly B, which upon evaporation gave a white solid (3.30 g). Recrystallization from hexane yielded *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 3.13 g, 66.5%) mp 105-106°. The infrared and nmr spectra are shown in Figure 1, page 23, and Figure 2, page 25, respectively. The mass spectrum exhibited very weak parent ion m/e 264 and fragment ions at m/e 132 (0.8%), 165 (0.8%), 178 (0.9%), 179 (14.5%), 180 (100%), and 181 (14.5%)

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.83; H, 9.22.

Irradiation of *trans*-stilbene in the presence of tetramethylethylene

A. *trans*-Stilbene (2.0 g, 0.011 mole, Scintillation grade, Matheson, Coleman and Bell) and tetramethylethylene (5.0 g, 0.06 mole) were dissolved in anhydrous ether (300 ml). The solution was degassed with nitrogen for 0.5 hr and irradiated in a quartz immersion irradiation apparatus using a 550-watt Hanovia Type A lamp for 6 hr. The reaction was followed by ultraviolet absorption until the maximum at 308 mμ was 6%

of its original value. The solvent was removed under reduced pressure yielding a yellow solid. The infrared spectrum (KBr) showed bands at 3.38, 6.25, 6.28, 6.92, 7.33, 9.75, 12.62, 13.43, 13.59, 14.28μ. The solid was dissolved in Skelly B and poured onto a 2.5" X 20" column prepared with 70 g of Alumina (Woelm, neutral activity I). The column was eluted with 400 ml of Skelly B which upon evaporation gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 1.98 g, 68%, mp 106-107°). The infrared spectrum (KBr) was superimposable on that of the adduct obtained from the photolysis of *cis*-α-phenylcinnamic acid in the presence of tetramethylethylene. A mixed melting point determination showed no depression.

B. A solution of *trans*-stilbene (500 mg, 0.0028 mole) in tetramethylethylene (40 ml) was placed in a quartz irradiation vessel and purged with nitrogen for 15 min. The solution was irradiated externally with a low pressure mercury lamp (Hanovia, model 688A45) for 19 hr. The reaction was monitored by periodically taking aliquots and measuring their ultraviolet absorption. The bands at 308 and 295 mμ were totally removed. The solvent was evaporated giving a yellow solid (0.74 g). Recrystallization from hexane gave LXXVIII (0.70 g, 95%, mp 105-106°). The infrared spectrum (KBr) was identical to that of the photoadduct described above.

Irradiation of *cis*-stilbene in the presence of tetramethylethylene

A solution of *cis*-stilbene (0.5 g, 0.0028 mole, Aldrich

Chemical Co.) in tetramethylethylene (40 ml) was placed in a quartz irradiation vessel and purged with nitrogen for 15 min. The solution was irradiated externally with a low pressure mercury arc lamp (Hanovia, model 688A45). The progress of the reaction was followed by periodically removing aliquots and measuring their ultraviolet absorption. The initial absorption at 276 mμ shifted to longer wavelength (290 mμ) and to a higher molar extinction value during the early course of the irradiation. After 44 hr the initial bands were completely removed. The solvent was evaporated under reduced pressure giving a yellow solid (0.70 g). Recrystallization from hexane gave trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 0.68 g, 93%, mp 106-107°). The infrared spectrum (KBr) was identical to that of the photo-adduct obtained from the photolysis of trans-stilbene in tetramethylethylene.

Irradiation of cis-α-phenylcinnamic acid (LXXVII)

A solution of LXXVII (4.0 g, 0.018 mole) in benzene (350 ml) was placed in a Pyrex immersion irradiation vessel. The solution was degassed with nitrogen for 0.5 hr and irradiated with a Hanovia Type A 550-watt lamp for 21 hr. The progress of the reaction was followed by periodically removing aliquots and measuring their infrared absorption. The carbonyl band of the acid (5.95μ) continually deminished throughout the course of the reaction and was replaced by a band at 5.42μ. At the end of the irradiation the acid carbonyl band was completely removed. The solvent was removed under reduced pressure giving a light yellow solid. The nmr ($CDCl_3$) of the crude photoproduct showed two AB proton patterns $\gamma_A = \delta 5.12$, $\gamma_B = \delta 5.68$ (J_{AB}=7.0 cps); $\gamma_A' = \delta 4.59$, $\gamma_B' = \delta 5.37$; (J_{AB}=4.5 cps) in the ratio of about 3:1 respectively. Recrystallization from benzene-pentane gave *cis*-α,β-diphenyl-β-propiolactone (LXXXIII, 3.10 g, 79%, mp 120-121°). The infrared and nmr spectra are shown in Figure 3, page 32, and Figure 5, page 47, respectively. The mass spectrum exhibited a very weak parent ion m/e 224 and the fragment ions are shown in Table 6.

Table 6. Mass spectrum of *cis*-α,β-diphenyl-β-propiolactone.

m/e	% of base	m/e	% of base
181	2.1	152	4.3
180	16.4	151	2.5
179	12.0	119	8.9
178	7.7	118	100
177	1.4	90	25.4
176	0.8	88	21.2
166	1.9	78	5.0
165	15.7	76	7.8
153	0.9	44	16.5

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 80.34; H, 5.39. Found: C, 80.48; H, 5.39.

Attempted photo-isomerization of cis and trans-α,β-diphenyl-β-propiolactone (LXXXIII):

A mixture of cis and trans-β-lactone obtained from the irradiation of cis-α-phenylcinnamic acid (LXXVII) in the ratio of 31:12 respectively was dissolved in benzene, placed in a Pyrex vessel and irradiated using a Hanovia Type A 550-watt lamp for 24 hr. The solvent was removed under reduced pressure giving a solid. The nmr spectrum ($CDCl_3$) showed the ratio of the β-lactone mixture was unchanged.

Irradiation of trans-α-phenylcinnamic acid (LXXXVIII)

A solution of LXXXVIII (2.0 g, 0.009 mole) in benzene (300 ml) was placed in a Pyrex immersion irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated for 46 hr using a Hanovia Type A 550-watt lamp. The progress of the reaction was followed by removing aliquots and observing the loss of the carbonyl absorption of the acid (5.90μ) and the appearance of the lactone carbonyl (5.42μ) in the infrared. At the end of the irradiation the acid carbonyl band was completely removed. Removal of the solvent under reduced pressure gave a red oil which was dissolved in boiling hexane, filtered and cooled, giving light yellow crystals (0.25 g, 12.5%, 120-121°). No attempt was made to maximize the yield of cis-lactone from the trans-α-phenylcinnamic acid. The infrared (KBr) was identical to that of cis-α,β-diphenyl-β-propiolactone (LXXXIII) obtained from the irradiation of the cis-acid.

Thermal decomposition of <u>cis</u>-α,β-diphenyl-β-propiolactone (LXXXIII)

A. The β-lactone LXXXIII (58.4 mg) was heated at 163° for 5 hr under a positive nitrogen atmosphere, and the evolved carbon dioxide was bubbled through a solution of 0.1 M barium hydroxide. The solution was filtered yielding barium carbonate (51.2 mg, 92%).

B. A benzene solution of LXXXIII was pyrolyzed on an Aerograph Model 512 vapor phase chromatograph using a 7 ft, 1/4" column packed with 20% SE-30 on Chromosorb P, 60-80 mesh. The column temperature was set at 205°, and the helium flow was maintained at 67 cc/min. The β-lactone gave two peaks with retention time of 4.5 and 8.0 min, with areas of 96±1 and 4±1 respectively. The largest peak corresponded to <u>cis</u>-stilbene and the smaller peak to <u>trans</u>-stilbene (determined by injection of the authentic compounds).

C. The reaction was carried out in vertical glass column packed with glass helices and heated by an electrical furnace. The β-lactone (0.1 g) in benzene (2.0 ml) was dropped onto the column from a 5 ml syringe attached to the top and collected in a Dry Ice cooled trap. The temperature of the furnace 280° (measured with a thermocouple). The system was flushed with nitrogen for 1 hr and the material was allowed to drop on the column over a 30 min period, the pressure difference being maintained by a flow of nitrogen.

When the reaction was complete, the column was cooled and the helices were washed with benzene. The solutions were combined and evaporated giving a colorless liquid (60 mg, 76%). The liquid was analyzed by vpc (20% SE-30 on Chromosorb P, column temperature 205, helium flow rate 67 cc/min). The *cis* : *trans*-stilbene isomer ratio was shown to be 99:1.

Irradiation of *cis*-α,β-diphenyl-β-propiolactone (LXXXIII)

A solution of the β-lactone LXXXIII (0.91 g, 0.004 mole) in anhydrous ether (250 ml) was degassed with nitrogen for 0.5 hr. The solution was irradiated in a quartz immersion irradiation vessel using a Hanovia Type A 550-watt lamp for 7 hr. The progress of the reaction was monitored by following the loss of the carbonyl absorption band of the lactone (5.45μ) in the infrared. The solvent was removed under reduced pressure giving a yellow oil. The infrared (CCl_4) showed bands at 3.40 (broad), 6.25, 6.90, 7.30, 9.00 (broad) μ. Analysis by tlc indicated at least 5 compounds were present. The oil was dissolved in a small volume of benzene and chromatographed on a Silica Gel column (25 g), 50 ml fractions being collected.

Eluent	Fraction number	Product composition
Skelly B	1	nil
"	2-4	solid (mp 77-92°)
"	5-8	oil
"	9-13	oil
"	14-16	oil
5% benzene in Skelly B	17-20	oil
"	21-26	oil
"	27-31	oil
50% benzene in Skelly B	32-40	nil

Eluent	Fraction number	Product composition
benzene	41-45	nil
ether	46-50	oil

The appropiate fractions were combined (analyzed by tlc) and the solvent removed under reduced pressure. Fractions 2-4 were recrystallized from 95% ethanol giving a white crystalline solid (0.27 g, 37.6%) mp 98.5-100°, lit (109) mp 98-99°; infrared (KBr) 6.87, 7.00, 7.70, 8.05, 9.78, 10.54, 11.46, 12.22, 13.65, 14.03 μ. The infrared spectrum was identical to that of phenanthrene. A mixture of the crystals with an authentic sample of phenanthrene failed to depress the melting point.

Fractions 14-31 and 46-50 showed bands in the infrared ($CHCl_3$) at 3.50, 5,85, 6.25, 6.70, 7.30, 9.25 μ. Fractions 5-13 were void of carbonyl absorption but gave bands at 6.25, 6.75, 6.92, 9.25 μ. These fractions were not characterized.

Irradiation of cis-α,β-diphenyl-β-propiolactone (LXXXIII) in the presence of tetramethylethylene

A solution of β-lactone LXXXIII (1.0 g, 0.0045 mole), tetramethylethylene (20 g) in ether (20 ml) was placed in a quartz irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated externally using a low pressure mercury lamp (Hanovia, Model 688A45) for 8 days. At the end of the irradiation the lactone carbonyl band in the infrared was completely removed. The solvent was evaporated under reduced pressure affording a yellow solid. The infrared spectrum (KBr) showed bands at 3.40, 6.23, 6.65, 6.90, 7.30, 9.73, 12.60, 13.40, 13.60, 14.27 μ. The solid was dissolved in a minimum volume of 1:1 Skelly B-benzene and chromatographed on a Silica Gel column (25 g), 100 ml fractions being collected.

Eluent	Fraction number	Product composition
Skelly B	1-2	nil
"	3	solid (mp 105-106°)
"	4	solid (mp 105-106°)
"	5-7	nil
10% benzene in Skelly B	8-11	nil
30% benzene in Skelly B	12-16	oil
benzene	17-21	oil
benzene	22-26	nil

Fractions 3 and 4 were combined and recrystallized from hexane giving trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 1.00 g, 85% mp 106-107°). The infrared spectrum (KBr) was superimposable on that of the photo-adduct obtained from the photolysis of trans-stilbene in the presence of tetramethylethylene.

The remaining fractions (total weight 0.17 g) were not characterized.

Reaction of trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) with bromine

A solution of LXXVIII (1.0 g, 0.0038 mole) and bromine (2.3 g, 0.0145 mole) in carbon tetrachloride (25 ml) was irradiated with a sun lamp for 4 hr. The solution was washed successively with a 20% aqueous solution of sodium thiosulfate and water. The organic layer was separated and concentrated under reduced pressure to give an oil. Crystallization from ethyl acetate gave 1,2-(di-*p*-bromophenyl)-3,3,4,4-tetramethylcyclobutene (LXXX, 0.5 g, [illegible]2%, mp 103-104°); infrared (KBr), 3.40, 6.75, 9.37, 9.52, 9.57, 11.97, 12.07, 12.25, 12.82μ; nmr (CCl_4) eight-proton A_2B_2 pattern, $\gamma_A = \delta\ 7.14$, $\gamma_B = \delta\ 7.39$, (J_{AB}= 8.5 cps), twelve-proton singlet δ 1.26 (methyl protons); λ max (95% ethanol) 289 mμ (ϵ 10,000), 240 (15,600). The mass spectrum exhibited an intense parent ion (m/e 418, 20% of base), and a P + 2 radical cation (m/e 420, 206% of parent ion).

Anal. Calcd. for $C_{20}H_{20}Br_2$: C, 57.41; H, 4.79; Br, 37.80. Found: C, 57.54; H, 4.89; Br, 37.86.

Reaction of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) with N-bromosuccinimide

The *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (1.4 g, 0.005 mole), N-bromosuccinimide (1.5 g, 0.008 mole) and benzoyl peroxide (0.1 g) were mixed in carbon tetrachloride (100 ml). The heterogeneous solution was irradiated with a sun lamp for 4 hr. The succinimide was filtered, and the filtrate was washed successively with sodium bicarbonate and sodium thiosulfate. The organic layer was dried over anhydrous magnesium sulfate, and the residue obtained upon evaporation of the solvent was crystallized from methanol giving 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXXIX, 1.1 g, 80%, mp 92-93°). The infrared and nmr spectra are shown Figure 1, page 23 and Figure 2, page 25, respectively. The mass spectrum showed an intense parent ion at m/e 262, (100% of base).

The ultraviolet spectrum gave λ max (95% ethanol), 278 mμ, (ε 6,300), 225 (10,000).

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.54; H, 8.36.

Irradiation of diphenylacetylene in the presence of tetramethylethylene

A solution of diphenylactylene (2.0 g, 0.011 mole), tetramethylethylene (5.0 g, 0.059 mole) in ether (100 ml) was degassed with nitrogen for 0.5 hr. The solution was irradiated in a quartz vessel using a Rayonet (Model RPR-100) reactor equipped with 3000 Å lamps. The progress of the reaction was followed by tlc until no change was observed upon further irradiation. After 13 hr the solution was concentrated under reduced pressure to give a light yellow oily residue. The nmr showed an aromatic multiplet at δ 7.60-7.00 and 5 singlets at δ 3.55, 1.50, 1.30, 1.10, and 0.80. The residue was dissolved in Skelly B, Alumina (Woelm, activity I, 4.0 g) was added and the solvent was removed under reduced pressure. The absorbed residue was placed on a 2.5" X 20" column, prepared with Alumina (Woelm, activity I, 150 g) and chromatographed, 100 ml fractions being collected.

Eluent	Fraction number	Product composition
Skelly B	1	nil
"	2-6	solid (mp 93-95°)
"	7-9	solid (mp 61-73°)
"	10-17	solid (mp 62-64°)
"	18	oil
10% benzene in Skelly B	19	oil

Fractions 2-6 were combined and recrystallized from methanol giving colorless crystals (0.7 g, mp 92-93°). Fractions 7-9 were a mixture of the photo-adduct and diphenylacetylene. Fractional recrystallization from methanol yielded crystals (0.1 g, mp 92-93°). These solid fractions were combined to give 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX, 0.8 g, 30%). The infrared spectrum (KBr) was superimposable on that of the authentic olefin. A mixed melting point determination gave no depression.

Fractions 10-17 were recrystallized from methanol-water to give diphenylacetylene (1.0 g). Fractions 18 and 19 were a mixture of three compounds (total weight 0.2 g) and were not characterized.

Reduction of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX)

This used procedure is similar to that of W. S. Johnson (110). 1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene (460 mg, 0.0017 mole) was dissolved in ether (20 ml) and liquid ammonia was added until the total volume was 100 ml. While the homogeneous solution was stirred, potassium (600 mg, 0.015 mole) was added over a 5 min period. The mixture was stirred for 20 min, then absolute ethanol (10 ml) in ether (7 ml) was added dropwise over another 20 min period. As soon as the blue color disappeared, the ammonia was evaporated, benzene and ice water were added, and the aqueous layer was extracted with benzene. The organic layers were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a solid (460 mg) which was crystallized from hexane to give *trans*- 1, 2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII, 440 mg, 95%, mp 105-106°). The infrared spectrum (KBr) was identical to that of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII) obtained from the photoaddition of *cis*-α-phenylcinnamic acid to tetramethylethylene. A mixed melting point determination gave no depression.

Erythro-3-bromo-2,3-diphenylpropanoic acid (LXXXIX)

Erythro-3-bromo-2,3-diphenylpropanoic acid was prepared following the procedure of Hagman (111). A solution of *cis*-α-phenylcinnamic acid (LXXVII, 10.0 g, 0.045 mole) in acetic acid was saturated with gaseous hydrogen bromide and allowed to stand for 7 days at room temperature. The heterogeneous solution was poured into cold water and extracted with chloroform. The organic layer was washed several times with water, dried over magnesium sulfate and concentrated under reduced pressure giving a solid (13.1 g). The solid was decolorized with charcoal and crystallized from acetone-water yielding LXXXIX (10.4 g, 73%, mp 201-202°); infrared (KBr) 2.80-3.90 (broad), 5.90, 6.25, 6.68, 6.88, 7.05, 7.85, 8.53, 9.34, 13.10, 13.75, 14.50 μ.

Anal. Calcd. for $C_{15}H_{13}BrO_2$: C, 59.00; H, 4.27; Br, 26.21. Found: C, 58.89; H, 4.28; Br, 26.26.

trans-α,β-Diphenyl-β-propiolactone (XC)

A solution of erythro-3-bromo-2,3-diphenylpropanoic acid

(LXXXIX, 1.0 g, 0.0033 mole), sodium carbonate (0.31 g, 0.003 mole) in water (20 ml) and chloroform (20 ml) was stirred for 2 hr at 0°. The solution was maintained at pH 8-9 throughout the course of the reaction by adding additional sodium carbonate. The organic layer was separated, washed successively with sodium bicarbonate solution and water, dried over magnesium sulfate and concentrated under reduced pressure affording a colorless solid (0.54 g). The nmr and infrared spectra showed the product to be a mixture of *trans*-stilbene and a small quantity of a β-lactone. Two successive recrystallizations from benzene-pentane gave *trans*-stilbene (0.32 g). The filtrate was concentrated under reduced pressure giving a solid (0.22 g). The infrared gave absorption bands at 5.46, 6.27, 6.70, 6.90, 9.36, 10.41, 13.10, 14.50μ. The nmr ($CDCl_3$) exhibited an aromatic multiplet at δ7.55-7.10, vinyl proton singlet (*trans*-stilbene) δ 7.05, an AB proton pattern γ_A=δ4.62, γ_B=δ5.39, (J_{AB}=4.5 cps). The β-lactone, *trans*-stilbene ratio was 3:7 respectively.

Irradiation of *cis*-α-(*p*-tolyl)-cinnamic acid (XCIII b)

A solution of XCIII b (2.0 g, 0.0084 mole) in benzene (250 ml) was placed in a Pyrex immersion irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated for 23.5 hr using a Hanovia Type A 550-watt lamp. The progress of the reaction was monitored by observing the loss of the carbonyl function of the acid (5.95μ) and the appearance of the β-lactone carbonyl band (5.45μ) in the infrared spectrum.

At the end of the irradiation the acid carbonyl band was completely removed. The solvent was removed under reduced pressure giving a yellow solid (2.0 g). The nmr ($CDCl_3$) of the crude material shows $\nu_A = \delta\ 5.03$, $\nu_B = \delta\ 5.60$, (J_{AB}=7.0 cps); $\nu_A' = \delta 4.50$, $\nu_B' = \delta\ 5.30$ (J_{AB}= 4.5 cps) in the ratio of 8:7 respectively. The solid was dissolved in benzene, decolorized with norite and concentrated under reduced pressure. Recrystallization from benzene-pentane gave cis-α-p-tolyl-β-phenyl-β-propiolactone (XCIV b, 0.4 g, 20%, mp 111-112.5°). The infrared spectrum (KBr) gave 5.47, 6.60, 6.90, 8.04, 8.95, 10.48, 10.58, 11.20, 12.05, 13.25, 13.85, 14.35 μ ; nmr ($CDCl_3$) five proton singlet δ 7.13, four proton singlet δ 6.87, AB proton pattern $\nu_A = \delta\ 5.25$, $\nu_B = \delta\ 5.83$, (J_{AB}=7.0 cps), three proton singlet δ 2.15. The mass spectrum exhibited a very weak parent ion at m/e 238 and the fragment ions are shown in Table 7.

Table 7. Mass spectrum of cis-α-(p-tolyl)-β-phenyl-β-propiolactone (XCIV b)

m/e	% of base	m/e	% of base
43	2.0	178	1.9
103	1.9	179	24.6
132	100	194	38.4
133	0.9		

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.65; H, 5.99.

Irradiation of cis-α-phenyl-p-methylcinnamic acid (XCIII b)

A solution of XCIII c (2.0 g, 0.0084 mole) in benzene (250 ml) was irradiated in a manner analogous to the procedure described above. After 28.5 hr the acid absorption in the infrared spectrum was about 5% of its original value. The solvent was removed under reduced pressure giving a solid (2.0 g). The nmr of the crude product showed two AB proton patterns $\nu_A = \delta$ 5.05, $\nu_B = \delta$ 5.62 (J_{AB}=7.0 cps); $\nu_A' = \delta$ 4.53, $\nu_B' = \delta$ 5.34 (J_{AB}=4.5 cps) in the ratio of 3:1 respectively. Recrystallization from benzene-pentane gave cis-α-phenyl-β-(p-tolyl)-β-propiolactone (XCIV c, 0.41 g, 21%, mp 98-99°). The infrared spectrum (KBr) gave absorption bands at 5.50, 6.66, 6.89, 7.94, 8.82, 8.92, 10.46, 11.66, 12.25, 12.45, 12.60, 13.50, 14.37 μ; nmr ($CDCl_3$) nine proton multiplet centered at δ 7.15, AB proton pattern $\nu_A = \delta$ 5.29, $\nu_B = \delta$ 5.84 (J_{AB}=7.0 cps), three proton singlet δ 2.19. The mass spectrum shows a very weak parent ion at m/e 238 (0.7%) and the fragment ions are shown in Table 8.

Table 8. Mass spectrum of cis-α-phenyl-β-(p-tolyl)-β-propiolactone (XCIV c)

m/e	% of base	m/e	% of base
44	30.3	179	57.6
88	13.0	193	18.0
95	11.1	194	100
118	40.6	195	15.6
178	39.6		

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.88. Found: C, 80.60, H, 5.97.

Irradiation of *cis*-α-phenyl-*p*-chlorocinnamic acid (XCIII d)

A solution of XCIII d (2.0 g, 0.0078 mole) in benzene (250 ml) was irradiated as described above for 26 hr. The acid carbonyl absorption (5.95 μ) was completely removed in the infrared spectrum. The solvent was removed under reduced pressure giving a semi-solid. The nmr ($CDCl_3$) of the crude product showed $\gamma_A = \delta\, 5.16$, $\gamma_B = \delta\, 5.69$ (J_{AB}=7.0 cps); $\gamma_A' = \delta\, 4.59$, $\gamma_B' = \delta\, 5.33$ (J_{AB}=4.5 cps) in the ratio of 5:6 respectively. Recrystallization from benzene-pentane gave *cis*-α-phenyl-β-(*p*-chlorophenyl)-β-propiolactone (XCIV d, 0.30 g, 15%, mp 103-104°). The infrared spectrum (KBr) gave absorption bands at 5.50, 6.70, 8.07, 8.67, 8.90, 9.20, 10.53, 11.17, 12.07, 12.26, 13.20, 14.02, 14.34μ ; nmr ($CDCl_3$) nine proton multiplet centered at $\delta\, 7.05$, AB proton pattern $\gamma_A = \delta\, 5.32$, $\gamma_B = \delta\, 5.86$ (J_{AB}= 7.0 cps). The mass spectrum exhibited a weak parent ion (m/e 258, 0.09% of base) and the fragment ions are shown in Table 9.

Table 9. Mass spectrum of *cis*-α-phenyl-β-(*p*-chlorophenyl)-β-propiolactone (XCIIId)

m/e	% of base	m/e	% of base
44	18.7	118	100
76	10.9	119	8.2
88	16.9	178	2.3
90	17.1	179	2.2

Anal. Calcd. for $C_{15}H_{11}ClO_2$: C, 69.77; H, 4.26; Cl, 13.52. Found: C, 69.82; H, 4.34; Cl, 13.38.

The filtrate was concentrated under reduced pressure and poured onto a 1.0" X 20" column prepared with 50 g of Silica Gel. The column was eluted with benzene (250 ml) which upon evaporation gave *trans*-*p*-chlorostilbene (0.3 g, 18%, mp 129-130°, lit. (112) mp 129°).

Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.50; H, 5.15; Cl, 16.40. Found: C, 78.31; H, 5.13; Cl, 16.38.

Irradiation of *cis*-α-(*p*-chlorophenyl)-cinnamic acid (XCII e)

A solution of XCIII e (2.0 g, 0.0078 mole) in benzene was irradiated as described above for 76 hr. The solvent was removed under reduced pressure giving an oil (2.0 g). The infrared spectrum ($CHCl_3$) showed bands at 2.80-3.75 (broad) 5.46, 5.80, 5.90, 6.25, 6.70, 8.50-9.50 (broad) 9.86, 10.40 μ. The nmr exhibited two AB proton patterns $\gamma_A = \delta\, 5.09$, $\gamma_B = \delta\, 5.67$ (J_{AB}=7.0 cps); $\gamma_A' = \delta\, 4.55$, $\gamma_B' = \delta\, 5.35$ (J_{AB}=4.5 cps) in the ratio of 9:5 respectively. Attempted crystallization from pentane, hexane, and benzene and mixtures thereof was futile.

Irradiation of *cis*-α-(*p*-fluorophenyl)-cinnamic acid (XCIII f)

A solution of XCIII f (2.0 g, 0.0083 mole) in benzene (250 ml) was irradiated for 41 hr using the method described above. The solvent was evaporated under reduced pressure giving a semi-solid (1.97 g). The infrared spectrum ($CHCl_3$) showed bands at 2.75-3.75 (broad) 5.45, 5.86, 6.25, 6.65, 6.90, 8.65, 8.95, 10.41, 11.22 μ. The nmr ($CDCl_3$) showed two AB proton patterns $\gamma_A = \delta\, 5.15$, $\gamma_B = \delta\, 5.72$ (J_{AB}=7.0 cps); $\gamma_A' = \delta\, 4.60$, $\gamma_B' = \delta\, 5.35$ (J_{AB}=4.5 cps) in the ratio of 1:1. Attempted crystallization from pentane-benzene or benzene was not successful.

Irradiation of *cis*-α-(*p*-cyanophenyl)-cinnamic acid (XCIII g)

A solution of XCIII g (2.0 g, 0.0080 mole) in benzene (250 ml) was irradiated using the procedure described above for 72 hr. The solvent was removed under reduced pressure giving a light, yellow oil. The infrared spectrum (cap film) showed bands at 2.80-3.70 (broad), 4.47, 5.45, 5.85 (broad), 6.21, 6.62, 6.87, 7.05, 8.00-9.00 (broad), 10.47, 12.00, 13.25, 14.30 μ. The nmr spectrum ($CDCl_3$) exhibited a single AB proton pattern $\gamma_A = \delta\, 5.37$, $\gamma_B = \delta\, 5.89$ (J_{AB}=7.0 cps). Attempts to crystallize the oily mixture failed.

Irradiation of *cis*-α-phenyl-*p*-cyanocinnamic acid (XCIII h)

A solution of XCIII h (2.0 g, 0.0080 mole) in benzene (250 ml) was irradiated for 5 hr. The solvent was removed under reduced pressure yielding a light, yellow oil (2.0 g). The infrared spectrum (cap film) showed bands at 4.50, 5.45, 9.05, 10.50, 11.15, 12.06, 13.25, 14.32 μ. The nmr spectrum ($CDCl_3$) exhibited two AB proton patterns $\gamma_A = \delta\, 5.37$, $\gamma_B = \delta\, 5.87$ (J_{AB}= 7.0 cps); $\gamma_A' = \delta\, 4.66$, $\gamma_B' = \delta\, 5.50$ (J_{AB}=4.5 cps) in the ratio of 3:2 respectively. All attempts to crystallize the oil failed.

Irradiation of cis-α-(p-nitrophenyl)-cinnamic acid (XCIII i)

A solution of XCIII i (2.0 g, 0.0074 mole) in benzene (250 ml) was irradiated for 94 hr using the procedure described above. Only a very small β-lactone absorption was observed in the infrared spectrum during the irradiation. The solvent was evaporated under reduced pressure giving a brown solid (2.0 g, mp 212-218°). The infrared spectrum (KBr) showed bands at 2.75-4.00 (broad), 6.00, 6.27, 6.60, 7.04, 7.45, 7.92, 13.35, 14.03, 14.45 μ. Recrystallization from ethanol gave cis-α-(p-nitrophenyl)-cinnamic acid (XCIII i), 1.4 g, mp 216-217°.

Irradiation of cis-α-phenyl-p-nitrocinnamic acid (XCIII j)

A solution of XCIII j (2.0 g, 0.0074 mole) in benzene (250 ml) was irradiated for 36 hr using the procedure described above. At the end of this period the β-lactone and acid carbonyl absorptions were approximately equal in the infrared spectrum. The solvent was removed under reduced pressure giving a dark brown-red oil (1.96 g). The infrared spectrum (cap film) showed bands at 2.75-3.75 (broad) 5.45, 5.93, 6.26, 6.60, 7.45, 9.05, 10.52, 11.13, 11.75, 13.30, 14.35 μ. The nmr spectrum ($CDCl_3$) exhibited two AB proton patterns $\gamma_A = \delta\, 5.35$, $\gamma_B = \delta\, 5.88$ (J_{AB}=7.0 cps); $\gamma_A' = \delta\, 4.69$, $\gamma_B' = \delta\, 5.52$ (J_{AB}=4.5 cps) in the ratio of 1:1. Crystallization from benzene-hexane gave a mixture of cis and trans-α-phenyl-p-nitrocinnamic acid (XCIII j, 200 mg, mp 209-211°). The infrared spectrum (KBr) showed bands at 2.75-4.25 (broad) 5.96, 6.18, 6.27, 6.57, 7.07, 7.40, 8.95, 11.73, 14.07, 14.67 μ.

Irradiation of *cis*-α-phenyl-*p*-methoxycinnamic acid (XCIII k)

A solution of XCIII k (2.0 g, 0.0078 mole) in benzene (250 ml) was irradiated for 96 hr. No lactone band was observed in the infrared spectrum throughout the course of the irradiation. The solvent was removed under reduced pressure giving a yellow solid (2.0 g, mp 164-176°); infrared (KBr) 2.75-4.25, 6.20, 6.45, 6.82, 7.25, 8.20, 8.72, 10.00, 12.25, 13.03, 14.50 μ. The nmr ($CDCl_3$) showed the photoproduct to be a mixture of *cis* and *trans*-α-phenyl-*p*-methoxyphenylcinnamic acid; *cis*: δ 7.90 (1H,s), δ 7.40-7.20 (5H,m), A_2B_2 proton pattern $\nu_A = \delta\, 6.65$, $\nu_B = \delta\, 7.00$ (J_{AB}=9.0 cps), δ 3.77 (3H,s); *trans*: δ 7.50-6.80 (10H,m), δ 3.70 (3H,s). The ultraviolet spectrum (95% ethanol) showed absorption bands at 312 and 222 mμ.

Recrystallization from ethanol-water gave a mixture of *cis* and *trans*-α-phenyl-p-methoxycinnamic acid (1.9 g, mp 183-187°).

Irradiation of *cis*-α-(*p*-methoxyphenyl)-cinnamic acid (XCIII l)

A solution of XCIII l (2.0 g, 0.0074 mole) in benzene (250 ml) was irradiated for 10.5 hr using the procedure described above. The solvent was removed under reduced pressure giving a yellow semi-solid (1.96 g). The infrared spectrum ($CHCl_3$) showed bands at 5.46, 6.20, 9.00, 10.50 μ. The nmr ($CDCl_3$) showed two AB proton patterns $\nu_A = \delta\, 5.05$, $\nu_B = \delta\, 5.62$

(J_{AB}=7.0 cps), $\gamma_A' = \delta\, 4.51$, $\gamma_B' = \delta\, 5.28$ (J_{AB}=4.5 cps) in the ratio of 1:1. Crystallization from acetonitrile gave *trans*-*p*-methoxystilbene (0.2 g, 12.8%, mp 134-135°, lit. (113), mp 136-137°); infrared (KBr) 6.25, 6.63, 8.05, 8.51, 9.74, 10.37, 12.10, 12.35, 13.37, 14.57 µ. The mass spectrum exhibited a strong parent ion at m/e 210, 100% of base.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.88; H, 6.75.

Irradiation of *trans*-cinnamic acid

A solution of *trans*-cinnamic acid (1.0 g, 0.0068 mole) in benzene (250 ml) was placed in a Pyrex immersion irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated with a Hanovia Type A 550-watt lamp for 56 hr. The progress of the reaction was monitored in the infrared spectrum and no band ascribable to a β-lactone was observed. The solvent was removed under reduced pressure giving a yellow solid (1.0 g). Recrystallization from benzene-pentane gave a mixture of *cis* and *trans*-cinnamic acid (0.96 g, mp 110-130°). The nmr ($CDCl_3$) exhibited two AB proton patterns; *trans*: $\gamma_A = \delta\, 6.37$, $\gamma_B = \delta\, 7.73$ (J_{AB}=16.0 cps), *cis*: $\gamma_A = \delta\, 5.90$, $\gamma_B = \delta\, 6.93$ (J_{AB}= 13.0 cps).

Irradiation of α-phenylcrotonic acid (XCV c)

A solution of XCV c (2.0 g, 0.0123 mole) in ether (250 ml) was placed in a quartz immersion irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated with a Hanovia Type A 550-watt lamp for 4 hr. The reaction was followed in the infrared spectrum and after 4 hr the β-lactone band (5.50 μ) was one-third that of the acid carbonyl absorption (5.85 μ). Longer irradiation periods destroyed the β-lactone. The solvent was removed under reduced pressure giving a yellow oil (2.0 g). The residue was dissolved in ether and extracted twice with an ice-cold sodium bicarbonate solution. The ethereal solution was washed with water, dried over magnesium sulfate and evaporated under reduced pressure giving an oil (1.0 g). The infrared (cap film) showed absorption bands at 2.75-3.50 (broad), 5.47, 5.66, 5.80-5.85 (broad), 6.25, 6.68, 6.87, 7.21, 8.90, 9.78, 12.04, 12.70, 13.20, 14.30μ. The nmr ($CDCl_3$) showed an aromatic multiplet δ 7.50-6.80, methine proton multiplet δ 5.00-4.20, methine proton doublet δ 4.30, (J=4.0 cps), methyl proton doublet δ 1.10 (J=6.0 cps). All attempts to crystallize the oil were futile.

Irradiation of α-methylcinnamic acid (XCV b)

A solution of XCV b (3.0 g, 0.0185 mole) in benzene (250 ml) was placed in a Pyrex immersion irradiation apparatus and degassed with nitrogen for 0.5 hr. The solution was irradiated using a Hanovia Type A 550-watt lamp for 16 days. The progress of the reaction was followed in the infrared spectrum until no further change in the intensity of the carbonyl bands of the acid and the β-lactone took place. At the end of the irradiation the intensity of the lactone carbonyl band was approximately one-half that of the carbonyl band of the acid. The solvent was removed under reduced pressure giving a light, yellow oil (2.9 g). The infrared spectrum (cap film) showed absorption bands at 2.45-4.00 (broad), 5.45, 5.95, 6.15, 6.70, 6.75, 6.90, 7.07, 7.90, 8.30, 8.87, 10.65, 13.10, 13.55, 14.35, 14.75 μ. The oil was dissolved in ether and extracted several times with cold sodium bicarbonate solution. The organic was washed with water, dried over magnesium sulfate and concentrated under reduced pressure giving a light, yellow oil (0.44 g). The infrared spectrum (cap film) gave a strong absorption band at 5.45 μ and less intense bands at 5.62 and 5.80 μ. The nmr ($CDCl_3$) showed an aromatic multiplet at δ 7.50-7.00, methine proton doublet δ 5.55 (J=6.5 cps), methine proton multiplet δ 4.18-3.30, methyl proton doublet δ 0.85 (J=8.0 cps). All attempts to crystallize the oil failed.

Irradiation of α-phenylacrylic acid (XCV e)

A solution of XCV e (1.0 g, 0.0067 mole) in ether (250 ml) was placed in a quartz irradiation vessel, degassed with nitrogen for 0.5 hr and irradiated using a Hanovia Type A 550-watt lamp for 12 hr. During the course of the irradiation a weak absorption band (5.47 μ) attributable to a β-lactone was observed in the infrared spectrum. The solvent was removed under reduced pressure giving a yellow oil (1.50 g). The nmr ($CDCl_3$) showed the mixture to be mainly a polymer with broad multiplets at δ 7.50-6.80, δ 4.00-3.00, and δ 1.50-0.70. The oil was dissolved in ether and extracted seven times with ice-cold solution of sodium bicarbonate. The ethereal solution was washed with water, dried over magnesium sulfate and concentrated under reduced pressure giving an oil (0.3 g). The infrared spectrum (cap film) gave absorption bands at 2.90-3.50 (broad), 5.45, 5.61, 5.80, 6.25, 6.68, 6.90, 7.30, 9.10 (broad), 13.20, 14.28 μ. The *nmr* was not very descriptive due to the presence of the polymer. Attempted crystallization from several aprotic solvents was futile.

Irradiation of crotonic acid

A solution of crotonic acid (2.0 g, 0.0125 mole) in ether (250 ml) was placed in a quartz immersion irradiation vessel and degassed with nitrogen for 0.5 hr. The solution was irradiated with a Hanovia Type A 550-watt lamp for 48 hr. The infrared spectrum failed to reveal an absorption band attributable to a β-lactone. The solvent was removed under reduced pressure yielding a light, yellow oil (2.2 g). The infrared spectrum (cap film) gave absorption bands at 2.75-4.00 (broad), 5.65 (broad), 6.10, 7.10, 7.75, 8.15, 9.10, 10.75 μ. The nmr spectrum ($CDCl_3$) revealed a mixture of cis and trans-crotonic acid and 3-butenoic acid (67); trans-crotonic acid: δ 7.30-6.90 (1H,m), δ 6.10-5.60 (1H,m), δ 2.00-1.80 (3H,q); cis-crotonic acid: δ 7.30-6.90 (1H,m), δ 6.10-5.60 (1H,m), δ 2.20-2.00 (3H, q); 3-butenoic acid: δ 5.90-5.60 (1H,m), δ 5.40-4.90 (2H,m), δ 3.25-3.00 (2H,m).

Irradiation of α, β-diphenylcinnamic acid (XCV d)

A solution of XCV d (1.0 g, 0.0033 mole) in benzene

(250 ml) was degassed with nitrogen for 0.5 hr. The solution was irradiated in a Pyrex immersion irradiation vessel using a Hanovia Type A 550-watt lamp. After 12 hr the infrared spectrum showed an intense β-lactone band (5.45μ) and a weak acid carbonyl band (5.90μ). The solvent was removed under reduced pressure giving a semi-solid (0.95 g). The nmr ($CDCl_3$) showed an aromatic multiplet at δ 7.50-6.90, and a methine proton singlet at δ 5.43. The residue was dissolved in benzene-pentane and cooled giving α,β-diphenylcinnamic acid (0.28 g). The filtrate was concentrated under reduced pressure yielding a yellow oil. The infrared and nmr spectra confirmed the presence of the β-lactone and also an increased amount of triphenylethylene. Crystallization of the oil from hexane gave triphenylethylene (0.16 g, mp 67-68°). The infrared spectrum (KBr) was superimposable in that of the authentic olefin. Further attempts to crystallize the residue failed.

Irradiation of β-phenylcinnamic acid

A solution of β-phenylcinnamic acid (2.0 g, 0.0089 mole) in benzene (250 ml) was placed in a Pyrex immersion irradiation vessel and purged with nitrogen for 0.5 hr. The solution was irradiated with a Hanovia Type A 550-watt lamp for 39 hr. The irradiation was monitored in the infrared spectrum and no change was observed. The solvent was removed under reduced pressure giving a yellow solid. Recrystallization from acetic acid gave β-phenylcinnamic acid (1.7 g, 85%).

Irradiation of biphenyleneacrylic acid

A solution of biphenyleneacrylic acid (2.0 g, 0.00. mole) in benzene (250 ml) was placed in a Pyrex immersion irradiation vessel and purged with nitrogen for 0.5 hr. The solution was irradiation with a Hanovia Type A 550-watt lamp for 40 hr. The infrared spectrum gave no evidence for the formation of a β-lactone. The solvent was removed under reduced pressure giving a yellow solid. Recrystallization from acetic acid gave biphenyleneacrylic acid (1.8 g, 90%).

Irradiation of cis-α-phenylcinnamamide (CIII)

A solution of CIII (4.0 g, 0.018 mole) in benzene (450 ml) was placed in a Pyrex immersion irradiation vessel and irradiated with a Hanovia Type A 550-watt lamp while being continuously degassed with purified nitrogen. The reaction was monitored by observing the change in the infrared spectrum during the irradiation. After 60 hr, bands at 5.68 μ and 5.96 μ failed to change on further irradiation. Total irradiation time was 70 hr. The solvent was removed under reduced pressure giving a yellow oil. Analysis by nmr and tlc of the crude photolysate showed at least 3 photoproducts were present. The oil was dissolved in a small volume of benzene and chromatographed on a Silica Gel column (300 g), 300 ml fractions being collected.

Eluent			Fraction number	Product composition
Benzene			1	nil
"			2-3	solid (mp 116-123°)
"			4-8	nil
5%	chloroform	in benzene	9-11	nil
10%	"	"	12-15	nil
20%	"	"	16-18	nil
30%	"	"	19-21	nil
40%	"	"	22-24	nil
50%	"	"	25	nil
50%	"	"	26	solid (mp 124-125°)
50%	"	"	27	solid (mp 112-122°)
50%	"	"	28	solid (mp 161-165°)
50%	"	"	29	solid (mp 155-170°)
60%	"	"	30	solid (mp 144-150°)
60%	"	"	31	solid (mp 118-127°)
60%	"	"	32	solid (mp 117-127°)
60%	"	"	33	solid (mp 120-126°)
60%	"	"	34	solid (mp 124-127°)
60%	"	"	35	solid (mp 124-127°)
60%	"	"	36	solid (mp 124-127°)

The nmr and tlc analysis showed all fractions to be a mixture of two or more compounds. Recrystallization of fractions 2 and 3 from hexane gave trans-stilbene (80 mg, 2.5%, mp 124-125°). The compound was identified by comparison with the infrared spectrum of an authentic sample of trans-stilbene.

Fraction 26 was recrystallized from benzene-pentane four times giving trans-3,4-diphenyl-2-azetidinone (CV, 110 mg, 3% mp 124-125°). The infrared and nmr spectra are shown in Figure 7, page 53, and Figure 8, page 55, respectively. The mass spectrum is shown in Table 10.

Table 10. Mass spectrum of trans-3,4-diphenyl-2-azetidinone(CV)

m/e	% of base	m/e	% of base
88	34.4	178	20.7
90	40.0	179	39.0
106	16.1	180	100
118	69.0	181	18.0
165	19.8	223	10.7

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28. Found: C, 80.82, H, 5.84; N, 6.27.

Repeated recrystallization of fraction 30 from benzene-pentane afforded an analytical sample of cis-3,4-diphenyl-2-azetidinone (CIV, 500 mg, 13%, mp 154-155°). All the yields are bases on unrecovered starting material. The infrared and nmr spectra are shown in Figure 7, page 53, and Figure 8, page 55, respectively. The mass spectrum is shown in Table 11.

Table 11. Mass spectrum of cis-3,4-diphenyl-2-azetidinone (CIV)

m/e	% of base	m/e	% of base
43	43.0	119	8.0
58	15.1	165	6.8
88	18.1	178	7.9
90	30.4	179	13.3
106	18.2	180	24.8
118	100	223	38.2

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28.

Found: C, 80.91; H, 5.89; N, 6.22.

Repeated recrystallization of fraction 28 from benzene-pentane gave colorless crystals (0.25 g, 6.2%, mp 164-165°). The product was very difficult to obtain in the pure state and sublimation at 140° gave an analytical sample. The infrared spectrum (KBr) 2.90 (broad), 5.96, 6.12, 6.26, 6.70, 7.23, 7.90, 13.20, 14.35 μ; nmr ($CDCl_3$) one proton multiplet centered at δ 9.15, an aromatic proton multiplet centered at δ 7.20 and an A_2B proton pattern $\gamma_A = \delta\, 3.18$, $\gamma_B = \delta\, 3.80$ (J=8.2 cps). The mass spectrum is shown in Table 12. The structure of the compound is tentatively assigned as 3-phenylhydrocarbostyril (CVI).

Table 12. Mass spectrum of 3-phenylhydrocarbostyril(CVI)

m/e	% of base	m/e	% of base
90	32.2	178	18.6
106	32.2	194	29.3
118	30.0	223	100
131	15.2		

<u>Anal</u>. Calcd. for $C_{15}H_{13}NO$: C, 80.72; H, 5.83; N, 6.28.
Found: C, 80.55; H, 5.89; N, 6.27.

Fractions 31-35 were combined and recrystallized from acetone-water giving cis-α-phenylcinnamamide (CIII, 1.10 g, mp 127-128°).

Irradiation of cis-α-phenylcinnamanilide (XCVI)

A solution of XCVI (3.0 g, 0.01 mole) in benzene (300 ml) was placed in a Pyrex immersion irradiation vessel and degassed with nitrogen for 1 hr. The solution was irradiated using a Hanovia Type A 550-watt lamp for 23 hr. The progress of the reaction was monitored by infrared analysis until no further change was observed. The amide absorption band (5.98μ) gradually diminished and was replaced by an intense band at 5.73μ. The solvent was evaporated under reduced pressure giving a solid (3.0 g). The nmr exhibited two overlapping AB proton patterns; $\nu_A = \delta\,4.25$, $\nu_B = \delta\,4.94$ (J_{AB}=3.0 cps), and $\nu_A' \doteq \delta\,4.96$, $\nu_B' = \delta\,5.44$ (J_{AB}=7.0 cps). The solid was dissolved in a small volume of benzene and chromatographed on a Silica Gel column (150 g), 250 ml fractions being collected.

Eluent	Fraction number	Product composition
Benzene	1-3	nil
"	4	solid (mp 110-143°)
"	5	solid (mp 116-156°)
"	6	solid (mp 118-163°)
"	7	solid (mp 119-174°)
"	8	solid (mp 162-180°)
"	9-13	nil
10% chloroform in benzene	14-18	nil
20% " "	19-23	nil
30% " "	24-27	nil
40% " "	27-29	solid (mp 219-220°)
50% " "	29-31	nil

Analysis of Fractions 4-8 by nmr and tlc revealed a mixture of two products. These fractions were combined and fractionally recrystallized from benzene-pentane giving <u>cis</u>-1,3,4-triphenyl-2-azetidinone (XCVII, 1.1 g, 37%, mp 182-183°). The infrared and nmr spectra are shown in Figure 6, page 49, and Figure 5, page 47, respectively. The mass spectrum is shown in Table 13.

Table 13. Mass spectrum of cis-1,3,4-triphenyl-2-azetidinone (XCVII)

m/e	% of base	m/e	% of base
165	8.4	181	100
178	14.0	182	18.6
179	24.4	299	30.0
180	86.0		

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.35; H, 5.71; N, 4.74.

The filtrate was concentrated under reduced pressure giving a solid (0.9 g). The fourth recrystallization from isopropyl alcohol gave trans-1,3,4-triphenyl-2-azetidinone (XCVIII, 700 mg, 2.3%, mp 127-128°). The infrared and nmr spectra are shown in Figure 6, page 49, and Figure 5, page 47, respectively. The mass spectrum is shown in Table 14.

Table 14. Mass spectrum of trans-1,3,4-triphenyl-2-azetidinone (XCVIII)

m/e	% of base	m/e	% of base
165	7.8	180	100
178	13.1	181	33.8
179	22.8	299	9.8

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.42; H, 5.70; N, 4.66.

Recrystallization of Fractions 27-29 from benzene-pentane gave colorless crystals (0.15 g, 5.0%, mp 219-220°); infrared spectrum (KBr) 2.87 (broad), 5.98, 6.28, 6.72, 6.89, 7.32, 13.10, 13.65, 14.28 μ; nmr ($CDCl_3$) one proton singlet at δ 9.35, an aromatic multiplet centered at δ 7.10 and an AB proton pattern $\gamma_A = \delta$ 4.17, $\gamma_B = \delta$ 4.43, (J_{AB}=6.0 cps). The mass spectrum exhibited an intense molecular ion at m/e 299 (100%) and fragment ions m/e 78 (40.0%), m/e 180 (67.0%). The structure was tentatively assigned as cis-3,4-diphenylhydrocarbostyril (XCIX) based on the small coupling constant.

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.29; H, 5.69; N, 4.68. Found: C, 84.25; H, 5.79; N, 4.75.

trans-1,3,4-Triphenyl-2-azetidinone (XCVIII)

To a solution of benzalaniline (1.81 g, 0.01 mole) and triethylamine (1.0 g, 0.01 mole) in anhydrous ether (35 ml) was added dropwise to a solution of α-phenylacetyl chloride (1.55 g, 0.01 mole) in ether (15 ml). A precipitate formed immediately, and the mixture was stirred for 0.5 hr. The reaction mixture was filtered and the filtrate was evaporated giving an oily residue. The oil was dissolved in a small volume of dichloromethane and poured onto 1.0" X 20" column prepared with 50 g of Silica Gel. The column was eluted with benzene (250 ml) which upon evaporation afforded an oil. Crystallization from iso-propyl alcohol gave trans-1,3,4-triphenyl-2-azetidinone (XCVIII, 180 mg, 6%, mp 127-128°, lit. (114,115), mp 133-134°).* The infrared spectrum (KBr) was superimposable on the trans-β-lactam XCVIII isolated from the photolysis of cis-α-phenylcinnamanilide (XCVI). A mixed melting point determination showed no depression.

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*The analysis of the trans-lactam XCVIII reported by Kirmse and Horner (114) leave much to be desired. They report the theoretical percent carbon in $C_{21}H_{17}NO$ to be 86.37% and found 86.17% whereas the correct carbon percentage should be 84.29%. The values reported by Pfleger and Jäger (115) were acceptable.

SUMMARY

Irradiation of cis-α-phenylcinnamic acid (LXXVII) in the presence of tetramethylethylene gave only trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII). The structure of the product was established by oxidation with N-bromosuccinimide to 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) which was identical to an authentic sample prepared by photocycloaddition of diphenylacetylene to tetramethylethylene. Reduction of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (LXXIX) with potassium in liquid ammonia gave trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII). The irradiation of cis or trans-α-phenylcinnamic acid (LXXVII, LXXXVIII) in benzene gave cis-α,β-diphenyl-β-propiolactone (LXXXIII). Irradiation of cis-α,β-diphenyl-β-propiolactone (LXXXIII) in the presence of tetramethylethylene afforded trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII), while irradiation in the absence of tetramethylethylene gave phenanthrene (XCII). Photocycloaddition of cis or trans-stilbene to tetramethylethylene gave only trans-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (LXXVIII). The scope and substituent effects of the β-lactone formation were investigated.

Irradiation of cis-α-phenylcinnamamide (CIII), and cis-α-phenylcinnamanilide (XCVI) gave cis and trans-β-lactams together with other products.

The bond orders and formal charge densities were calculated for the acid and amide systems. Alternative mechanisms for the β-lactone and β-lactam formation are discussed in light of these results.

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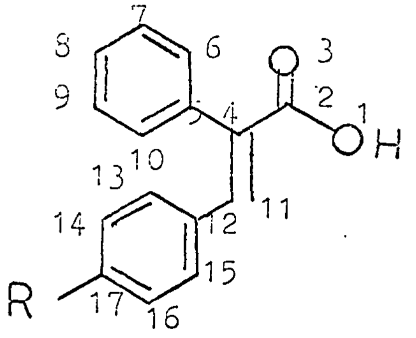
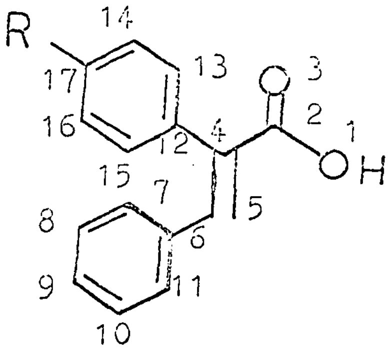
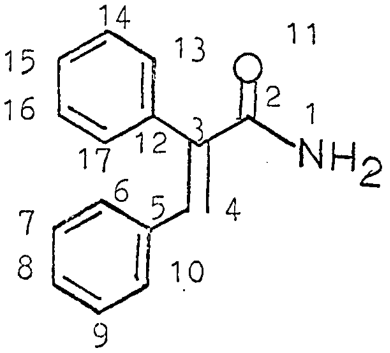
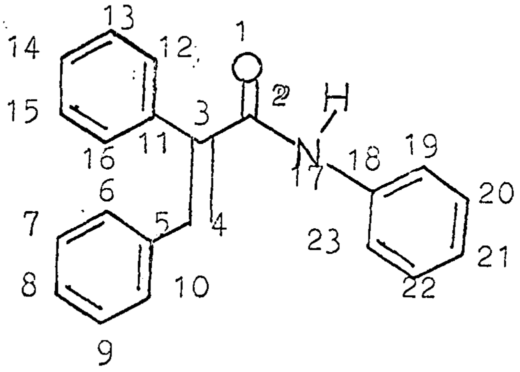
APPENDIX

The acid and amide systems
were numbered as shown below.









α-Phenylcinnamic acid

```
PSI( 1) = 0.4375 ( 1) + 0.4763 ( 2) + 0.4375 ( 3)
        + 0.3935( 4)+ 0.2777( 5)+ 0.1476( 6)
        + 0.0882( 7)+ 0.0711( 8)+ 0.0882( 9)
        + 0.1476(10)+ 0.2218(11)+ 0.1565(12)
        + 0.0832(13)+ 0.0497(14)+ 0.0832(15)
        + 0.0497(16)+ 0.0401(17)+
PSI( 2) =-0.2973 ( 1) +-0.2075 ( 2) +-0.2973 ( 3)
        + 0.0936( 4)+ 0.1632( 5)+ 0.1269( 6)
        + 0.1068( 7)+ 0.1003( 8)+ 0.1068( 9)
        + 0.1269(10)+ 0.2435(11)+ 0.4246(12)
        + 0.3300(13)+ 0.2777(14)+ 0.3300(15)
        + 0.2777(16)+ 0.2610(17)+
PSI( 3) =-0.1862 ( 1) +-0.1139 ( 2) +-0.1362 ( 3)
        + 0.1015( 4)+ 0.3815( 5)+ 0.3404( 6)
        + 0.3166( 7)+ 0.3087( 8)+ 0.3166( 9)
        + 0.3404(10)+-0.0594(11)+-0.2234(12)
        +-0.1993(13)+-0.1854(14)+-0.1993(15)
        +-0.1854(16)+-0.1808(17)+
PSI( 4) =-0.2148 ( 1) +-0.0010 ( 2) +-0.2148 ( 3)
        + 0.3851( 4)+ 0.1947( 5)+-0.0461( 6)
        +-0.2641( 7)+-0.3511( 8)+-0.2641( 9)
        +-0.0461(10)+ 0.3856(11)+ 0.1950(12)
        +-0.0462(13)+-0.2644(14)+-0.0462(15)
        +-0.2644(16)+-0.3516(17)+
PSI( 5) =-0.7071 ( 1) +-0.0000 ( 2) + 0.7071 ( 3)
        + 0.0000( 4)+ 0.0000( 5)+-0.0000( 6)
        +-0.0000( 7)+-0.0000( 8)+-0.0000( 9)
        +-0.0000(10)+ 0.0000(11)+ 0.0000(12)
        +-0.0000(13)+-0.0000(14)+-0.0000(15)
        +-0.0000(16)+-0.0000(17)+
PSI( 6) = 0.0797 ( 1) +-0.0300 ( 2) + 0.0797 ( 3)
        +-0.1784( 4)+-0.3710( 5)+-0.1262( 6)
        + 0.2245( 7)+ 0.3869( 8)+ 0.2246( 9)
        +-0.1262(10)+ 0.1940(11)+ 0.4036(12)
        + 0.1373(13)+-0.2443(14)+ 0.1373(15)
        +-0.2442(16)+-0.4208(17)+
PSI( 7) =-0.0000 ( 1) + 0.0000 ( 2) + 0.0000 ( 3)
        +-0.0000( 4)+-0.0000( 5)+ 0.5000( 6)
        + 0.5000( 7)+ 0.0000( 8)+-0.5000( 9)
        +-0.5000(10)+ 0.0000(11)+ 0.0000(12)
        + 0.0030(13)+ 0.0030(14)+-0.0030(15)
        +-0.0030(16)+-0.0000(17)+
PSI( 8) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
        +-0.0000( 4)+ 0.0000( 5)+ 0.0030( 6)
        + 0.0030( 7)+-0.0000( 8)+-0.0030( 9)
        +-0.0030(10)+-0.0000(11)+ 0.0000(12)
        +-0.5000(13)+-0.5000(14)+ 0.5000(15)
        + 0.5000(16)+ 0.0000(17)+
PSI( 9) = 0.1733 ( 1) +-0.1760 ( 2) + 0.1733 ( 3)
        +-0.4151( 4)+ 0.2691( 5)+ 0.2864( 6)
```

```
          +-0.1013( 7)+-0.3457( 8)+-0.1013( 9)
          + 0.2864(10)+-0.3363(11)+ 0.2180(12)
          + 0.2320(13)+-0.0821(14)+ 0.2320(15)
          +-0.0821(16)+-0.2801(17)+
PSI(10) = 0.2141 ( 1) +-0.4213 ( 2) + 0.2141 ( 3)
          +-0.2711( 4)+-0.0591( 5)+ 0.1436( 6)
          + 0.0202( 7)+-0.1490( 8)+ 0.0202( 9)
          + 0.1436(10)+ 0.5539(11)+ 0.1208(12)
          +-0.2933(13)+-0.0413(14)+-0.2933(15)
          +-0.0413(16)+ 0.3043(17)+
PSI(11) = 0.1951 ( 1) +-0.5221 ( 2) + 0.1951 ( 3)
          + 0.1231( 4)+ 0.4379( 5)+-0.2604( 6)
          +-0.2013( 7)+ 0.4433( 8)+-0.2013( 9)
          +-0.2604(10)+-0.0276(11)+-0.0980(12)
          + 0.0583(13)+ 0.0451(14)+ 0.0583(15)
          + 0.0451(16)+-0.0993(17)+
PSI(12) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          + 0.0000( 4)+ 0.0000( 5)+ 0.5000( 6)
          +-0.5000( 7)+ 0.0000( 8)+ 0.5000( 9)
          +-0.5000(10)+-0.0000(11)+-0.0000(12)
          +-0.0060(13)+ 0.0060(14)+ 0.0060(15)
          +-0.0060(16)+-0.0000(17)+
PSI(13) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
          +-0.0000( 4)+ 0.0000( 5)+ 0.0060( 6)
          +-0.0060( 7)+ 0.0000( 8)+ 0.0060( 9)
          +-0.0060(10)+-0.0000(11)+ 0.0000(12)
          + 0.5000(13)+-0.5000(14)+-0.5000(15)
          + 0.5000(16)+ 0.0000(17)+
PSI(14) =-0.0733 ( 1) + 0.2199 ( 2) +-0.0733 ( 3)
          +-0.1318( 4)+ 0.2198( 5)+-0.0659( 6)
          +-0.1407( 7)+ 0.2347( 8)+-0.1407( 9)
          +-0.0659(10)+-0.2816(11)+ 0.4696(12)
          +-0.1408(13)+-0.3007(14)+-0.1408(15)
          +-0.3007(16)+ 0.5015(17)+
PSI(15) =-0.1024 ( 1) + 0.3611 ( 2) +-0.1024 ( 3)
          +-0.4200( 4)+ 0.0650( 5)+ 0.1556( 6)
          +-0.3253( 7)+ 0.3889( 8)+-0.3254( 9)
          + 0.1556(10)+ 0.2766(11)+-0.0428(12)
          +-0.1024(13)+ 0.2143(14)+-0.1024(15)
          + 0.2143(16)+-0.2561(17)+
PSI(16) =-0.0157 ( 1) + 0.0624 ( 2) +-0.0157 ( 3)
          +-0.1010( 4)+ 0.2836( 5)+-0.2431( 6)
          + 0.2200( 7)+-0.2124( 8)+ 0.2200( 9)
          +-0.2431(10)+-0.1369(11)+ 0.3845(12)
          +-0.3297(13)+ 0.2983(14)+-0.3297(15)
          + 0.2983(16)+-0.2881(17)+
PSI(17) =-0.0544 ( 1) + 0.2290 ( 2) +-0.0544 ( 3)
          +-0.4256( 4)+ 0.4178( 5)+-0.2648( 6)
          + 0.1876( 7)+-0.1641( 8)+ 0.1876( 9)
          +-0.2648(10)+ 0.3262(11)+-0.3202(12)
          + 0.2030(13)+-0.1438(14)+ 0.2030(15)
          +-0.1438(16)+ 0.1258(17)+
```

Electron Densities

```
Atom( 1)=1.7941        Atom( 2)=0.6296        Atom( 3)=1.7941
Atom( 4)=1.0527        Atom( 5)=0.9946        Atom( 6)=1.0076
Atom( 7)=0.9996        Atom( 8)=1.0058        Atom( 9)=0.9996
Atom(10)=1.0076        Atom(11)=0.8230        Atom(12)=1.0062
Atom(13)=0.9607        Atom(14)=1.0006        Atom(15)=0.9607
Atom(16)=1.0006        Atom(17)=0.9631
```

Bond Orders

```
Bond( 1, 2)=0.5173        Bond( 2, 4)=0.4690
Bond( 4, 5)=0.3855        Bond( 5, 6)=0.6129
Bond( 6, 7)=0.6783        Bond( 7, 8)=0.6587
Bond( 8, 9)=0.6587        Bond( 9,10)=0.6783
Bond(10, 5)=0.6129        Bond( 4,11)=0.7151
Bond(11,12)=0.4631        Bond(12,13)=0.5893
Bond(13,14)=0.6848        Bond(14,17)=0.6535
Bond(17,16)=0.6535        Bond(16,15)=0.6848
Bond(15,12)=0.5893        Bond( 2, 3)=0.5173
```

α-Phenyl-p-methoxycinnamic acid

```
PSI( 1) = 0.3125 ( 1) + 0.3469 ( 2) + 0.3125 ( 3)
          + 0.3043( 4)+ 0.2096( 5)+ 0.1097( 6)
          + 0.0646( 7)+ 0.0517( 8)+ 0.0646( 9)
          + 0.1097(10)+ 0.2039(11)+ 0.2053(12)
          + 0.1545(13)+ 0.1808(14)+ 0.1545(15)
          + 0.1808(16)+ 0.2974(17)+ 0.4769(18)
PSI( 2) = 0.3198 ( 1) + 0.3367 ( 2) + 0.3198 ( 3)
          + 0.2486( 4)+ 0.1831( 5)+ 0.0998( 6)
          + 0.0612( 7)+ 0.0500( 8)+ 0.0612( 9)
          + 0.0998(10)+ 0.0887(11)+-0.0315(12)
          +-0.0829(13)+-0.1715(14)+-0.0829(15)
          +-0.1715(16)+-0.3368(17)+-0.6017(18)
PSI( 3) = 0.3411 ( 1) + 0.2209 ( 2) + 0.3411 ( 3)
          +-0.1540( 4)+-0.3804( 5)+-0.3191( 6)
          +-0.2843( 7)+-0.2730( 8)+-0.2843( 9)
          +-0.3191(10)+-0.1612(11)+-0.1818(12)
          +-0.1087(13)+-0.0446(14)+-0.1087(15)
          +-0.0446(16)+ 0.0158(17)+ 0.1526(18)
PSI( 4) = 0.0533 ( 1) + 0.0273 ( 2) + 0.0533 ( 3)
          +-0.0424( 4)+ 0.1607( 5)+ 0.1788( 6)
          + 0.1899( 7)+ 0.1937( 8)+ 0.1899( 9)
          + 0.1768(10)+-0.2712(11)+-0.4895(12)
          +-0.3444(13)+-0.1859(14)+-0.3444(15)
          +-0.1859(16)+-0.0202(17)+ 0.4153(18)
PSI( 5) = 0.7071 ( 1) + 0.0000 ( 2) +-0.7071 ( 3)
          +-0.0000( 4)+-0.0000( 5)+ 0.0000( 6)
          + 0.0000( 7)+ 0.0000( 8)+ 0.0000( 9)
          + 0.0000(10)+-0.0000(11)+-0.0000(12)
          + 0.0000(13)+ 0.0000(14)+ 0.0000(15)
          + 0.0000(16)+ 0.0000(17)+-0.0000(18)
PSI( 6) = 0.2192 ( 1) +-0.0168 ( 2) + 0.2192 ( 3)
          +-0.4186( 4)+-0.2788( 5)+ 0.0098( 6)
          + 0.2929( 7)+ 0.4093( 8)+ 0.2929( 9)
          + 0.0098(10)+-0.3034(11)+-0.0156(12)
          + 0.1406(13)+ 0.2167(14)+ 0.1406(15)
          + 0.2167(16)+ 0.1696(17)+-0.2385(18)
PSI( 7) = 0.0198 ( 1) +-0.0100 ( 2) + 0.0198 ( 3)
          +-0.0460( 4)+-0.3371( 5)+-0.1533( 6)
          + 0.1769( 7)+ 0.3382( 8)+ 0.1768( 9)
          +-0.1533(10)+ 0.2990(11)+ 0.3587(12)
          + 0.0381(13)+-0.3189(14)+ 0.0381(15)
          +-0.3189(16)+-0.3716(17)+ 0.3115(18)
PSI( 8) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+ 0.0000( 5)+ 0.5000( 6)
          + 0.5000( 7)+-0.0000( 8)+-0.5000( 9)
          +-0.5000(10)+-0.0000(11)+-0.0000(12)
          +-0.0070(13)+-0.0069(14)+ 0.0070(15)
          + 0.0070(16)+ 0.0000(17)+-0.0000(18)
PSI( 9) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          +-0.0000( 4)+-0.0000( 5)+-0.0070( 6)
```

```
          +-0.0070( 7)+ 0.0000( 8)+ 0.0070( 9)
          + 0.0070(10)+ 0.0000(11)+ 0.0000(12)
          +-0.5000(13)+-0.5000(14)+ 0.5000(15)
          + 0.5000(16)+-0.0000(17)+ 0.0000(18)
PSI(10) =-0.1761 ( 1) + 0.1861 ( 2) +-0.1761 ( 3)
          + 0.4192( 4)+-0.2402( 5)+-0.2755( 6)
          + 0.0890( 7)+ 0.3243( 8)+ 0.0890( 9)
          +-0.2755(10)+ 0.2841(11)+-0.2632(12)
          +-0.2143(13)+ 0.1456(14)+-0.2143(15)
          + 0.1456(16)+ 0.2942(17)+-0.1622(18)
PSI(11) = 0.2130 ( 1) +-0.4252 ( 2) + 0.2130 ( 3)
          +-0.2573( 4)+-0.0623( 5)+ 0.1379( 6)
          + 0.0214( 7)+-0.1442( 8)+ 0.0214( 9)
          + 0.1379(10)+ 0.5638(11)+ 0.0902(12)
          +-0.2953(13)+-0.0026(14)+-0.2953(15)
          +-0.0026(16)+ 0.2960(17)+-0.1031(18)
PSI(12) =-0.1917 ( 1) + 0.5134 ( 2) +-0.1917 ( 3)
          +-0.1223( 4)+-0.4444( 5)+ 0.2634( 6)
          + 0.2047( 7)+-0.4497( 8)+ 0.2047( 9)
          + 0.2634(10)+ 0.0423(11)+ 0.0838(12)
          +-0.0593(13)+-0.0298(14)+-0.0593(15)
          +-0.0298(16)+ 0.0864(17)+-0.0238(18)
PSI(13) = 0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+-0.0000( 5)+ 0.3572( 6)
          +-0.3572( 7)+-0.0000( 8)+ 0.3572( 9)
          +-0.3572(10)+ 0.0000(11)+-0.0000(12)
          +-0.3499(13)+ 0.3499(14)+ 0.3499(15)
          +-0.3499(16)+-0.0000(17)+ 0.0000(18)
PSI(14) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          + 0.0000( 4)+-0.0000( 5)+-0.3499( 6)
          + 0.3499( 7)+-0.0000( 8)+-0.3499( 9)
          + 0.3499(10)+ 0.0000(11)+-0.0000(12)
          +-0.3572(13)+ 0.3572(14)+ 0.3572(15)
          +-0.3572(16)+-0.0000(17)+ 0.0000(18)
PSI(15) =-0.0796 ( 1) + 0.2431 ( 2) +-0.0796 ( 3)
          +-0.1605( 4)+ 0.2109( 5)+-0.0515( 6)
          +-0.1466( 7)+ 0.2346( 8)+-0.1466( 9)
          +-0.0515(10)+-0.2536(11)+ 0.4773(12)
          +-0.1714(13)+-0.2632(14)+-0.1714(15)
          +-0.2632(16)+ 0.5002(17)+-0.1231(18)
PSI(16) = 0.0985 ( 1) +-0.3488 ( 2) + 0.0985 ( 3)
          + 0.4107( 4)+-0.0512( 5)+-0.1622( 6)
          + 0.3246( 7)+-0.3851( 8)+ 0.3246( 9)
          +-0.1622(10)+-0.2923(11)+ 0.0821(12)
          + 0.0770(13)+-0.2118(14)+ 0.0770(15)
          +-0.2118(16)+ 0.2802(17)+-0.0608(18)
PSI(17) =-0.0187 ( 1) + 0.0746 ( 2) +-0.0187 ( 3)
          +-0.1219( 4)+ 0.2939( 5)+-0.2454( 6)
          + 0.2179( 7)+-0.2090( 8)+ 0.2179( 9)
          +-0.2454(10)+-0.1143(11)+ 0.3603(12)
          +-0.3185(13)+ 0.3038(14)+-0.3185(15)
          + 0.3038(16)+-0.3151(17)+ 0.0617(18)
```

```
PSI(18) = 0.0536 ( 1) +-0.2258 ( 2) + 0.0536 ( 3)
        + 0.4202( 4)+-0.4099( 5)+ 0.2591( 6)
        +-0.1830( 7)+ 0.1599( 8)+-0.1830( 9)
        + 0.2591(10)+-0.3262(11)+ 0.3265(12)
        +-0.2105(13)+ 0.1555(14)+-0.2105(15)
        + 0.1555(16)+-0.1453(17)+ 0.0271(18)
```

Electron Densities

```
Atom( 1)=1.7972          Atom( 2)=0.6366          Atom( 3)=1.7972
Atom( 4)=1.0659          Atom( 5)=0.9942          Atom( 6)=1.0106
Atom( 7)=0.9996          Atom( 8)=1.0087          Atom( 9)=0.9996
Atom(10)=1.0106          Atom(11)=0.8223          Atom(12)=1.0279
Atom(13)=0.9566          Atom(14)=1.0370          Atom(15)=0.9566
Atom(16)=1.0370          Atom(17)=0.9118          Atom(18)=1.9308
```

Bond Orders

```
Bond( 1, 2)=0.5125          Bond( 2, 4)=0.4792
Bond( 4, 5)=0.3852          Bond( 5, 6)=0.6131
Bond( 6, 7)=0.6783          Bond( 7, 8)=0.6587
Bond( 8, 9)=0.6587          Bond( 9,10)=0.6783
Bond(10, 5)=0.6131          Bond( 4,11)=0.7055
Bond(11,12)=0.4766          Bond(12,13)=0.5811
Bond(13,14)=0.6963          Bond(14,17)=0.6253
Bond(17,16)=0.6253          Bond(16,15)=0.6963
Bond(15,12)=0.5811          Bond( 2, 3)=0.5125
Bond(17,18)=0.2692
```

α-Phenyl-o-cyanocinnamic acid

```
PSI( 1) = 0.4338 ( 1) + 0.4729 ( 2) + 0.4338 ( 3)
        + 0.3923( 4)+ 0.2764( 5)+ 0.1467( 6)
        + 0.0876( 7)+ 0.0706( 8)+ 0.0876( 9)
        + 0.1467(10)+ 0.2240(11)+ 0.1636(12)
        + 0.0909(13)+ 0.0619(14)+ 0.0909(15)
        + 0.0619(16)+ 0.0627(17)+ 0.0317(18)
        + 0.0160(19)+
PSI( 2) =-0.2056 ( 1) +-0.1614 ( 2) +-0.2056 ( 3)
        + 0.0140( 4)+ 0.0171( 5)+ 0.0119( 6)
        + 0.0092( 7)+ 0.0083( 8)+ 0.0092( 9)
        + 0.0119(10)+ 0.1750(11)+ 0.3723(12)
        + 0.3232(13)+ 0.3408(14)+ 0.3232(15)
        + 0.3408(16)+ 0.4289(17)+ 0.2647(18)
        + 0.1551(19)+
PSI( 3) = 0.2850 ( 1) + 0.1798 ( 2) + 0.2850 ( 3)
        +-0.1414( 4)+-0.4140( 5)+-0.3573( 6)
        +-0.3247( 7)+-0.3141( 8)+-0.3247( 9)
        +-0.3573(10)+-0.0581(11)+ 0.0213(12)
        + 0.0510(13)+ 0.0843(14)+ 0.0510(15)
        + 0.0843(16)+ 0.1232(17)+ 0.0862(18)
        + 0.0550(19)+
PSI( 4) = 0.1402 ( 1) + 0.0335 ( 2) + 0.1402 ( 3)
        +-0.1949( 4)+-0.0094( 5)+ 0.0893( 6)
        + 0.1627( 7)+ 0.1897( 8)+ 0.1627( 9)
        + 0.0893(10)+-0.3583(11)+-0.4197(12)
        +-0.1808(13)+ 0.1096(14)+-0.1808(15)
        + 0.1096(16)+ 0.3688(17)+ 0.4134(18)
        + 0.3402(19)+
PSI( 5) =-0.7071 ( 1) +-0.0000 ( 2) + 0.7071 ( 3)
        + 0.0000( 4)+ 0.0000( 5)+-0.0000( 6)
        +-0.0000( 7)+-0.0000( 8)+-0.0000( 9)
        + 0.0000(10)+ 0.0000(11)+-0.0000(12)
        +-0.0000(13)+-0.0000(14)+-0.0000(15)
        +-0.0000(16)+ 0.0000(17)+ 0.0000(18)
        + 0.0000(19)+
PSI( 6) = 0.1913 ( 1) +-0.0296 ( 2) + 0.1913 ( 3)
        +-0.3847( 4)+-0.3286( 5)+-0.0313( 6)
        + 0.2861( 7)+ 0.4205( 8)+ 0.2861( 9)
        +-0.0313(10)+-0.1651(11)+ 0.1600(12)
        + 0.1914(13)+ 0.1004(14)+ 0.1914(15)
        + 0.1004(16)+-0.0547(17)+-0.2754(18)
        +-0.3199(19)+
PSI( 7) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
        +-0.0000( 4)+-0.1689( 5)+-0.1459( 6)
        + 0.0230( 7)+ 0.1689( 8)+ 0.1459( 9)
        +-0.0230(10)+ 0.1689(11)+ 0.1689(12)
        + 0.3918(13)+ 0.2229(14)+-0.3918(15)
        +-0.5607(16)+-0.1689(17)+ 0.1689(18)
        + 0.3378(19)+
PSI( 8) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
```

```
          + 0.0000( 4)+-0.0123( 5)+-0.4967( 6)
          +-0.4844( 7)+ 0.0123( 8)+ 0.4967( 9)
          + 0.4844(10)+ 0.0123(11)+ 0.0123(12)
          +-0.0942(13)+-0.1065(14)+ 0.0942(15)
          + 0.0819(16)+-0.0123(17)+ 0.0123(18)
          + 0.0246(19)+
 PSI( 9) =-0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+ 0.2196( 5)+ 0.0351( 6)
          +-0.1845( 7)+-0.2196( 8)+-0.0351( 9)
          + 0.1845(10)+-0.2196(11)+-0.2196(12)
          + 0.2960(13)+ 0.5157(14)+-0.2960(15)
          +-0.0764(16)+ 0.2196(17)+-0.2196(18)
          +-0.4393(19)+
 PSI(10) =-0.1671 ( 1) + 0.1709 ( 2) +-0.1671 ( 3)
          + 0.3998( 4)+-0.2535( 5)+-0.2733( 6)
          + 0.0951( 7)+ 0.3284( 8)+ 0.0951( 9)
          +-0.2733(10)+ 0.3141(11)+-0.2178(12)
          +-0.2201(13)+ 0.0902(14)+-0.2201(15)
          + 0.0902(16)+ 0.2724(17)+-0.0227(18)
          +-0.2855(19)+
 PSI(11) =-0.1950 ( 1) + 0.3674 ( 2) +-0.1950 ( 3)
          + 0.2791( 4)+ 0.0425( 5)+-0.1437( 6)
          +-0.0143( 7)+ 0.1465( 8)+-0.0143( 9)
          +-0.1437(10)+-0.4644(11)+-0.1881(12)
          + 0.2506(13)+ 0.1391(14)+ 0.2506(15)
          + 0.1391(16)+-0.2779(17)+-0.2238(18)
          + 0.3217(19)+
 PSI(12) = 0.1348 ( 1) +-0.3259 ( 2) + 0.1348 ( 3)
          +-0.0226( 4)+-0.0202( 5)+ 0.0181( 6)
          + 0.0079( 7)+-0.0235( 8)+ 0.0079( 9)
          + 0.0181(10)+ 0.3614(11)+-0.2214(12)
          +-0.1059(13)+ 0.2930(14)+-0.1059(15)
          + 0.2930(16)+-0.0919(17)+-0.5238(18)
          + 0.4457(19)+
 PSI(13) = 0.1714 ( 1) +-0.4606 ( 2) + 0.1714 ( 3)
          + 0.1149( 4)+ 0.4646( 5)+-0.2709( 6)
          +-0.2156( 7)+ 0.4691( 8)+-0.2156( 9)
          +-0.2709(10)+-0.1096(11)+-0.0142(12)
          + 0.0613(13)+-0.0422(14)+ 0.0613(15)
          +-0.0422(16)+-0.0225(17)+ 0.1051(18)
          +-0.0740(19)+
 PSI(14) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
          +-0.0000( 4)+ 0.0000( 5)+ 0.5000( 6)
          +-0.5000( 7)+ 0.0000( 8)+ 0.5000( 9)
          +-0.5000(10)+ 0.0000(11)+ 0.0000(12)
          + 0.0030(13)+-0.0030(14)+-0.0030(15)
          + 0.0030(16)+ 0.0000(17)+-0.0000(18)
          + 0.0000(19)+
 PSI(15) = 0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+-0.0000( 5)+-0.0030( 6)
          + 0.0030( 7)+-0.0000( 8)+-0.0030( 9)
          + 0.0030(10)+ 0.0000(11)+-0.0000(12)
```

```
         + 0.5000(13)+-0.5000(14)+-0.5000(15)
         + 0.5000(16)+-0.0000(17)+ 0.0000(18)
         +-0.0000(19)+
PSI(16) =-0.0977 ( 1) + 0.3187 ( 2) +-0.0977 ( 3)
         +-0.2815( 4)+ 0.1847( 5)+ 0.0082( 6)
         +-0.1965( 7)+ 0.2738( 8)+-0.1965( 9)
         + 0.0082(10)+-0.0994(11)+ 0.4242(12)
         +-0.2547(13)+-0.0587(14)+-0.2547(15)
         +-0.0587(16)+ 0.3389(17)+-0.3690(18)
         + 0.1907(19)+
PSI(17) =-0.0755 ( 1) + 0.2722 ( 2) +-0.0755 ( 3)
         +-0.3397( 4)+-0.0156( 5)+ 0.1834( 6)
         +-0.3048( 7)+ 0.3491( 8)+-0.3049( 9)
         + 0.1834(10)+ 0.3367(11)+-0.2484(12)
         + 0.0486(13)+ 0.1635(14)+ 0.0486(15)
         + 0.1635(16)+-0.3342(17)+ 0.2567(18)
         +-0.1143(19)+
PSI(18) =-0.0296 ( 1) + 0.1196 ( 2) +-0.0296 ( 3)
         +-0.2024( 4)+ 0.3351( 5)+-0.2569( 6)
         + 0.2139( 7)+-0.2002( 8)+ 0.2139( 9)
         +-0.2569(10)+-0.0223(11)+ 0.2500(12)
         +-0.2560(13)+ 0.2970(14)+-0.2560(15)
         + 0.2970(16)+-0.3788(17)+ 0.2155(18)
         +-0.0817(19)+
PSI(19) =-0.0494 ( 1) + 0.2086 ( 2) +-0.0494 ( 3)
         +-0.3912( 4)+ 0.3714( 5)+-0.2317( 6)
         + 0.1618( 7)+-0.1406( 8)+ 0.1618( 9)
         +-0.2317(10)+ 0.3202(11)+-0.3455(12)
         + 0.2375(13)+-0.2009(14)+ 0.2375(15)
         +-0.2009(16)+ 0.2249(17)+-0.1157(18)
         + 0.0413(19)+
```

Electron Densities

```
Atom( 1)=1.7918       Atom( 2)=0.6264       Atom( 3)=1.7918
Atom( 4)=1.0397       Atom( 5)=0.9947       Atom( 6)=1.0045
Atom( 7)=0.9997       Atom( 8)=1.0027       Atom( 9)=0.9997
Atom(10)=1.0044       Atom(11)=0.8310       Atom(12)=0.9838
Atom(13)=0.9662       Atom(14)=0.9686       Atom(15)=0.9662
Atom(16)=0.9686       Atom(17)=0.9864       Atom(18)=0.8052
Atom(19)=1.2693
```

Bond Orders

```
Bond( 1, 2)=0.5201          Bond( 2, 4)=0.4621
Bond( 4, 5)=0.3883          Bond( 5, 6)=0.6117
Bond( 6, 7)=0.6787          Bond( 7, 8)=0.6583
Bond( 8, 9)=0.6583          Bond( 9,10)=0.6787
Bond(10, 5)=0.6117          Bond( 4,11)=0.7150
```

```
Bond(11,12)=0.4661          Bond(12,13)=0.5814
Bond(13,14)=0.6992          Bond(14,17)=0.5938
Bond(17,16)=0.5938          Bond(16,15)=0.6992
Bond(15,12)=0.5814          Bond( 2, 3)=0.5201
Bond(17,18)=0.4211          Bond(18,19)=0.8706
```

α-(p-Methoxyphenyl)-cinnamic acid

```
PSI( 1) = 0.1496 ( 1) + 0.1855 ( 2) + 0.1496 ( 3)
          + 0.2228( 4)+ 0.1240( 5)+ 0.0861( 6)
          + 0.0453( 7)+ 0.0268( 8)+ 0.0215( 9)
          + 0.0268(10)+ 0.0453(11)+ 0.2458(12)
          + 0.1949(13)+ 0.2398(14)+ 0.1949(15)
          + 0.2398(16)+ 0.4027(17)+ 0.6549(18)
PSI( 2) =-0.3753 ( 1) +-0.4045 ( 2) +-0.3753 ( 3)
          +-0.3552( 4)+-0.2336( 5)+-0.1967( 6)
          +-0.1155( 7)+-0.0762( 8)+-0.0645( 9)
          +-0.0762(10)+-0.1155(11)+-0.2008(12)
          +-0.0596(13)+ 0.0600(14)+-0.0596(15)
          + 0.0600(16)+ 0.2013(17)+ 0.4445(18)
PSI( 3) = 0.2794 ( 1) + 0.2103 ( 2) + 0.2794 ( 3)
          +-0.0048( 4)+-0.2153( 5)+-0.4478( 6)
          +-0.3631( 7)+-0.3155( 8)+-0.3001( 9)
          +-0.3155(10)+-0.3631(11)+-0.0051(12)
          +-0.0030(13)+-0.0012(14)+-0.0030(15)
          +-0.0012(16)+ 0.0006(17)+ 0.0044(18)
PSI( 4) = 0.3027 ( 1) + 0.1567 ( 2) + 0.3027 ( 3)
          +-0.1844( 4)+-0.0553( 5)+ 0.0785( 6)
          + 0.1028( 7)+ 0.1182( 8)+ 0.1235( 9)
          + 0.1182(10)+ 0.1028(11)+-0.4543(12)
          +-0.3426(13)+-0.2015(14)+-0.3426(15)
          +-0.2015(16)+-0.0430(17)+ 0.4007(18)
PSI( 5) = 0.7071 ( 1) + 0.0000 ( 2) +-0.7071 ( 3)
          +-0.0000( 4)+-0.0000( 5)+-0.0000( 6)
          +-0.0000( 7)+ 0.0000( 8)+ 0.0000( 9)
          + 0.0000(10)+-0.0000(11)+ 0.0000(12)
          + 0.0000(13)+ 0.0000(14)+ 0.0000(15)
          + 0.0000(16)+ 0.0000(17)+-0.0000(18)
PSI( 6) = 0.1834 ( 1) +-0.0163 ( 2) + 0.1834 ( 3)
          +-0.3168( 4)+-0.4184( 5)+-0.2809( 6)
          + 0.0085( 7)+ 0.2931( 8)+ 0.4102( 9)
          + 0.2931(10)+ 0.0085(11)+-0.0180(12)
          + 0.1456(13)+ 0.2260(14)+ 0.1456(15)
          + 0.2260(16)+ 0.1773(17)+-0.2483(18)
PSI( 7) = 0.1341 ( 1) +-0.0725 ( 2) + 0.1341 ( 3)
          +-0.2919( 4)+ 0.0744( 5)+ 0.3713( 6)
          + 0.1609( 7)+-0.1995( 8)+-0.3739( 9)
          +-0.1995(10)+ 0.1610(11)+-0.3134(12)
          +-0.0213(13)+ 0.2907(14)+-0.0213(15)
          + 0.2907(16)+ 0.3316(17)+-0.2844(18)
PSI( 8) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          +-0.0000( 4)+-0.0000( 5)+ 0.0000( 6)
          + 0.0276( 7)+ 0.0276( 8)+-0.0000( 9)
          +-0.0276(10)+-0.0275(11)+-0.0000(12)
          + 0.4992(13)+ 0.4993(14)+-0.4992(15)
          +-0.4992(16)+ 0.0000(17)+-0.0000(18)
PSI( 9) =-0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+-0.0000( 5)+-0.0000( 6)
```

```
         +-0.4992( 7)+-0.4992( 8)+ 0.0000( 9)
         + 0.4992(10)+ 0.4992(11)+ 0.0000(12)
         + 0.0276(13)+ 0.0275(14)+-0.0276(15)
         +-0.0276(16)+-0.0000(17)+ 0.0000(18)
PSI(10) =-0.1597 ( 1) + 0.1913 ( 2) +-0.1597 ( 3)
         + 0.3592( 4)+ 0.3261( 5)+-0.1825( 6)
         +-0.2125( 7)+ 0.0674( 8)+ 0.2490( 9)
         + 0.0674(10)+-0.2125(11)+-0.3229(12)
         +-0.2670(13)+ 0.1782(14)+-0.2670(15)
         + 0.1782(16)+ 0.3636(17)+-0.1994(18)
PSI(11) =-0.2179 ( 1) + 0.4732 ( 2) +-0.2179 ( 3)
         + 0.2362( 4)+-0.5552( 5)+-0.1043( 6)
         + 0.2900( 7)+ 0.0354( 8)+-0.2984( 9)
         + 0.0354(10)+ 0.2900(11)+ 0.0259(12)
         +-0.1212(13)+ 0.0029(14)+-0.1212(15)
         + 0.0029(16)+ 0.1205(17)+-0.0431(18)
PSI(12) = 0.1769 ( 1) +-0.5326 ( 2) + 0.1769 ( 3)
         + 0.2010( 4)+-0.0448( 5)+-0.1603( 6)
         + 0.0953( 7)+ 0.0737( 8)+-0.1623( 9)
         + 0.0737(10)+ 0.0952(11)+ 0.3947(12)
         +-0.2799(13)+-0.1403(14)+-0.2799(15)
         +-0.1403(16)+ 0.4074(17)+-0.1120(18)
PSI(13) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
         + 0.0000( 4)+-0.0000( 5)+-0.0000( 6)
         + 0.0048( 7)+-0.0048( 8)+-0.0000( 9)
         + 0.0048(10)+-0.0048(11)+ 0.0000(12)
         + 0.5000(13)+-0.5000(14)+-0.5000(15)
         + 0.5000(16)+ 0.0000(17)+-0.0000(18)
PSI(14) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
         + 0.0000( 4)+-0.0000( 5)+ 0.0000( 6)
         +-0.5000( 7)+ 0.5000( 8)+ 0.0000( 9)
         +-0.5000(10)+ 0.5000(11)+ 0.0000(12)
         + 0.0048(13)+-0.0048(14)+-0.0048(15)
         + 0.0048(16)+ 0.0000(17)+-0.0000(18)
PSI(15) = 0.0443 ( 1) +-0.1500 ( 2) + 0.0443 ( 3)
         + 0.1104( 4)+ 0.2871( 5)+-0.4572( 6)
         + 0.1327( 7)+ 0.2969( 8)+-0.4914( 9)
         + 0.2969(10)+ 0.1327(11)+-0.2704(12)
         + 0.1082(13)+ 0.1397(14)+ 0.1082(15)
         + 0.1397(16)+-0.2769(17)+ 0.0691(18)
PSI(16) =-0.0844 ( 1) + 0.3364 ( 2) +-0.0844 ( 3)
         +-0.4330( 4)+ 0.2758( 5)+-0.0326( 6)
         +-0.1104( 7)+ 0.2189( 8)+-0.2593( 9)
         + 0.2189(10)+-0.1104(11)+ 0.1190(12)
         + 0.1160(13)+-0.3150(14)+ 0.1160(15)
         +-0.3150(16)+ 0.4158(17)+-0.0902(18)
PSI(17) = 0.0098 ( 1) +-0.0438 ( 2) + 0.0098 ( 3)
         + 0.0754( 4)+ 0.1513( 5)+-0.3900( 6)
         + 0.3296( 7)+-0.2952( 8)+ 0.2841( 9)
         +-0.2952(10)+ 0.3296(11)+-0.2642(12)
         + 0.2369(13)+-0.2283(14)+ 0.2369(15)
         +-0.2283(16)+ 0.2376(17)+-0.0466(18)
```

```
PSI(18) =-0.0452 ( 1) + 0.2141 ( 2) +-0.0452 ( 3)
         +-0.4172( 4)+ 0.3196( 5)+-0.3136( 6)
         + 0.1987( 7)+-0.1407( 8)+ 0.1231( 9)
         +-0.1407(10)+ 0.1987(11)+ 0.4201(12)
         +-0.2717(13)+ 0.2012(14)+-0.2717(15)
         + 0.2012(16)+-0.1883(17)+ 0.0351(18)
```

Electron Densities

```
Atom( 1)=1.8201      Atom( 2)=0.6179      Atom( 3)=1.8201
Atom( 4)=1.0488      Atom( 5)=0.8126      Atom( 6)=1.0059
Atom( 7)=0.9578      Atom( 8)=1.0006      Atom( 9)=0.9601
Atom(10)=1.0006      Atom(11)=0.9578      Atom(12)=1.0200
Atom(13)=1.0037      Atom(14)=1.0381      Atom(15)=1.0037
Atom(16)=1.0381      Atom(17)=0.9562      Atom(18)=1.9386
```

Bond Orders

```
Bond( 1, 2)=0.4850        Bond( 2, 4)=0.5003
Bond( 4, 5)=0.6996        Bond( 5, 6)=0.4687
Bond( 6, 7)=0.5869        Bond( 7, 8)=0.6855
Bond( 8, 9)=0.6528        Bond( 9,10)=0.6528
Bond(10,11)=0.6855        Bond(11, 6)=0.5869
Bond( 4,12)=0.3822        Bond(12,13)=0.6116
Bond(13,14)=0.6826        Bond(14,17)=0.6371
Bond(17,16)=0.6371        Bond(16,15)=0.6826
Bond(15,12)=0.6116        Bond( 2, 3)=0.4850
Bond(17,18)=0.2503
```

α-(p-Cyanophenyl)-cinnamic acid

```
PSI( 1) = 0.3558 ( 1) + 0.4067 ( 2) + 0.3558 ( 3)
        + 0.4125( 4)+ 0.2514( 5)+ 0.1944( 6)
        + 0.1090( 7)+ 0.0687( 8)+ 0.0559( 9)
        + 0.0687(10)+ 0.1090(11)+ 0.3379(12)
        + 0.2017(13)+ 0.1490(14)+ 0.2017(15)
        + 0.1490(16)+ 0.1500(17)+ 0.0835(18)
        + 0.0436(19)+
PSI( 2) =-0.2950 ( 1) +-0.2357 ( 2) +-0.2950 ( 3)
        +-0.0322( 4)+-0.0641( 5)+-0.1049( 6)
        +-0.0802( 7)+-0.0666( 8)+-0.0622( 9)
        +-0.0666(10)+-0.0802(11)+ 0.2308(12)
        + 0.2630(13)+ 0.3318(14)+ 0.2630(15)
        + 0.3318(16)+ 0.4468(17)+ 0.2922(18)
        + 0.1783(19)+
PSI( 3) = 0.2683 ( 1) + 0.2020 ( 2) + 0.2683 ( 3)
        +-0.0047( 4)+-0.2172( 5)+-0.4519( 6)
        +-0.3664( 7)+-0.3184( 8)+-0.3029( 9)
        +-0.3184(10)+-0.3664(11)+ 0.0053(12)
        + 0.0080(13)+ 0.0114(14)+ 0.0080(15)
        + 0.0114(16)+ 0.0160(17)+ 0.0108(18)
        + 0.0067(19)+
PSI( 4) = 0.2657 ( 1) + 0.0653 ( 2) + 0.2657 ( 3)
        +-0.3143( 4)+-0.1966( 5)+-0.0192( 6)
        + 0.0820( 7)+ 0.1583( 8)+ 0.1866( 9)
        + 0.1583(10)+ 0.0820(11)+-0.4020(12)
        +-0.1838(13)+ 0.0901(14)+-0.1838(15)
        + 0.0901(16)+ 0.3366(17)+ 0.3910(18)
        + 0.3268(19)+
PSI( 5) =-0.7071 ( 1) + 0.0000 ( 2) + 0.7071 ( 3)
        +-0.0000( 4)+-0.0000( 5)+-0.0000( 6)
        + 0.0000( 7)+ 0.0000( 8)+ 0.0000( 9)
        + 0.0000(10)+ 0.0000(11)+-0.0000(12)
        +-0.0000(13)+-0.0000(14)+-0.0000(15)
        + 0.0000(16)+ 0.0000(17)+ 0.0000(18)
        + 0.0000(19)+
PSI( 6) = 0.0981 ( 1) +-0.0182 ( 2) + 0.0951 ( 3)
        +-0.1815( 4)+-0.3863( 5)+-0.3407( 6)
        +-0.0371( 7)+ 0.2905( 8)+ 0.4298( 9)
        + 0.2905(10)+-0.0371(11)+ 0.1591(12)
        + 0.1983(13)+ 0.1090(14)+ 0.1983(15)
        + 0.1090(16)+-0.0510(17)+-0.2868(18)
        +-0.3368(19)+
PSI( 7) = 0.1299 ( 1) +-0.0776 ( 2) + 0.1299 ( 3)
        +-0.2872( 4)+ 0.0203( 5)+ 0.3080( 6)
        + 0.1472( 7)+-0.1575( 8)+-0.3082( 9)
        +-0.1575(10)+ 0.1472(11)+-0.2363(12)
        + 0.0229(13)+ 0.2596(14)+ 0.0229(15)
        + 0.2596(16)+ 0.2425(17)+-0.2714(18)
        +-0.5199(19)+
PSI( 8) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
```

```
          + 0.0000( 4)+-0.0000( 5)+-0.0000( 6)
          + 0.0026( 7)+ 0.0026( 8)+ 0.0000( 9)
          +-0.0026(10)+-0.0026(11)+ 0.0000(12)
          + 0.5000(13)+ 0.5000(14)+-0.5000(15)
          +-0.5000(16)+-0.0000(17)+ 0.0000(18)
          + 0.0000(19)+
 PSI( 9) =-0.0000 ( 1) + 0.0000 ( 2) + 0.0000 ( 3)
          + 0.0000( 4)+ 0.0000( 5)+ 0.0000( 6)
          + 0.5000( 7)+ 0.5000( 8)+ 0.0000( 9)
          +-0.5000(10)+-0.5000(11)+-0.0000(12)
          +-0.0026(13)+-0.0026(14)+ 0.0026(15)
          + 0.0026(16)+ 0.0000(17)+-0.0000(18)
          +-0.0000(19)+
 PSI(10) = 0.1651 ( 1) +-0.1883 ( 2) + 0.1651 ( 3)
          +-0.3748( 4)+-0.3023( 5)+ 0.1972( 6)
          + 0.2091( 7)+-0.0743( 8)+-0.2527( 9)
          +-0.0743(10)+ 0.2091(11)+ 0.2703(12)
          + 0.2668(13)+-0.1134(14)+ 0.2668(15)
          +-0.1134(16)+-0.3335(17)+ 0.0309(18)
          + 0.3516(19)+
 PSI(11) = 0.1945 ( 1) +-0.4177 ( 2) + 0.1945 ( 3)
          +-0.2200( 4)+ 0.5652( 5)+ 0.0967( 6)
          +-0.2932( 7)+-0.0328( 8)+ 0.3003( 9)
          +-0.0328(10)+-0.2932(11)+-0.0996(12)
          + 0.1209(13)+ 0.0732(14)+ 0.1209(15)
          + 0.0732(16)+-0.1368(17)+-0.1165(18)
          + 0.1623(19)+
 PSI(12) =-0.1411 ( 1) + 0.3562 ( 2) +-0.1411 ( 3)
          + 0.0405( 4)+-0.0389( 5)+-0.0203( 6)
          + 0.0247( 7)+ 0.0074( 8)+-0.0286( 9)
          + 0.0074(10)+ 0.0247(11)+-0.3384(12)
          + 0.0677(13)+ 0.3032(14)+ 0.0677(15)
          + 0.3032(16)+-0.2253(17)+-0.4892(18)
          + 0.4796(19)+
 PSI(13) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          + 0.0000( 4)+ 0.0000( 5)+-0.0000( 6)
          + 0.4931( 7)+-0.4931( 8)+-0.0000( 9)
          + 0.4931(10)+-0.4931(11)+ 0.0000(12)
          + 0.0827(13)+-0.0827(14)+-0.0827(15)
          + 0.0827(16)+ 0.0000(17)+-0.0000(18)
          + 0.0000(19)+
 PSI(14) =-0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
          +-0.0000( 4)+-0.0000( 5)+ 0.0000( 6)
          +-0.0827( 7)+ 0.0827( 8)+ 0.0000( 9)
          +-0.0827(10)+ 0.0827(11)+-0.0000(12)
          + 0.4931(13)+-0.4931(14)+-0.4931(15)
          + 0.4931(16)+-0.0000(17)+ 0.0000(18)
          +-0.0000(19)+
 PSI(15) = 0.1561 ( 1) +-0.4991 ( 2) + 0.1561 ( 3)
          + 0.2788( 4)+ 0.0600( 5)+-0.3424( 6)
          + 0.1512( 7)+ 0.1822( 8)+-0.3442( 9)
          + 0.1822(10)+ 0.1513(11)+ 0.1439(12)
```

```
         +-0.2156(13)+ 0.0844(14)+-0.2156(15)
         + 0.0844(16)+ 0.1262(17)+-0.3024(18)
         + 0.1940(19)+
PSI(16) =-0.0274 ( 1) + 0.0960 ( 2) +-0.0274 ( 3)
         +-0.0812( 4)+ 0.3312( 5)+-0.3552( 6)
         + 0.0625( 7)+ 0.2688( 8)+-0.4127( 9)
         + 0.2688(10)+ 0.0625(11)+-0.3214(12)
         + 0.2499(13)+-0.0042(14)+ 0.2499(15)
         +-0.0042(16)+-0.2445(17)+ 0.3269(18)
         +-0.1813(19)+
PSI(17) =-0.0736 ( 1) + 0.3036 ( 2) +-0.0736 ( 3)
         +-0.4283( 4)+ 0.2092( 5)+ 0.0520( 6)
         +-0.1514( 7)+ 0.2203( 8)+-0.2449( 9)
         + 0.2203(10)+-0.1514(11)+ 0.2577(12)
         +-0.0176(13)+-0.2260(14)+-0.0176(15)
         +-0.2260(16)+ 0.4242(17)+-0.3110(18)
         + 0.1353(19)+
PSI(18) =-0.0040 ( 1) + 0.0182 ( 2) +-0.0040 ( 3)
         +-0.0319( 4)+ 0.2109( 5)+-0.4132( 6)
         + 0.3305( 7)+-0.2843( 8)+ 0.2694( 9)
         +-0.2843(10)+ 0.3305(11)+-0.1618(12)
         + 0.1866(13)+-0.2321(14)+ 0.1866(15)
         +-0.2321(16)+ 0.3031(17)+-0.1755(18)
         + 0.0672(19)+
PSI(19) = 0.0421 ( 1) +-0.2001 ( 2) + 0.0421.( 3)
         + 0.3939( 4)+-0.2887( 5)+ 0.2717( 6)
         +-0.1688( 7)+ 0.1174( 8)+-0.1018( 9)
         + 0.1174(10)+-0.1688(11)+-0.4193(12)
         + 0.2863(13)+-0.2407(14)+ 0.2863(15)
         +-0.2407(16)+ 0.2687(17)+-0.1379(18)
         + 0.0491(19)+
```

Electron Densities

```
Atom( 1)=1.8200          Atom( 2)=0.6156          Atom( 3)=1.8200
Atom( 4)=1.0520          Atom( 5)=0.7883          Atom( 6)=1.0063
Atom( 7)=0.9521          Atom( 8)=1.0006          Atom( 9)=0.9546
Atom(10)=1.0006          Atom(11)=0.9521          Atom(12)=0.9665
Atom(13)=1.0095          Atom(14)=0.9654          Atom(15)=1.0095
Atom(16)=0.9654          Atom(17)=1.0217          Atom(18)=0.8046
Atom(19)=1.2957
```

Bond Orders

```
Bond( 1, 2)=0.4857       Bond( 2, 4)=0.5001
Bond( 4, 5)=0.6923       Bond( 5, 6)=0.4716
Bond( 6, 7)=0.5856       Bond( 7, 8)=0.6859
Bond( 8, 9)=0.6524       Bond( 9,10)=0.6524
Bond(10,11)=0.6859       Bond( 4,12)=0.3919
```

```
Bond(12,13)=0.6021           Bond(13,14)=0.6963
Bond(14,17)=0.5951           Bond(17,16)=0.5951
Bond(16,15)=0.6963           Bond(15,12)=0.6021
Bond( 2, 3)=0.4857           Bond(17,18)=0.4282
Bond(18,19)=0.8643           Bond(11, 6)-0.5856
```

α-Phenylcinnamamide

```
PSI( 1) = 0.3840 ( 1) + 0.4354 ( 2) + 0.4313 ( 3)
        + 0.2654( 4)+ 0.2076( 5)+ 0.1171( 6)
        + 0.0743( 7)+ 0.3617( 8)+ 0.0743( 9)
        + 0.1171(10)+ 0.3094(11)+ 0.3373(12)
        + 0.1903(13)+ 0.1207(14)+ 0.1903(15)
        + 0.1207(16)+ 0.1903(17)+
PSI( 2) =-0.2744 ( 1) +-0.2042 ( 2) +-0.0219 ( 3)
        + 0.2065( 4)+ 0.4546( 5)+ 0.3730( 6)
        + 0.3270( 7)+ 0.3121( 8)+ 0.3270( 9)
        + 0.3730(10)+-0.1864(11)+-0.0482(12)
        +-0.0396(13)+-0.0347(14)+-0.0331(15)
        +-0.0347(16)+-0.0396(17)+
PSI( 3) =-0.3963 ( 1) +-0.2590 ( 2) + 0.0464 ( 3)
        +-0.0081( 4)+-0.0626( 5)+-0.0593( 6)
        +-0.0574( 7)+-0.0567( 8)+-0.0574( 9)
        +-0.0593(10)+-0.2532(11)+ 0.3608(12)
        + 0.3417(13)+ 0.3305(14)+ 0.3267(15)
        + 0.3305(16)+ 0.3417(17)+
PSI( 4) = 0.4496 ( 1) + 0.0021 ( 2) +-0.3607 ( 3)
        +-0.3610( 4)+-0.1833( 5)+ 0.0431( 6)
        + 0.2481( 7)+ 0.3299( 8)+ 0.2481( 9)
        + 0.0431(10)+ 0.0042(11)+-0.1827(12)
        + 0.0430(13)+ 0.2473(14)+ 0.3290(15)
        + 0.2473(16)+ 0.0430(17)+
PSI( 5) =-0.5709 ( 1) + 0.1731 ( 2) + 0.0020 ( 3)
        +-0.1731( 4)+-0.2197( 5)+-0.0516( 6)
        + 0.1548( 7)+ 0.2463( 8)+ 0.1548( 9)
        +-0.0516(10)+ 0.6723(11)+ 0.0026(12)
        + 0.0006(13)+-0.0018(14)+-0.0029(15)
        +-0.0018(16)+ 0.0006(17)+
PSI( 6) = 0.1017 ( 1) +-0.0449 ( 2) + 0.1733 ( 3)
        +-0.1523( 4)+-0.3479( 5)+-0.1233( 6)
        + 0.2064( 7)+ 0.3601( 8)+ 0.2064( 9)
        +-0.1233(10)+-0.3062(11)+ 0.3959(12)
        + 0.1403(13)+-0.2349(14)+-0.4098(15)
        +-0.2349(16)+ 0.1403(17)+
PSI( 7) =-0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
        +-0.0000( 4)+-0.0000( 5)+-0.4997( 6)
        +-0.4997( 7)+-0.0000( 8)+ 0.4997( 9)
        + 0.4997(10)+ 0.0000(11)+ 0.0000(12)
        +-0.0165(13)+-0.0165(14)+-0.0000(15)
        + 0.0165(16)+ 0.0165(17)+
PSI( 8) = 0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
        +-0.0000( 4)+ 0.0000( 5)+ 0.0165( 6)
        + 0.0165( 7)+-0.0000( 8)+-0.0165( 9)
        +-0.0165(10)+ 0.0000(11)+-0.0000(12)
        +-0.4997(13)+-0.4997(14)+-0.0000(15)
        + 0.4997(16)+ 0.4997(17)+
PSI( 9) =-0.1011 ( 1) + 0.1189 ( 2) + 0.4172 ( 3)
        + 0.3620( 4)+-0.2147( 5)+-0.2410( 6)
```

```
        + 0.0799( 7)+ 0.2857( 8)+ 0.0799( 9)
        +-0.2410(10)+-0.2698(11)+-0.2475(12)
        +-0.2778(13)+ 0.0921(14)+ 0.3293(15)
        + 0.0921(16)+-0.2778(17)+
PSI(10) =-0.1642 ( 1) + 0.3709 ( 2) + 0.3014 ( 3)
        +-0.5393( 4)+-0.1359( 5)+ 0.2905( 6)
        + 0.0468( 7)+-0.3048( 8)+ 0.0468( 9)
        + 0.2905(10)+-0.2838(11)+ 0.0759(12)
        +-0.1623(13)+-0.0261(14)+ 0.1703(15)
        +-0.0261(16)+-0.1623(17)+
PSI(11) = 0.1679 ( 1) +-0.5119 ( 2) + 0.0825 ( 3)
        +-0.0130( 4)+-0.0703( 5)+ 0.0395( 6)
        + 0.0332( 7)+-0.0707( 8)+ 0.0332( 9)
        + 0.0395(10)+ 0.2639(11)+ 0.4473(12)
        +-0.2513(13)+-0.2112(14)+ 0.4497(15)
        +-0.2112(16)+-0.2513(17)+
PSI(12) = 0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
        +-0.0000( 4)+ 0.0000( 5)+-0.4999( 6)
        + 0.4999( 7)+ 0.0000( 8)+-0.4999( 9)
        + 0.4999(10)+ 0.0000(11)+ 0.0000(12)
        +-0.0123(13)+ 0.0123(14)+ 0.0000(15)
        +-0.0123(16)+ 0.0123(17)+
PSI(13) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
        + 0.0000( 4)+-0.0000( 5)+-0.0123( 6)
        + 0.0123( 7)+-0.0000( 8)+-0.0123( 9)
        + 0.0123(10)+ 0.0000(11)+ 0.0000(12)
        + 0.4999(13)+-0.4999(14)+ 0.0000(15)
        + 0.4999(16)+-0.4999(17)+
PSI(14) = 0.0705 ( 1) +-0.2384 ( 2) + 0.1225 ( 3)
        + 0.2901( 4)+-0.4718( 5)+ 0.1390( 6)
        + 0.3044( 7)+-0.5056( 8)+ 0.3044( 9)
        + 0.1390(10)+ 0.1081(11)+-0.1992(12)
        + 0.0587(13)+ 0.1285(14)+-0.2135(15)
        + 0.1285(16)+ 0.0587(17)+
PSI(15) = 0.0939 ( 1) +-0.3737 ( 2) + 0.4141 ( 3)
        +-0.2675( 4)+ 0.0358( 5)+ 0.1036( 6)
        +-0.2101( 7)+ 0.2498( 8)+-0.2101( 9)
        + 0.1036(10)+ 0.1393(11)+-0.0554(12)
        +-0.1604(13)+ 0.3253(14)+-0.3868(15)
        + 0.3253(16)+-0.1604(17)+
PSI(16) =-0.0144 ( 1) + 0.0642 ( 2) +-0.1006 ( 3)
        +-0.1377( 4)+ 0.3858( 5)+-0.3307( 6)
        + 0.2991( 7)+-0.2888( 8)+ 0.2991( 9)
        +-0.3307(10)+-0.0209(11)+ 0.2818(12)
        +-0.2416(13)+ 0.2185(14)+-0.2110(15)
        + 0.2185(16)+-0.2416(17)+
PSI(17) = 0.0497 ( 1) +-0.2356 ( 2) + 0.4278 ( 3)
        +-0.3259( 4)+ 0.3181( 5)+-0.2011( 6)
        + 0.1421( 7)+-0.1242( 8)+ 0.1421( 9)
        +-0.2011(10)+ 0.0716(11)+-0.4175(12)
        + 0.2639(13)+-0.1865(14)+ 0.1630(15)
        +-0.1865(16)+ 0.2639(17)+
```

Electron Densities

```
Atom( 1)=1.8568          Atom( 2)=0.6888          Atom( 3)=1.0457
Atom( 4)=0.8564          Atom( 5)=1.0053          Atom( 6)=0.9684
Atom( 7)=1.0005          Atom( 8)=0.9705          Atom( 9)=1.0005
Atom(10)=0.9684          Atom(11)=1.6263          Atom(12)=0.9953
Atom(13)=1.0066          Atom(14)=0.9997          Atom(15)=1.0050
Atom(16)=0.9997          Atom(17)=1.0066
```

Bond Orders

```
Bond( 1, 2)=0.4228          Bond( 2, 3)=0.4433
Bond( 3, 4)=0.7287          Bond( 4, 5)=0.4581
Bond( 5, 6)=0.5914          Bond( 6, 7)=0.6841
Bond( 7, 8)=0.6541          Bond( 8, 9)=0.6541
Bond( 9,10)=0.6841          Bond(10, 5)=0.5914
Bond( 3,12)=0.3890          Bond(12,13)=0.6117
Bond(13,14)=0.6787          Bond(14,15)=0.6584
Bond(15,16)=0.6584          Bond(16,17)=0.6787
Bond(17,12)=0.6117          Bond( 2,11)=0.6728
```

α-Phenylcinnamanilide

```
PSI( 1) = 0.2779 ( 1) + 0.4217 ( 2) + 0.3239 ( 3)
        + 0.1756( 4)+ 0.1182( 5)+ 0.0610( 6)
        + 0.0354( 7)+ 0.0281( 8)+ 0.0354( 9)
        + 0.0610(10)+ 0.2181(11)+ 0.1126(12)
        + 0.0653(13)+ 0.0519(14)+ 0.0653(15)
        + 0.1126(16)+ 0.5750(17)+ 0.3097(18)
        + 0.1599(19)+ 0.0928(20)+ 0.0737(21)
        + 0.0928(22)+ 0.1599(23)+
PSI( 2) =-0.0134 ( 1) +-0.0163 ( 2) +-0.2686 ( 3)
        +-0.2606( 4)+-0.3091( 5)+-0.2123( 6)
        +-0.1615( 7)+-0.1457( 8)+-0.1615( 9)
        +-0.2123(10)+-0.3186(11)+-0.2188(12)
        +-0.1665(13)+-0.1502(14)+-0.1665(15)
        +-0.2188(16)+ 0.3074(17)+ 0.2917(18)
        + 0.2003(19)+ 0.1524(20)+ 0.1375(21)
        + 0.1524(22)+ 0.2003(23)+
PSI( 3) = 0.0560 ( 1) + 0.0599 ( 2) + 0.0993 ( 3)
        +-0.1337( 4)+-0.3763( 5)+-0.3228( 6)
        +-0.2921( 7)+-0.2821( 8)+-0.2921( 9)
        +-0.3228(10)+ 0.2795(11)+ 0.2398(12)
        + 0.2170(13)+ 0.2096(14)+ 0.2170(15)
        + 0.2398(16)+-0.0390(17)+-0.0878(18)
        +-0.0753(19)+-0.0681(20)+-0.0658(21)
        +-0.0681(22)+-0.0753(23)+
PSI( 4) =-0.3329 ( 1) +-0.3041 ( 2) +-0.1008 ( 3)
        +-0.0304( 4)+ 0.0427( 5)+ 0.0560( 6)
        + 0.0645( 7)+ 0.0674( 8)+ 0.0645( 9)
        + 0.0560(10)+ 0.1416(11)+ 0.1859(12)
        + 0.2141(13)+ 0.2237(14)+ 0.2141(15)
        + 0.1859(16)+-0.1853(17)+ 0.2083(18)
        + 0.2734(19)+ 0.3149(20)+ 0.3291(21)
        + 0.3149(22)+ 0.2734(23)+
PSI( 5) =-0.1811 ( 1) +-0.1017 ( 2) +-0.3220 ( 3)
        +-0.2751( 4)+-0.1076( 5)+ 0.0536( 6)
        + 0.1912( 7)+ 0.2450( 8)+ 0.1912( 9)
        + 0.0536(10)+-0.1259(11)+ 0.0627(12)
        + 0.2238(13)+ 0.2867(14)+ 0.2238(15)
        + 0.0627(16)+ 0.4305(17)+ 0.1346(18)
        +-0.0671(19)+-0.2394(20)+-0.3066(21)
        +-0.2394(22)+-0.0671(23)+
PSI( 6) = 0.6176 ( 1) + 0.2170 ( 2) +-0.1300 ( 3)
        +-0.2778( 4)+-0.2454( 5)+-0.0269( 6)
        + 0.2090( 7)+ 0.3094( 8)+ 0.2090( 9)
        +-0.0269(10)+-0.1148(11)+-0.0126(12)
        + 0.0978(13)+ 0.1448(14)+ 0.0978(15)
        +-0.0126(16)+-0.2431(17)+-0.1718(18)
        +-0.0188(19)+ 0.1463(20)+ 0.2166(21)
        + 0.1463(22)+-0.0188(23)+
PSI( 7) = 0.2294 ( 1) + 0.0342 ( 2) +-0.1779 ( 3)
        + 0.1616( 4)+ 0.3636( 5)+ 0.1281( 6)
```

```
          +-0.2164( 7)+-0.3760( 8)+-0.2164( 9)
          + 0.1281(10)+-0.4002(11)+-0.1410(12)
          + 0.2382(13)+ 0.4147(14)+ 0.2382(15)
          +-0.1410(16)+-0.0153(17)+-0.0275(18)
          +-0.0097(19)+ 0.0164(20)+ 0.0285(21)
          + 0.0164(22)+-0.0097(23)+
 PSI( 8) =-0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
          + 0.0000( 4)+-0.0000( 5)+ 0.0248( 6)
          + 0.0248( 7)+ 0.0000( 8)+-0.0248( 9)
          +-0.0248(10)+-0.0000(11)+ 0.4994(12)
          + 0.4994(13)+ 0.0000(14)+-0.4994(15)
          +-0.4994(16)+-0.0000(17)+ 0.0000(18)
          + 0.0003(19)+ 0.0003(20)+-0.0000(21)
          +-0.0003(22)+-0.0003(23)+
 PSI( 9) = 0.0000 ( 1) + 0.0000 ( 2) +-0.0000 ( 3)
          + 0.0000( 4)+ 0.0000( 5)+-0.4993( 6)
          +-0.4993( 7)+-0.0000( 8)+ 0.4993( 9)
          + 0.4993(10)+-0.0000(11)+ 0.0248(12)
          + 0.0248(13)+ 0.0000(14)+-0.0248(15)
          +-0.0248(16)+ 0.0000(17)+ 0.0000(18)
          + 0.0066(19)+ 0.0066(20)+-0.0000(21)
          +-0.0066(22)+-0.0066(23)+
 PSI(10) =-0.0000 ( 1) +-0.0000 ( 2) +-0.0000 ( 3)
          +-0.0000( 4)+ 0.0000( 5)+ 0.0066( 6)
          + 0.0066( 7)+-0.0000( 8)+-0.0066( 9)
          +-0.0066(10)+-0.0000(11)+-0.0006(12)
          +-0.0006(13)+ 0.0000(14)+ 0.0006(15)
          + 0.0006(16)+ 0.0000(17)+-0.0000(18)
          + 0.5000(19)+ 0.5000(20)+ 0.0000(21)
          +-0.5000(22)+-0.5000(23)+
 PSI(11) = 0.3141 ( 1) +-0.0714 ( 2) +-0.0430 ( 3)
          +-0.0202( 4)+ 0.0274( 5)+ 0.0207( 6)
          +-0.0114( 7)+-0.0295( 8)+-0.0114( 9)
          + 0.0207(10)+ 0.0583(11)+ 0.0441(12)
          +-0.0243(13)+-0.0628(14)+-0.0243(15)
          + 0.0441(16)+-0.4077(17)+ 0.4420(18)
          + 0.3339(19)+-0.1839(20)+-0.4760(21)
          +-0.1839(22)+ 0.3339(23)+
 PSI(12) =-0.2368 ( 1) + 0.1057 ( 2) + 0.4133 ( 3)
          + 0.3638( 4)+-0.2119( 5)+-0.2406( 6)
          + 0.0787( 7)+ 0.2841( 8)+ 0.0787( 9)
          +-0.2406(10)+-0.2407(11)+-0.2733(12)
          + 0.0894(13)+ 0.3228(14)+ 0.0894(15)
          +-0.2733(16)+-0.1474(17)+ 0.0687(18)
          + 0.0780(19)+-0.0255(20)+-0.0921(21)
          +-0.0255(22)+ 0.0780(23)+
 PSI(13) =-0.2869 ( 1) + 0.3738 ( 2) + 0.2957 ( 3)
          +-0.5367( 4)+-0.1332( 5)+ 0.2885( 6)
          + 0.0458( 7)+-0.3024( 8)+ 0.0458( 9)
          + 0.2885(10)+ 0.0734(11)+-0.1589(12)
          +-0.0252(13)+ 0.1666(14)+-0.0252(15)
          +-0.1589(16)+-0.1525(17)+-0.0303(18)
```

```
             + 0.0556(19)+ 0.0104(20)+-0.0687(21)
             + 0.0104(22)+ 0.0656(23)+
    PSI(14) =-0.2496 ( 1) + 0.4757 ( 2) +-0.1152 ( 3)
             + 0.0264( 4)+ 0.0913( 5)+-0.0546( 6)
             +-0.0419( 7)+ 0.0925( 8)+-0.0419( 9)
             +-0.0545(10)+-0.3978(11)+ 0.2377(12)
             + 0.1825(13)+-0.4030(14)+ 0.1825(15)
             + 0.2377(16)+-0.0825(17)+-0.2278(18)
             + 0.1361(19)+ 0.1045(20)+-0.2307(21)
             + 0.1045(22)+ 0.1361(23)+
    PSI(15) =-0.0000 ( 1) + 0.0000 ( 2) + 0.0000 ( 3)
             +-0.0000( 4)+ 0.0000( 5)+ 0.0001( 6)
             +-0.0001( 7)+-0.0000( 8)+ 0.0001( 9)
             +-0.0001(10)+-0.0000(11)+ 0.0035(12)
             +-0.0035(13)+-0.0000(14)+ 0.0035(15)
             +-0.0035(16)+-0.0000(17)+ 0.0000(18)
             +-0.5000(19)+ 0.5000(20)+ 0.0000(21)
             +-0.5000(22)+ 0.5000(23)+
    PSI(16) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
             + 0.0000( 4)+-0.0000( 5)+ 0.4954( 6)
             +-0.4954( 7)+-0.0000( 8)+ 0.4954( 9)
             +-0.4954(10)+-0.0000(11)+ 0.0678(12)
             +-0.0678(13)+-0.0000(14)+ 0.0678(15)
             +-0.0678(16)+ 0.0000(17)+ 0.0000(18)
             + 0.0006(19)+-0.0006(20)+ 0.0000(21)
             + 0.0006(22)+-0.0006(23)+
    PSI(17) = 0.0000 ( 1) +-0.0000 ( 2) + 0.0000 ( 3)
             + 0.0000( 4)+-0.0000( 5)+-0.0678( 6)
             + 0.0678( 7)+-0.0000( 8)+-0.0678( 9)
             + 0.0678(10)+ 0.0000(11)+ 0.4954(12)
             +-0.4954(13)+ 0.0000(14)+ 0.4954(15)
             +-0.4954(16)+-0.0000(17)+ 0.0000(18)
             + 0.0034(19)+-0.0034(20)+ 0.0000(21)
             + 0.0034(22)+-0.0034(23)+
    PSI(18) = 0.0591 ( 1) +-0.1244 ( 2) +-0.0740 ( 3)
             +-0.0345( 4)+ 0.1120( 5)+-0.0446( 6)
             +-0.0629( 7)+ 0.1139( 8)+-0.0629( 9)
             +-0.0446(10)+ 0.2405(11)+-0.0957(12)
             +-0.1349(13)+ 0.2446(14)+-0.1349(15)
             +-0.0957(16)+ 0.1901(17)+-0.4944(18)
             + 0.1967(19)+ 0.2774(20)+-0.5027(21)
             + 0.2774(22)+ 0.1967(23)+
    PSI(19) = 0.1168 ( 1) +-0.2584 ( 2) + 0.1004 ( 3)
             + 0.2928( 4)+-0.4556( 5)+ 0.1299( 6)
             + 0.2980( 7)+-0.4914( 8)+ 0.2980( 9)
             + 0.1299(10)+-0.1562(11)+ 0.0445(12)
             + 0.1022(13)+-0.1684(14)+ 0.1022(15)
             + 0.0445(16)+ 0.1204(17)+-0.1498(18)
             + 0.0427(19)+ 0.0980(20)+-0.1616(21)
             + 0.0980(22)+ 0.0427(23)+
    PSI(20) =-0.1387 ( 1) + 0.3720 ( 2) +-0.4106 ( 3)
             + 0.2647( 4)+-0.0349( 5)+-0.1030( 6)
```

```
          + 0.2082( 7)+-0.2475( 8)+ 0.2082( 9)
          +-0.1030(10)+ 0.0542(11)+ 0.1597(12)
          +-0.3229(13)+ 0.3838(14)+-0.3229(15)
          + 0.1597(16)+-0.0961(17)+ 0.0131(18)
          + 0.0299(19)+-0.0604(20)+ 0.0718(21)
          +-0.0604(22)+ 0.0299(23)+
PSI(21) =-0.0138 ( 1) + 0.0418 ( 2) + 0.0156 ( 3)
          + 0.0052( 4)+-0.0262( 5)+ 0.0241( 6)
          +-0.0228( 7)+ 0.0224( 8)+-0.0228( 9)
          + 0.0241(10)+-0.0738(11)+ 0.0724(12)
          +-0.0687(13)+ 0.0675(14)+-0.0687(15)
          + 0.0724(16)+-0.1087(17)+ 0.4389(18)
          +-0.4034(19)+ 0.3826(20)+-0.3757(21)
          + 0.3826(22)+-0.4034(23)+
PSI(22) = 0.0230 ( 1) +-0.0705 ( 2) + 0.0980 ( 3)
          + 0.1395( 4)+-0.3870( 5)+ 0.3312( 6)
          +-0.2993( 7)+ 0.2889( 8)+-0.2993( 9)
          + 0.3312(10)+-0.2721(11)+ 0.2328(12)
          +-0.2104(13)+ 0.2031(14)+-0.2104(15)
          + 0.2328(16)+ 0.0314(17)+-0.0697(18)
          + 0.0597(19)+-0.0539(20)+ 0.0521(21)
          +-0.0539(22)+ 0.0597(23)+
PSI(23) = 0.0729 ( 1) +-0.2400 ( 2) + 0.4283 ( 3)
          +-0.3248( 4)+ 0.3156( 5)+-0.1991( 6)
          + 0.1405( 7)+-0.1227( 8)+ 0.1405( 9)
          +-0.1991(10)+-0.4162(11)+ 0.2626(12)
          +-0.1852(13)+ 0.1617(14)+-0.1852(15)
          + 0.2626(16)+ 0.0606(17)+-0.0471(18)
          + 0.0297(19)+-0.0210(20)+ 0.0183(21)
          +-0.0210(22)+ 0.0297(23)+
```

Electron Densities

```
Atom( 1)=1.6260      Atom( 2)=0.6981      Atom( 3)=1.0439
Atom( 4)=0.8586      Atom( 5)=1.0052      Atom( 6)=0.9688
Atom( 7)=1.0005      Atom( 8)=0.9708      Atom( 9)=1.0005
Atom(10)=0.9688      Atom(11)=0.9955      Atom(12)=1.0064
Atom(13)=0.9997      Atom(14)=1.0049      Atom(15)=0.9997
Atom(16)=1.0064      Atom(17)=1.7873      Atom(18)=0.9611
Atom(19)=1.0373      Atom(20)=0.9982      Atom(21)=1.0276
Atom(22)=0.9982      Atom(23)=1.0373
```

Bond Orders

```
Bond( 1, 2)=0.6696        Bond( 2, 3)=0.4456
Bond( 3, 4)=0.7276        Bond( 4, 5)=0.4585
Bond( 5, 6)=0.5912        Bond( 6, 7)=0.6842
Bond( 7, 8)=0.6540        Bond( 8, 9)=0.6540
```

```
Bond( 9,10)=0.6842          Bond(10, 5)=0.5912
Bond( 3,11)=0.3887          Bond(11,12)=0.6118
Bond(12,13)=0.6787          Bond(13,14)=0.6584
Bond(14,15)=0.6584          Bond(15,16)=0.6787
Bond(16,11)=0.6118          Bond( 2,17)=0.4160
Bond(17,18)=0.2848          Bond(18,19)=0.6378
Bond(19,20)=0.6726          Bond(20,21)=0.6628
Bond(21,22)=0.6628          Bond(22,23)=0.6726
Bond(23,18)=0.6378
```