0.4% benzocyclooctatetraene. One recrystallization of 96.3% pure benzobicyclo[2.2.2]octatriene[32] (0.85 g) from a methanol (30 ml)–water (10 ml) mixture gave 0.53 g of pure (glpc) benzobicyclo-[2.2.2]octatriene (white needles, mp 65.6–66.5°). The ultraviolet and infrared spectra agreed with those reported previously.[12]

Pyrolysis of Phthalic Anhydride. Reagent grade phthalic anhydride (0.08 to 0.09 *M* in benzene or benzene-d_6) was pyrolyzed at 690° (3–5-sec contact time) to give 35–45% recovered phthalic anhydride. Phthalic anhydride was removed from the pyrolysate by washing with 10% aqueous sodium hydroxide. The following results were obtained for a typical run in benzene. In order of retention time, naphthalene (100),[33] biphenyl (358), acenaphthylene (6.3), and acenaphthene (4.7) were identified by infrared, ultraviolet, and mass spectra. In addition, the following products were tentatively identified by retention time: fluorenone (0.9),[34] *o*-terphenyl (1.5), 1-phenylnaphthalene (2.8), 2-phenylnaphthalene (1.4), and a poorly resolved peak containing fluoranthrene, *m*-terphenyl, and *p*-terphenyl (total, 3.9). Of the five other extremely small peaks and shoulders, four were unidentified and the fifth may have been triphenylene. Mass spectral data confirmed the assignments of fluorenone, terphenyl, phenylnaphthalene, and fluoranthene. In addition a peak, *m/e* 178, corresponding to anthracene was observed.

Pyrolysis of Benzocyclooctatetraene. A 0.098 *M* solution of benzocyclooctatetraene in benzene-d_6 was passed through the flow system under the usual pyrolysis conditions. In order of retention time the products were naphthalene (40),[33] biphenyl-d_{10}, an unknown (2), acenaphthylene (39), and acenaphthene (19). Benzocyclooctatetraene was not recovered. Ultraviolet spectra and low-voltage mass spectrometry confirmed the identity of the products. The biphenyl was contaminated with only trace amounts of d_5–d_7 species. Pyrolysis of benzocyclooctatetraene (4 mg) in an evacuated sealed tube for 2 hr at 352–370° produced a complex mixture which was not investigated further.

Pyrolysis of Benzobicyclo[2.2.2]octatriene. A 0.091 *M* solution of benzobicyclo[2.2.2]octatriene in benzene-d_6 was passed through the flow system under the usual pyrolytic conditions. The products were only naphthalene and biphenyl (containing only trace amounts of d_5–d_7 species) as analyzed by glpc and low-voltage mass spectrometry. Benzobicyclo[2.2.2]octatriene was not recovered. Pyrolysis of benzobicyclo[2.2.2]octatriene (7 mg) in an evacuated sealed tube[12] at 352–370° for 2 hr afforded essentially pure naphthalene.

Pyrolysis of Acenaphthylene. A 0.097 *M* solution of commercial acenaphthylene (14.5% acenaphthene, 85.5% acenaphthylene) in benzene-d_6 was passed through the flow system under the usual pyrolysis conditions. In addition to biphenyl-d_{10}, the pyrolysate contained a mixture of 10.5% acenaphthene and 89.8% acenaphthylene.

Pyrolysis of Acenaphthene. A 0.100 *M* solution of pure acenaphthene in benzene-d_6 was passed through the flow system under the usual pyrolytic conditions. In addition to biphenyl-d_{10}, the pyrolysate contained a mixture of 69% recovered acenaphthene and 29% acenaphthylene confirmed by ultraviolet spectra and low-voltage mass spectrometry. Two minor peaks were also observed. These products had retention times corresponding to naphthalene (0.6%) and the unknown (1.4%) from the pyrolysis of benzocyclooctatetraene.

Acknowledgment. The authors are indebted to Mr. Linwood B. Crider, B. F. Goodrich Company, for mass spectral analyses.

---

[32] A sample from another run which was contaminated with 3.7% benzocyclooctatetraene.

[33] Glpc, relative number of moles.

[34] Peak area relative to naphthalene (100).

Photoisomerization of Substituted Acrylic[1] Acids and Acrylamides to β-Lactones and β-Lactams

O. L. Chapman and W. R. Adams

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. Received October 5, 1967

Abstract: Irradiation of *cis*-α-phenylcinnamic acid in the presence of tetramethylethylene in degassed ether gives *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane. The mechanistic path of the reaction is shown to involve initial isomerization of *cis*-α-phenylcinnamic acid to the *trans*- and *cis*-β-lactones. The *cis*-β-lactone is isolated in 79% yield. Irradiation of the *cis*-β-lactone in the presence of tetramethylethylene gives *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (85%). Irradiation of either *trans*- or *cis*-stilbene in tetramethylethylene gives *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (95 and 93%, respectively). The photoisomerization of α,β-disubstituted acrylic acids to β-lactones is shown to be quite general when one substituent is phenyl. A qualitative study of the effect of *para* substituents in the α- and β-phenyl rings of *cis*-α-phenylcinnamic acid has revealed a striking dependence on the nature of the substituent. In the α-phenyl group electron-donating substituents facilitate reaction and electron-withdrawing substituents retard reaction. In the β-phenyl ring the substituent effect is reversed. Irradiation of *cis*-α-phenylcinnamamide and *cis*-α-phenylcinnamanilide in degassed benzene gives in each case the *cis*- and *trans*-β-lactams.

As one aspect of our study of the photocycloaddition reactions of compounds of the type $C_6H_5CH{=}CXY$,[2] we attempted to add tetramethylethylene to *cis*-α-phenylcinnamic acid. In this case, the reaction took a different course and led to a general investigation of the photochemistry of substituted acrylic acids and amides.

Irradiation of *cis*-α-phenylcinnamic acid (1) in the presence of tetramethylethylene in degassed solution[3]

---

[1] Photochemical Transformations. XXII. A preliminary account of this work has been published: O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **89**, 4243 (1967).

[2] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *J. Pure Appl. Chem.*, **9**, 585 (1964); O. L. Chapman, Abstracts, 20th National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 18–22, 1967, p 111.

[3] Irradiations of *cis*-α-phenylcinnamic acid in the presence of iodine[4a] and *cis*-α-phenylcinnamamide in the presence of oxygen[4b] give the corresponding phenanthrene derivatives in good yield. Oxidative cyclization of 3,4-dihydroxycinnamic acid to 6,7-dihydroxycoumarin has also been observed.[4c] These oxidative cyclizations have been

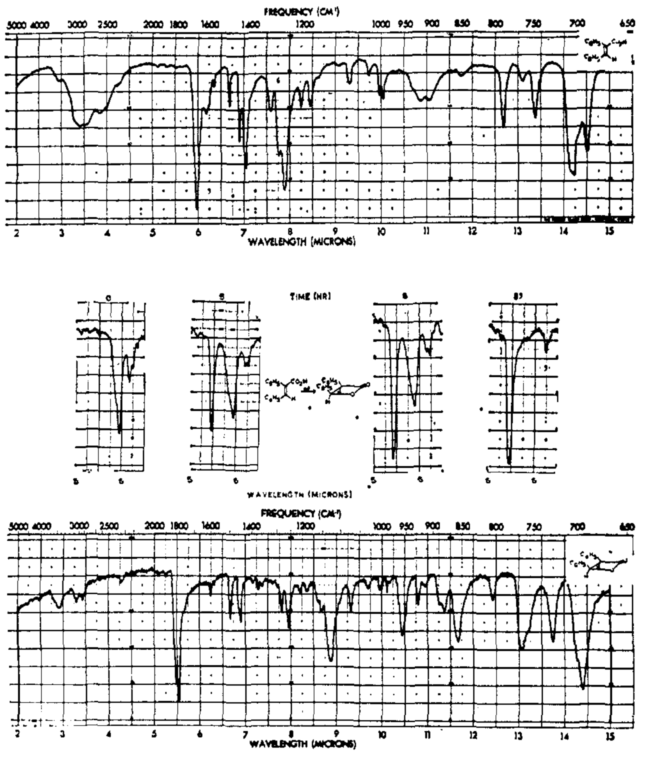
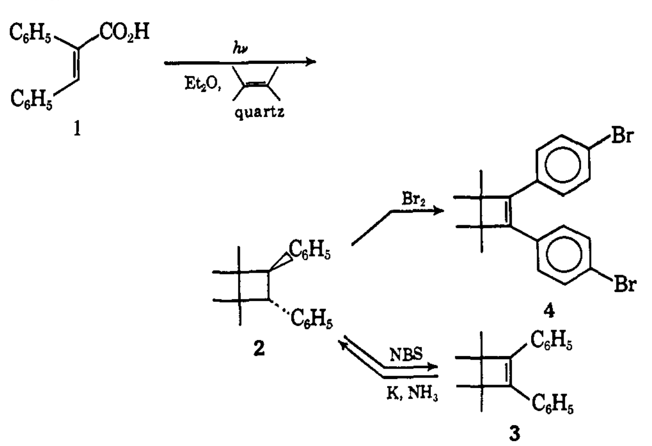
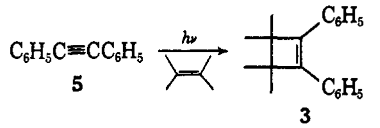


Figure 1. Top, infrared spectrum (KBr) of *cis*-α-phenylcinnamic acid. Middle, carbonyl region at 0-, 5-, 8-, and 21-hr irradiation. Bottom, infrared spectrum (KBr) of *cis*-2,3-diphenyl-3-propiolactone.

in ether gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (**2**) in 67% yield. The structure of the product was established by the mass spectrum, the nmr spectrum, and oxidation to 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**3**) which was synthesized independently. The mass spectrum established the molecular weight (264) and thus the loss of CO_2 in the formation of **2**. The nmr spectrum showed singlets at δ 7.07 (10 H, aromatic protons), 3.55 (2 H, methine protons), 1.12 (6 H, methyl protons), and 0.77 (6 H, methyl protons). Treatment of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane with bromine gave 1,2-di-(*p*-bromophenyl)-3,3,4,4-tetramethylcyclobutene (**4**, 32%) which showed the expected A_2B_2 (δ 7.14 and 7.39) pattern for the aromatic protons, a singlet for the four equivalent methyl groups (δ 1.26), and ultraviolet absorption consistent with a 1,2-diarylcyclobutene structure (λ_{max} 240 (ε 15,600) and 289 mμ (ε 10,100)). Oxidation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane with N-bromosuccinimide in carbon tetrachloride gave directly the desired 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**3**) in 80% yield. This product showed aromatic protons (δ 7.25, m) and four equivalent methyl groups (δ 1.32, s); λ_{max} 225 (ε 10,000) and 278 mμ (ε 6300); and mass spectrometric molecular weight 262. An authentic sample of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene was prepared in 30% yield by photocycloaddition of diphenylacetylene (**5**) to tetramethylethylene. Reduction of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**3**) with potassium in liquid ammonia gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (**2**, 95%). This reduction should give the more stable (*trans*) isomer. Confirmation of the *trans* stereochemistry is available by comparison of the chemical shift of the methine protons (δ 3.55) of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane with the chemical shifts of the benzylic methine protons of *cis*- (δ 3.94)[5] and *trans*-1,2-diphenylcyclobutanes (δ 3.55)[5] and by the fact that the aromatic protons in *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane appear as a singlet. In *trans*-1,2-diphenylcyclopentane the aromatic protons give rise to a singlet while the aromatic protons in *cis*-1,2-diphenylcyclopentane give rise to a complex multiplet.[6]





All attempts to produce *cis*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane by reduction of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**3**) catalytically (Pt, Pd–C) at various pressures or using diimide failed. This is presumed to be due to steric effects of the four methyl groups.

In an effort to gain insight to the mechanism of the transformation *cis*-α-phenylcinnamic acid (**1**) was irradiated in degassed benzene in the absence of tetramethylethylene. The progress of the reaction was monitored by the infrared spectrum. The carbonyl absorption of the carboxyl group (5.95 μ) gradually diminished during the course of the reaction and was replaced by an intense band at 5.45 μ (Figure 1). The nuclear magnetic resonance spectrum of the crude product showed, besides aromatic protons, two AB patterns of different intensity (δ_A 5.12, δ_B 5.68, J_{AB} = 7.0 cps; $\delta_{A'}$ 4.59, $\delta_{B'}$ 5.37, $J_{A'B'}$ = 4.5 cps). The area ratio for the two AB patterns was approximately 3:1. Crystallization of the crude product gave *cis*-2,3-diphenyl-3-propiolactone (**6**) in 79% yield. The infrared spectrum of the product showed a 5.45-μ band characteristic of the β-lactone carbonyl. The nmr spectrum showed aromatic protons (δ 7.10, 10 H, m) and two methine protons (δ_A 5.30, δ_B 5.84, J_{AB} = 7.0 cps). Element analysis and the mass spectrum showed that the product was an isomer of *cis*-α-phenylcinnamic acid. The

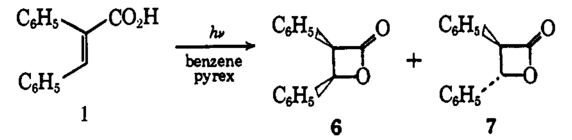
---

averted in the present work by removing oxygen from the solutions prior to irradiation.

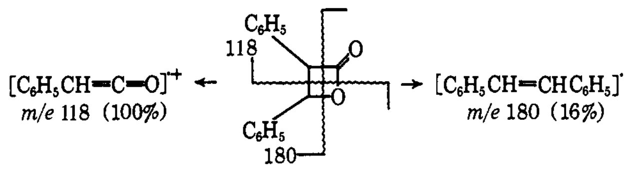
(4) (a) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964); (b) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964); (c) J. Kagan, *J. Am. Chem. Soc.*, **88**, 2617 (1966).

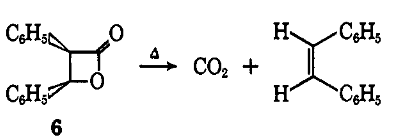
(5) R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 28 (1967).

(6) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

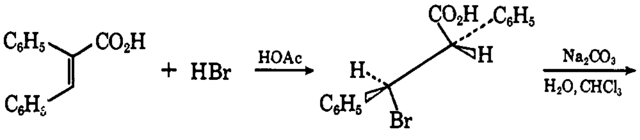


fragmentations of the parent ion, *m/e* 118 (100%) and *m/e* 180 (16%), are consistent with the β-lactone structure. The *cis* stereochemistry is assigned on the basis of thermal decomposition of the β-lactone to carbon dioxide and *cis*-stilbene.[7] The minor product which is apparent in the nmr spectrum of the crude product from the irradiation of *cis*-α-phenylcinnamic acid (1) is tentatively identified as *trans*-2,3-diphenyl-3-propiolactone (7). Attempts to prepare this substance by an alternate route were only partially successful. Solvolysis of *erythro*-3-bromo-2,3-diphenylpropanoic acid (8) gave *trans*-2,3-diphenyl-3-propiolactone in low yield. The product proved quite labile and was easily converted to *trans*-stilbene. The nmr spectrum of *trans*-2,3-diphenyl-3-propiolactone in solutions which still contained *trans*-stilbene showed the characteristic AB pattern (δ_A 4.62, δ_B 5.39, J_{AB} = 5.0 cps) and the characteristic β-lactone carbonyl absorption at 5.46 μ. These observations leave little doubt that the minor product is *trans*-2,3-diphenyl-3-propiolactone (7).

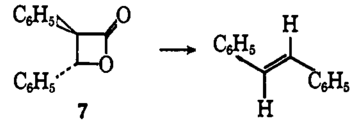




6



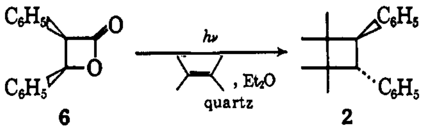
8



7

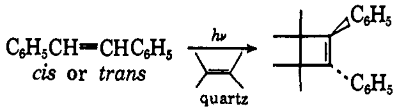
Irradiation of *trans*-α-phenylcinnamic acid in benzene gave *cis*-2,3-diphenyl-3-propiolactone as the only isolated product. The yield was substantially lower than that from *cis*-α-phenylcinnamic acid, and the reaction was slower. The lower yield of lactone is probably due to product destruction in the longer irradiation.

Irradiation of *cis*-2,3-diphenyl-3-propiolactone (6) in a degassed ether solution containing tetramethylethylene gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (2) in 85% yield. This result shows that *cis*-2,3-diphenyl-3-propiolactone is a plausible intermediate in the formation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane.



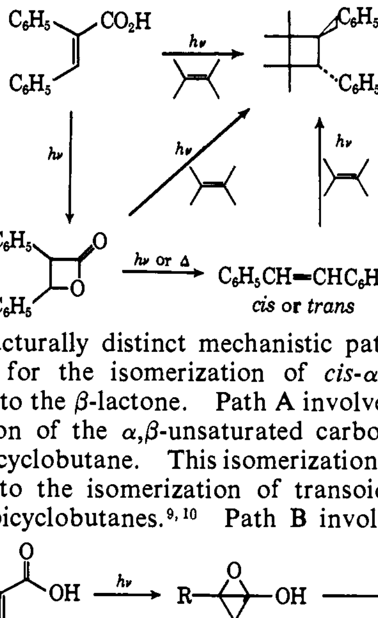
Irradiation of *cis*-2,3-diphenyl-3-propiolactone in ether in the absence of tetramethylethylene gave a complex mixture from which phenanthrene was isolated. This process presumably involves loss of carbon dioxide and formation of *cis*- and/or *trans*-stilbene. The isomeric stilbenes are interconverted under the conditions of the experiment, and *cis*-stilbene is known to undergo cyclization to phenanthrene.[8]

In the formation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (2) from *cis*-α-phenylcinnamic acid (1) and tetramethylethylene, it is not clear whether the excited *cis*-β-lactone loses carbon dioxide and gives a ground-state stilbene molecule or loses carbon dioxide and gives an excited stilbene which can add to tetramethylethylene without a separate excitation. In any event, irradiation of either *cis*- or *trans*-stilbene in tetramethylethylene gives only *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane. The yields of the adduct are excellent in each case, 95% from *trans*-stilbene and 93% from *cis*-stilbene. The addition requires a significantly longer irradiation time for *cis*-stilbene (44 hr) than for *trans*-stilbene (19 hr).

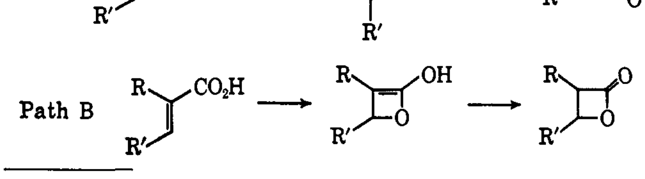


The processes responsible for formation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane from *cis*-α-phenylcinnamic acid are summarized in Chart I.

Chart I



Two structurally distinct mechanistic paths may be considered for the isomerization of *cis*-α-phenylcinnamic acid to the β-lactone. Path A involves an initial isomerization of the α,β-unsaturated carbonyl system to an oxabicyclobutane. This isomerization is formally analogous to the isomerization of transoid 1,3-butadienes to bicyclobutanes.[9,10] Path B involves forma-



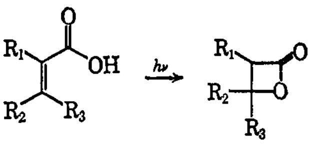
---

[7] Thermal elimination of carbon dioxide from β-lactones has been shown to be stereospecific: (a) D. S. Noyce and E. H. Banitt, *J. Org. Chem.*, 31, 4043 (1966); (b) P. G. Cleveland, Ph.D. Thesis, Iowa State University of Science and Technology, 1967.

[8] F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 247.

[9] W. G. Dauben and F. G. Willey, *Tetrahedron Letters*, 893 (1962).

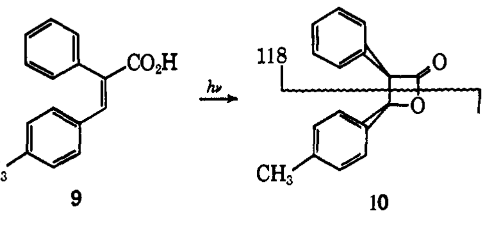
Table I. β-Lactone Formation from Arylacrylic Acids[a]



Acid	λ_{max} (ε)[b]	Irradiation time, hr[c]	β-Lactone *trans/cis* ratio[d]
$R_1 = R_2 = C_6H_5$; $R_3 = H$	286 (16,000)	21	0.3
$R_1 = p\text{-}CH_3C_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	284 (18,000)	23.5	0.9
$R_1 = C_6H_5$; $R_2 = p\text{-}CH_3C_6H_4$; $R_3 = H$	297 (20,000)	28.5	0.3
$R_1 = p\text{-}ClC_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	290 (17,000)	72[f]	0.6
$R_1 = C_6H_5$; $R_2 = p\text{-}ClC_6H_4$; $R_3 = H$	296 (20,000)	26	0.8
$R_1 = p\text{-}FC_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	288 (17,000)	41	1.0
$R_1 = p\text{-}CNC_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	293 (16,000)	72[f]	All *cis*
$R_1 = C_6H_5$; $R_2 = p\text{-}CNC_6H_4$; $R_3 = H$	289 (20,000)	5	0.7
$R_1 = p\text{-}NO_2C_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	293 (sh) (16,000)	72	No lactone
$R_1 = C_6H_5$; $R_2 = p\text{-}NO_2C_6H_4$; $R_3 = H$	310 (16,000)	36[f]	1.0
$R_1 = p\text{-}CH_3OC_6H_4$; $R_2 = C_6H_5$; $R_3 = H$	318 (sh) (7000)	10.5	1.0
$R_1 = C_6H_5$; $R_2 = p\text{-}CH_3OC_6H_4$; $R_3 = H$	313 (22,000)	96	No lactone
$R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = H$	265 (6650)[e]	16 days[f]	All *cis*
$R_1 = C_6H_5$; $R_2 = CH_3$; $R_3 = H$	240 (sh) (4700)[e]	4[f,g]	All *trans*
$R_1 = R_2 = R_3 = C_6H_5$	292 (10,200)[e]	12	Only one β-lactone possible

[a] The acids (2.0 g) in degassed benzene (250 ml) were irradiated in a Pyrex vessel with a Hanovia Type A 550-W lamp unless otherwise noted. The solutions were degassed with nitrogen throughout the irradiation. [b] The ultraviolet spectra were taken in spectroscopic grade cyclohexane unless otherwise noted. [c] The time required to completely remove the infrared carbonyl absorption of the starting acid. [d] Determined by integration of the nmr spectra of the crude products. [e] The ultraviolet spectrum was taken in 95% ethanol. [f] Reaction did not go to completion. [g] Irradiation of the acid (2.0 g) was carried out in ether solution using a quartz vessel. The solutions were degassed with nitrogen throughout the irradiation and were irradiated with a Hanovia Type A 550-W lamp.

tion of a hydroxyoxetene. This process could involve either the carbonyl oxygen or the hydroxyl oxygen. In the case of *cis*-α-phenylcinnamic acid ($R = R' = C_6H_5$) the two paths are indistinguishable in terms of the β-lactone structure. In the case of *cis*-α-phenyl-*p*-methylcinnamic acid ($R = C_6H_5$; $R' = p\text{-}C_6H_4CH_3$), however, the two paths predict different products. Irradiation of *cis*-α-phenyl-*p*-methylcinnamic acid (**9**) gives *cis*-2-phenyl-3-(*p*-tolyl)-3-propiolactone (**10**, 21% yield). The *trans*-β-lactone is also formed but was not isolated. This result (and others to be described below) is consistent only with path B. The mass spectrum of the product shows a fragment ion at *m/e* 118 (40.6%) which is due to phenylketene radical cation. No significant fragment ion (*m/e* 132) corresponding to *p*-tolylketene radical cation is observed.



9 **10**

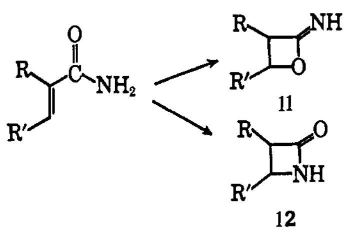
Questions naturally arise about the generality of the photoisomerization of α,β-unsaturated acids to β-lactones. We have found that a variety of α-substituted cinnamic and α-substituted crotonic acids give β-lactones on irradiation. β-Lactones have not been observed in the irradiation of cinnamic acid or crotonic acid. The results of the survey irradiations are summarized in Table I. The *cis*-2,3-disubstituted 3-propiolactones from the first four acids listed in Table I have been isolated in crystalline form and fully characterized. The β-lactones in the other instances were characterized only by their spectroscopic properties. The β-lactones (especially the *trans*-2,3-disubstituted isomers) proved to be rather labile. Other workers have encountered similar difficulties in isolating substituted β-lactones.[7a] The infrared spectra of the crude products showed characteristic β-lactone carbonyl absorption and the nmr spectra showed the methine protons of both *cis*- and *trans*-2,3-disubstituted 3-propiolactones. The *trans*:*cis* ratios were determined approximately by integration of the methine proton resonances.

Formation of β-lactones seems to require an α substituent which in the cases cited in Table I has been either a phenyl group, a substituted phenyl group, or a methyl group. The presence of β substituent on the α,β-unsaturated acid also facilitates photoisomerization to the β-lactone. A substantial substituent effect is apparent in both the α-(*p*-X-phenyl)cinnamic acids and the α-phenyl-*p*-X-cinnamic acids. Electron-releasing groups (methoxyl) in the α-phenyl group facilitate the photoisomerization while electron-withdrawing groups (cyano) retard the photoisomerization. In the β-phenyl group the effects are stronger and are reversed. A methoxyl group retards the reaction to such an extent that no β-lactone is observed, while a cyano group facilitates the reaction.

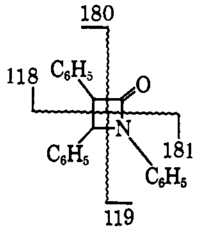
The photoisomerization of α-substituted cinnamic and crotonic acids to β-lactones suggested that irradiation of the corresponding amides ought to give either iminolactones (**11**) or β-lactams (**12**). The product of such a reaction should give a clue to one aspect of the cyclization, *i.e.*, whether the carbonyl oxygen or the nitrogen is involved in the cyclization.

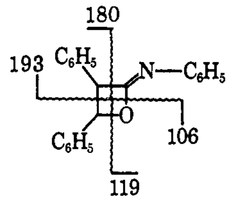
---

(10) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).

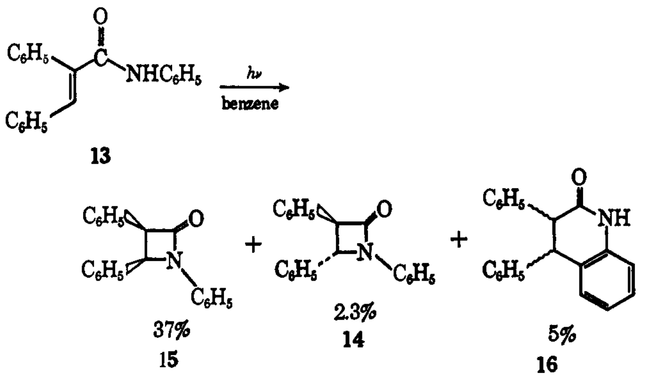


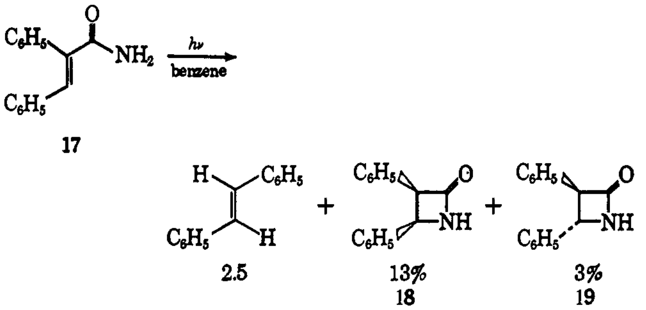
Irradiation of *cis*-α-phenylcinnamanilide (**13**) in benzene[3] for 23 hr gave *trans*-1,3,4-triphenyl-2-azetidinone (**14**, 2.3%), *cis*-1,3,4-triphenyl-2-azetidinone (**15**, 37%), and a third substance which is tentatively identified as 3,4-diphenyl-3,4-dihydrocarbostyril (**16**, 5%). The identity of *trans*-1,3,4-triphenyl-2-azetidinone (**14**) was confirmed by comparison with an authentic sample prepared by addition of phenylketene to benzalaniline.[11] *cis*-1,3,4-Triphenyl-2-azetidinone had the expected spectral characteristics including carbonyl absorption ($CHCl_3$) at 5.73 μ. The mass spectra of the *trans*- and *cis*-β-lactams gave the expected parent ion at *m*/*e* 299 and fragment ions at 180 (*trans*, 100%; *cis*, 86%) and 181 (*trans*, 33.8%; *cis*, 100%). The fragmentation patterns exclude the iminolactone structure for the products and are in accord with expectation for the β-lactam structures.[12a,b,d] It has been established by Singer and Davis[12a] that β-lactams and iminolactones give easily distinguishable mass spectra. Attempts to pyrolyze the β-lactams to the corresponding stilbenes were not successful. The stereochemical assignments are based on the *trans* assignment made earlier. The smaller J_{AB} (3.0 cps) for *trans*-methine protons as compared to *cis*-methine protons (7.0 cps) is in accord with expectation based on the β-lactone nmr spectra and literature values for *trans*-3,4-disubstituted β-lactams.[12c]



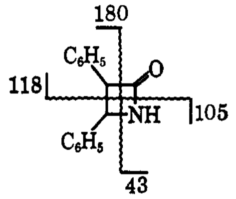


The third product isolated from the irradiation of *cis*-α-phenylcinnamanilide is tentatively identified as 3,4-diphenyl-3,4-dihydrocarbostyril. The mass spectrum of the product shows a parent ion at *m*/*e* 299 (100%) which establishes that it is an isomer of the starting anilide. The lactam carbonyl absorption (KBr) is at 5.98 μ. The nmr spectrum consists of an N–H proton singlet at δ 9.35, a multiplet centered at 7.10 (aromatic protons), and an AB pattern (δ_A 4.17, δ_B 4.43, J_{AB} = 6.0 cps). Cyclization of *cis*-α-phenylcinnamanilide to 3,4-diphenyl-3,4-dihydrocarbostyril on irradiation is analogous to other nonoxidative photocyclizations of acrylanilides observed by Cleveland.[13]





Irradiation of *cis*-α-phenylcinnamamide (**17**) in degassed benzene for 70 hr gave a complex mixture from which it was possible to isolate *trans*-stilbene (2.5%), *cis*-3,4-diphenyl-2-azetidinone (**18**, 13%), *trans*-3,4-diphenyl-2-azetidinone (**19**, 3%), and an unidentified product (6.2%). The mass spectra of the two isomers show parent ions at *m*/*e* 223 and fragment ions at *m*/*e* 180 (*trans*, 100%; *cis*, 24.8%) and 118 (*trans*, 69%; *cis*, 100%) in accord with expectation for the β-lactam structures. It is worth noting that in the fragmentation of the N-phenyl β-lactams the charge goes to the $C_6H_5CH{=}NC_6H_5$ moiety rather than to the phenylketene moiety while in the unsubstituted β-lactams the charge goes to the phenylketene moiety rather than the $C_6H_5CH{=}NH$ moiety.



The intense, long-wavelength ultraviolet absorption bands of the cinnamic acids together with the position assigned to the n → π* transition of acrylic acids[14,15] leaves little doubt that the lowest excited singlet state of the cinnamic acids is π,π* in configuration. The multiplicity of the excited state responsible for β-lactone formation is not known. The formation of the β-lactones is probably not related to the addition of alcohols to olefins reported by Kropp[16] and Marshall[17] because these additions occur only with cyclic olefins.

---

(11) W. Kirmse and L. Horner, *Chem. Ber.*, **89**, 2759 (1956); R. Pfleger and A. Jäger, *ibid.*, **90**, 2460 (1957); B. Kurtev, N. Mollov, Ek. Simova, and J. Stefanovski, *Compt. Rend. Acad. Bulgare Sci.*, **13**, 167 (1960).

(12) (a) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 940 (1967); (b) H. E. Audier, M. Fetizon, H. B. Kagan, and J. L. Luche, *Bull. Soc. Chim. France*, 2297 (1967); (c) H. B. Kagan, J. J. Basselier, and J. L. Luche, *Tetrahedron Letters*, 941 (1964); (d) H. E. Audier, M. Fetizon, H. B. Kagan, and J. L. Luche, *Bull. Soc. Chim. France*, 2297 (1967).

(13) P. G. Cleveland, Ph.D. Thesis, Iowa State University of Science and Technology, 1967; P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967).

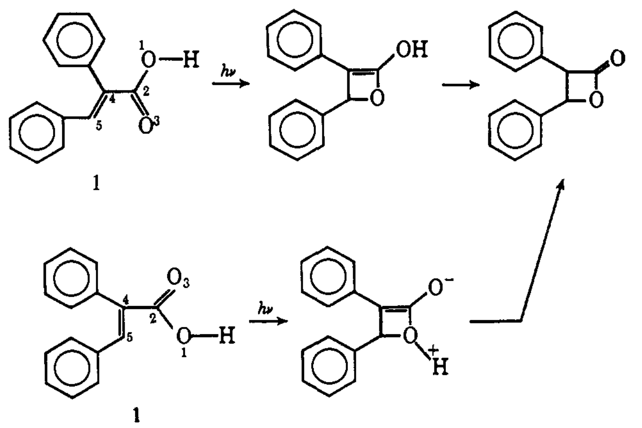
(14) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).

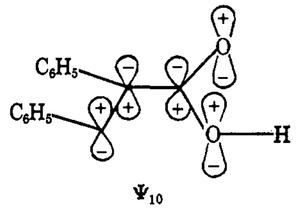
(15) For a recent discussion of the electronic excitation of carboxylic acids see H. H. Jaffé, D. L. Beveridge, and M. Orchin, *J. Chem. Educ.*, 383 (1967).

(16) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

(17) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

The formation of the β-lactones (and β-lactams) is best viewed as a cyclization process. Such processes belong to the general class of electrocyclic reactions.[18] The symmetry of the highest occupied molecular orbital in the excited state of α-phenylcinnamic acids and amides is such that two disrotatory closures leading to cyclized products are available. The dangers of basing arguments solely on the highest occupied molecular orbitals have been pointed out.[19,20] Calculation of the 1,5 and 3,5 bond orders for the acids shows that both are antibonding in the ground state. Both bond orders increase on excitation but are still antibonding in the first π,π* excited state.[21] The increase in 1,5 and 3,5 bonding is due to the fact that Ψ_9 from which an electron is excited is 1,5 and 3,5 antibonding while Ψ_{10} is 1,5 and 3,5 bonding. It is probably artificial to make a distinction between the two oxygens of the acid since most carboxylic acids exist as hydrogen-bonded dimers in benzene solution. Calculations in which equivalent parameters are used for the two oxygen atoms also give over-all negative 1,5 bond orders for the ground and excited states but show an increase in bonding on promotion of an electron from Ψ_9 to Ψ_{10}.

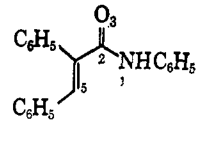


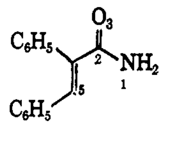


Ψ_{10}

The stereochemistry of the products is determined in the protonation of the hydroxyoxetene. The predominance of *cis* products suggests that this is a kinetically controlled protonation.

In the case of α-phenylcinnamanilide and α-phenylcinnamamide the distinction between 1,5 and 3,5 bonding is real. HMO calculations give negative 1,5 and 3,5 bond orders for the ground states of α-phenylcinnamanilide and α-phenylcinnamamide. In the case of α-phenylcinnamanilide the 3,5 bond order decreases on excitation (becomes more negative) while the 1,5 bond order increases. In α-phenylcinnamamide both 1,5 and 3,5 bond orders increase although the 3,5 bond is still favored substantially. The simple calculations thus correctly predict β-lactam formation from α-phenylcinnamanilide but incorrectly predict iminolactone from the α-phenylcinnamamide.





Experimental Section

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 using tetramethylsilane as an internal standard. Chemical shifts are reported as δ values.

The mass spectra were recorded at 70 eV on an Atlas CH4 mass spectrometer using a direct solid inlet system (TO-4 ion source). Mass spectra are reported as *m/e* (per cent of base).

Irradiation of *cis*-α-Phenylcinnamic Acid in the Presence of Tetramethylethylene. A solution of *cis*-α-phenylcinnamic acid (4.0 g, 0.018 mol), tetramethylethylene (10 g, 0.12 mol), and ether (250 ml) was purged with purified nitrogen for 0.5 hr.[23] The solution was irradiated in a quartz immersion irradiation apparatus using a Hanovia Type A 550-W 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, and 14.28 μ. The solid was dissolved in Skellysolve B and poured onto a 2.5 × 20 in. column prepared with 200 g of silica gel. The column was eluted with 500 ml of Skellysolve B, which upon evaporation gave a white solid (3.30 g). Recrystallization from hexane yielded *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (3.13 g, 67%), mp 105–106°. The nmr spectrum showed aromatic protons (δ 7.07, 10 H, s), methine protons (δ 3.55, 2 H, s), and methyl protons (δ 1.12, 6 H, s; δ 0.77, 6 H, s). The mass spectrum exhibited a very weak parent ion at *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 mol, scintillation grade, Matheson Coleman and Bell) and tetramethylethylene (5.0 g, 0.06 mol) 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-W 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, and 14.28 μ. The solid was dissolved in Skellysolve B and poured onto a 2.5 × 20 in. column prepared with 70 g of alumina (Woelm, neutral activity I). The column was eluted with 400 ml of Skellysolve B which upon evaporation gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (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 mixture melting point determination showed no depression.

B. A solution of *trans*-stilbene (500 mg, 0.0028 mol) 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

---

(18) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).

(19) H. E. Zimmerman, *ibid.*, 88, 1566 (1966).

(20) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, 87, 2046 (1965).

(21) Other cases have been reported where calculations show net antibonding between two atoms (but strong bonding in the highest occupied molecular orbital) of the excited state, and photochemical bond formation is observed.[19,22]

(22) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, 86, 1436 (1964); H. E. Zimmerman, *Pure Appl. Chem.*, 9, 493 (1964).

(23) Purging with purified nitrogen reduced the oxygen concentration to a sufficiently low level to preclude oxidative cyclizations. This procedure was more convenient for preparative work than freeze–thaw degassing.

evaporated giving a yellow solid (0.74 g). Recrystallization from hexane gave 1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (0.70 g, 95%, mp 105–106°). The infrared spectrum (KBr) was identical with 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 mol, 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 (0.68 g, 93%, mp 106–107°). The infrared spectrum (KBr) was identical with that of the photoadduct obtained from the photolysis of *trans*-stilbene in tetramethylethylene.

Irradiation of *cis*-α-Phenylcinnamic Acid. A solution of *cis*-α-phenylcinnamic acid (4.0 g, 0.018 mol) 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-W 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 (5.95 μ) continually diminished throughout the course of the reaction and was replaced by a band at 5.42 μ. 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, δ_A 5.12, δ_B 5.68 (J_{AB} = 7.0 cps); $\delta_{A'}$ 4.59, $\delta_{B'}$ 5.37 ($J_{A'B'}$ = 4.5 cps), in the ratio of about 3:1, respectively. Recrystallization from benzene–pentane gave *cis*-2,3-diphenyl-3-propiolactone (3.10 g, 79%, mp 120–121°). The nmr spectrum showed aromatic protons (δ 6.90–7.20, 10 H) and methine protons (δ_A 5.30, δ_B 5.84, J_{AB} = 7.0 cps, 2 H). The infrared spectrum showed carbonyl absorption at 5.45 μ (KBr). The mass spectrum exhibited a very weak parent ion at *m/e* 224 and fragment ions at *m/e* 181 (2.1), 180 (16.4), 179 (12.0), 178 (7.7), 177 (1.4), 176 (0.8), 166 (1.9), 165 (15.7), 153 (0.9), 152 (4.3), 151 (2.5), 119 (8.9), 118 (100), 90 (25.4), 88 (21.2), 78 (5.0), 76 (7.8), and 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 Photoisomerization of *cis*- and *trans*-2,3-Diphenyl-3-propiolactones. A mixture of *cis*- and *trans*-β-lactones obtained from the irradiation of *cis*-α-phenylcinnamic acid in the ratio of 31:12, respectively, was dissolved in benzene, placed in a Pyrex vessel, and irradiated using a Hanovia Type A 550-W 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-lactones was unchanged.

Irradiation of *trans*-α-Phenylcinnamic Acid. A solution of *trans*-α-phenylcinnamic acid (2.0 g, 0.009 mol) 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-W lamp. The progress of the reaction was followed by removing aliquots and observing the loss of the carbonyl absorption of the acid (5.90 μ) and the appearance of the lactone carbonyl (5.42 μ) 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 spectrum (KBr) was identical with that of *cis*-2,3-diphenyl-3-propiolactone obtained from the irradiation of *cis*-α-phenylcinnamic acid.

Thermal Decomposition of *cis*-2,3-Diphenyl-3-propiolactone. A. The β-lactone (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. The reaction was carried out in vertical glass column packed with glass helices and heated by an electric 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 was 280° (measured with a thermocouple). The system was flushed with nitrogen for 1 hr, and the material was allowed to drop onto 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*-2,3-Diphenyl-3-propiolactone. A solution of the β-lactone (0.91 g, 0.004 mol) 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-W lamp for 7 hr. The progress of the reaction was monitored by following the loss of the carbonyl absorption band of the lactone (5.45 μ) 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 that at least five 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.

The following solvents were used for elution: Skellysolve B (fractions 1–16), 5% benzene in Skellysolve B (17–31), 50% benzene in Skellysolve B (32–40), benzene (41–45), ether (46–50). The appropriate fractions (analyzed by tlc) were combined, and the solvent was 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.[24] mp 98–99°); infrared (KBr) 6.87, 7.00, 7.70, 8.05, 9.78, 10.54, 11.46, 12.22, 13.65, and 14.03 μ. The infrared spectrum was identical with 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, and 9.25 μ. Fractions 5–13 were void of carbonyl absorption but showed bands at 6.25, 6.75, 6.92, and 9.25 μ. These fractions were not characterized.

Irradiation of *cis*-2,3-Diphenyl-3-propiolactone in the Presence of Tetramethylethylene. A solution of β-lactone (1.0 g, 0.0045 mol) and 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, and 14.27 μ. The solid was dissolved in a minimum volume of 1:1 Skellysolve B–benzene and chromatographed on a silica gel column. Elution with Skellysolve B gave *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane which was recrystallized from hexane (1.00 g, 85%, mp 106–107°). The infrared spectrum (KBr) was superimposable on that of the photoadduct obtained from the photolysis of *trans*-stilbene in the presence of tetramethylethylene.

Reaction of *trans*-1,2-Diphenyl-3,3,4,4-tetramethylcyclobutane with Bromine. A solution of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (1.0 g, 0.0038 mol) and bromine (2.3 g, 0.0145 mol) 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 (0.5 g, 32%, mp 103–104°); infrared (KBr) 3.40, 6.75, 9.37, 9.52, 9.57, 11.97, 12.07, 12.25, and 12.82 μ; nmr (CCl_4) 8-proton A_2B_2 pattern, δ_A 7.14, δ_B 7.39 ($J_{AB} \sim$ 8.5 cps), 12-proton singlet, δ 1.26 (methyl protons); λ_{max} (95% ethanol) 289 mμ (ϵ 10,000) and 240 mμ (ϵ 15,600). The mass spectrum exhibited an intense parent ion (*m/e* 418, 50% of base) and a P + 2 ion (*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 with N-Bromosuccinimide. The *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane (1.4 g, 0.005 mol), N-bromosuccinimide (1.5 g, 0.008 mol), 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

---

[24] L. F. Fieser and E. B. Herschberg, *J. Am. Chem. Soc.*, 57, 1508 (1935).

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 (1.1 g, 80%, mp 92–93°). The nmr spectrum showed aromatic protons (δ 7.25, m) and four equivalent methyl groups (δ 1.32, s). 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 6300) and 225 mμ (ε 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 diphenylacetylene (2.0 g, 0.011 mol) and tetramethylethylene (5.0 g, 0.059 mol) 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 five singlets at δ 3.55, 1.50, 1.30, 1.10, and 0.80. The residue was dissolved in Skellysolve B, alumina (Woelm, activity I, 4.0 g) was added, and the solvent was removed under reduced pressure. The adsorbed residue was placed on a 2.5 × 20 in. column, prepared with alumina (Woelm, activity I, 150 g), and chromatographed. Elution with Skellysolve B gave 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene which was recrystallized from methanol (0.8 g, 30%). The infrared spectrum (KBr) was superimposable on that of the olefin prepared by oxidation of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane. A mixture melting point determination gave no depression.

Reduction of 1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene. The procedure used is similar to that of Johnson.[25] 1,2-Diphenyl-3,3,4,4-tetramethylcyclobutene (460 mg, 0.0017 mol) 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 g-atom) 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 (440 mg, 95%, mp 105–106°). The infrared spectrum (KBr) was identical with that of *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane obtained from the photoaddition of *cis*-α-phenylcinnamic acid to tetramethylethylene. A mixture melting point determination gave no depression.

***erythro*-3-Bromo-2,3-diphenylpropanoic Acid.** *erythro*-3-Bromo-2,3-diphenylpropanoic acid was prepared following the procedure of Hagman.[26] A solution of *cis*-α-phenylcinnamic acid (10.0 g, 0.045 mol) 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 *erythro*-3-bromo-2,3-diphenylpropanoic acid (10.4 g, 73%, mp 201–202°); infrared spectrum (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, and 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*-2,3-Diphenyl-3-propiolactone.** A solution of *erythro*-3-bromo-2,3-diphenylpropanoic acid (1.0 g, 0.0033 mol) and sodium carbonate (0.13 g, 0.003 mol) 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 showed absorption bands at 5.46, 6.27, 6.70, 6.90, 9.36, 10.41, 13.10, and 14.50 μ. The nmr ($CDCl_3$) exhibited an aromatic multiplet at δ 7.55–7.10, a vinyl proton singlet (*trans*-stilbene) at δ 7.05, and an AB proton pattern, δ_A 4.62, δ_B 5.39 (J_{AB} = 4.5 cps). The β-lactone:*trans*-stilbene ratio was 3:7.

***cis*-α-(*p*-Tolyl)cinnamic Acid.** A mixture of *p*-tolylacetic acid (14.0 g, 0.093 mol), benzaldehyde (14.0 g, 0.132 mol), 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, and 14.42 μ; nmr ($CDCl_3$) δ 11.15 (1 H, m), 7.90 (1 H, s), 7.30–6.95 (9 H, m), 2.35 (3 H, s); λ_{max} (cyclohexane) 284 mμ (ε 18,000), 226 (24,000), and 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.** A mixture of phenylacetic acid (7.5 g, 0.055 mol), *p*-methylbenzaldehyde (8.0 g, 0.067 mol), 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, and 14.25 μ; nmr ($CDCl_3$) δ 11.09 (1 H, m), 7.92 (1 H, s), 7.30 (5 H, m), 6.95 (4 H, s), and 2.25 (3 H, s); λ_{max} (cyclohexane) 297 mμ (ε 20,000), 229 (18,000), and 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.** A mixture of *p*-fluorophenylacetic acid (12.0 g, 0.078 mol), benzaldehyde (14.0 g, 0.13 mol), 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, and 14.51 μ; nmr ($CDCl_3$) δ 12.39 (1 H, s), 7.95 (1 H, s), and 7.40–6.90 (9 H, m); λ_{max} (cyclohexane) 288 mμ (ε 17,000), 225 (18,000), and 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.** A mixture of *p*-cyanophenylacetic acid (9.25 g, 0.057 mol), benzaldehyde (9.0 g, 0.085 mol), triethylamine (6.3 ml), and acetic anhydride (6.3 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 (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, and 14.47 μ; nmr ($CDCl_3$) δ 11.29 (1 H, m), 8.04 (1 H, s), A_2B_2 pattern, δ_A 7.35, δ_B 7.67 (J_{AB} = 8.0 cps), 7.30–6.95 (5 H, m); λ_{max} (cyclohexane) 293 mμ (ε 16,000), 247 (sh) (15,000), and 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.** A mixture of *p*-cyanobenzaldehyde (10.0 g, 0.076 mol), phenylacetic acid (6.5 g, 0.049 mol), 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 chloroform solution was washed twice with water and then several times with 5% aqueous sodium hydroxide. The alkaline extract was acidified to pH 6 with acetic acid. The precipitated acid was collected and recrystallized from ethanol giving light yellow crystals (3.2 g, 26%, mp 178–180°); infrared spectrum (KBr) 2.75–4.00

---

[25] W. S. Johnson, A. D. Kemp, R. Pappo, J. Ackerman, and W. F. Johns, *J. Am. Chem. Soc.*, **78**, 6312 (1956).

[26] S. M. Hagman, *Diss., Lund.*, 96 (1924); *Chem. Abstr.*, **18**, 2497 (1924).

(broad), 4.50, 4.96, 6.17, 7.07, 7.95, 11.90, 12.00, and 14.25 μ; nmr ($CDCl_3$) δ 11.19 (1 H), 7.89 (1 H, s), and 7.50–7.00 (9 H, m); λ_{max} (cyclohexane) 289 mμ (ε 20,000), 226 (19,000), and 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.

Irradiation of *cis*-α-(*p*-Tolyl)cinnamic Acid. A solution of *cis*-α-(*p*-tolyl)cinnamic acid (2.0 g, 0.0084 mol) 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-W lamp. The progress of the reaction was monitored by observing the loss of the carbonyl absorption of the acid (5.95 μ) and the appearance of the β-lactone carbonyl band (5.45 μ) 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 δ_A 5.03, δ_B 5.60 (J_{AB} = 7.0 cps); $\delta_{A'}$ 4.50, $\delta_{B'}$ 5.30 ($J_{A'B'}$ = 4.5 cps), in the ratio of 8:7, respectively. The solid was dissolved in benzene, decolorized with Norit, and concentrated under reduced pressure. Recrystallization from benzene–pentane gave *cis*-2-*p*-tolyl-3-phenyl-3-propiolactone (0.4 g, 20%, mp 111–112.5°). The infrared spectrum (KBr) showed bands at 5.47, 6.60, 6.90, 8.04, 8.95, 10.48, 10.58, 11.20, 12.05, 13.25, 13.85, and 14.35 μ; nmr ($CDCl_3$) five-proton singlet at δ 7.13, four-proton singlet at δ 6.87, AB proton pattern, δ_A 5.25, δ_B 5.83 (J_{AB} = 7.0 cps), three-proton singlet at δ 2.15. The mass spectrum exhibited a very weak parent ion at *m/e* 238 and fragment ions at *m/e* 194 (38.4), 179 (24.6), 178 (1.9), 133 (0.9), 132 (100), 103 (1.9), and 43 (2.0).

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. A solution of *cis*-α-phenyl-*p*-methylcinnamic acid (2.0 g, 0.0084 mol) 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, δ_A 5.05, δ_B 5.62 (J_{AB} = 7.0 cps); $\delta_{A'}$ 4.53, $\delta_{B'}$ 5.34 ($J_{A'B'}$ = 4.5 cps), in the ratio of 3:1, respectively. Recrystallization from benzene–pentane gave *cis*-2-phenyl-3-(*p*-tolyl)-3-propiolactone (0.51 g, 21%, mp 98–99°). The infrared spectrum (KBr) showed 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, and 14.37 μ; nmr ($CDCl_3$) nine-proton multiplet centered at δ 7.15, AB proton pattern, δ_A 5.29, δ_B 5.84 (J_{AB} = 7.0 cps), three-proton singlet at δ 2.19. The mass spectrum showed a very weak parent ion at *m/e* 238 (0.7%) and fragment ions at *m/e* 195 (15.6), 194 (100), 193 (18.0), 179 (57.6), 178 (39.6), 118 (40.6), 95 (11.1), 88 (13.0), and 44 (30.3).

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. A solution of *cis*-α-phenyl-*p*-chlorocinnamic acid (2.0 g, 0.0078 mol) in benzene (250 ml) was irradiated as described above for 26 hr. The acid carbonyl absorption (5.95 μ) had disappeared from the infrared spectrum. The solvent was removed under reduced pressure giving a semisolid. The nmr ($CDCl_3$) of the crude product showed δ_A 5.16, δ_B 5.69 (J_{AB} = 7.0 cps); $\delta_{A'}$ 4.59, $\delta_{B'}$ 5.33 ($J_{A'B'}$ = 4.5 cps), in the ratio of 5:6, respectively. Recrystallization from benzene–pentane gave *cis*-2-phenyl-3-(*p*-chlorophenyl)-3-propiolactone (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, and 14.34 μ; nmr ($CDCl_3$) nine-proton multiplet centered at δ 7.05, AB proton pattern, δ_A 5.32, δ_B 5.86 (J_{AB} = 7.0 cps). The mass spectrum exhibited a weak parent ion (*m/e* 258, 0.09% of base) and fragment ions at *m/e* 179 (2.2), 178 (2.3), 119 (8.2), 118 (100), 90 (17.1), 88 (16.9), 76 (10.9), and 44 (18.7).

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 × 20 in. 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.[27] 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 Other Acids. Irradiations of the other acids (2.0 g) were carried out in degassed benzene (250 ml) as described above. The crude products were characterized by infrared and nmr spectra. The results are summarized in Table I.

Irradiation of *cis*-α-Phenylcinnamamide. A solution of *cis*-α-phenylcinnamamide (4.0 g, 0.018 mol) in benzene (450 ml) was placed in a Pyrex immersion irradiation vessel and irradiated with a Hanovia Type A 550-W 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 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 three 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. The following solvents were used for elution: benzene (fractions 1–8), 5% chloroform in benzene (9–11), 10% chloroform in benzene (12–15), 20% chloroform in benzene (16–18), 30% chloroform in benzene (19–21), 40% chloroform in benzene (22–24), 50% chloroform in benzene (25–29), 60% chloroform in benzene (30–36). Recrystallization of fractions 2 and 3 gave *trans*-stilbene (80 mg, 2.5%, mp 124–125°) which was identified by infrared comparison with an authentic sample. Fractions 4–25 did not contain products. All other fractions were shown by nmr and tlc analysis to be mixtures of 2 or more compounds. Recrystallization of fraction 26 four times from benzene–pentane gave *trans*-3,4-diphenyl-2-azetidinone (110 mg, 3%, mp 124–125°). The infrared spectrum ($CHCl_3$) showed carbonyl absorption at 5.67 μ. The nmr spectrum showed aromatic protons (δ 7.34, 10 H), N–H (δ 6.90), and methine protons (δ_A 4.15, δ_B 4.62, J_{AB} = 3.0 cps). The mass spectrum showed peaks at *m/e* 223 (M^+, 10.7), 181 (18.0), 180 (100), 179 (39.0), 178 (20.7), 165 (19.8), 118 (69.0), 106 (16.1), 90 (40.0), and 88 (34.4).

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 (500 mg, 13%, mp 154–155°). All the yields are based on unrecovered starting material. The infrared spectrum showed carbonyl absorption at 5.67 μ ($CHCl_3$). The nmr spectrum showed aromatic protons (δ 7.00, 10 H, m), two methine protons and one N–H as an ABX system (δ_A 4.87, δ_B 5.12, δ_X 6.83, J_{AB} = 6.0 cps, J_{AX} = 1.8 cps, J_{BX} ∼ 0). The N–H is obscured by the aromatic multiplet and was located by a double resonance experiment. The mass spectrum showed peaks at *m/e* 223 (M^+, 38.2), 180 (24.8), 179 (13.3), 178 (7.9), 165 (6.8), 119 (8.0), 118 (100), 106 (18.2), 90 (30.4), 88 (18.1), 58 (15.1), and 43 (43.0).

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 of an unidentified substance (0.25 g, 6.2%, mp 164–165°). The product was very difficult to obtain in the pure state. Sublimation at 140° gave an analytical sample; infrared spectrum (KBr) 2.90 (broad), 5.96, 6.12, 6.26, 6.70, 7.23, 7.90, 13.20, and 14.35 μ; nmr ($CDCl_3$) one-proton multiplet centered at δ 9.15, an aromatic multiplet centered at δ 7.20, and an A_2B proton pattern, δ_A 3.18, δ_B 3.80 (J_{AB} = 8.2 cps). The mass spectrum showed peaks at *m/e* 223 (M^+, 100), 194 (29.3), 178 (18.6), 131 (15.2), 118 (30.0), 106 (32.2), and 90 (32.2).

Anal. 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 (1.10 g, mp 127–128°).

Irradiation of *cis*-α-Phenylcinnamanilide. A solution of *cis*-α-phenylcinnamanilide (3.0 g, 0.01 mol) 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-W lamp for 23 hr. The progress of the reaction was monitored by infrared analysis until no further change was observed. The amide absorption band (5.98 μ) gradually diminished and was replaced by an intense band at 5.73 μ. The solvent was evaporated under reduced pressure giving a solid (3.0 g). The nmr exhibited two overlapping AB proton patterns: δ_A 4.25, δ_B 4.94 (J_{AB} = 3.0 cps), and $\delta_{A'}$ 4.96, $\delta_{B'}$ 5.44 ($J_{A'B'}$ = 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 (Table II).

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 *cis*-1,3,4-triphenyl-2-azetidinone (1.1 g, 37%, mp 182–183°). The infrared showed car-

---

[27] F. Bergman, J. Weizman, and D. Sharpiro, *J. Org. Chem.*, **9**, 408 (1944).

Table II

Eluent	Fraction no.	Prodt compn
Benzene	1–3	Nil
Benzene	4	Solid (mp 110–143°)
Benzene	5	Solid (mp 116–156°)
Benzene	6	Solid (mp 118–163°)
Benzene	7	Solid (mp 119–174°)
Benzene	8	Solid (mp 162–180°)
Benzene	9–13	Nil
Chloroform in benzene		
10%	14–18	Nil
20%	19–23	Nil
30%	24–27	Nil
40%	27–29	Solid (mp 219–220°)
50%	29–31	Nil

bonyl absorption at 5.73 μ ($CHCl_3$). The nmr spectrum showed aromatic protons (δ 7.20, 15 H) and methine protons (δ_A 4.96, δ_B 5.44, J_{AB} = 7.0 cps). The mass spectrum showed peaks at *m/e* 299 (M^+, 30.0), 182 (18.6), 181 (100), 180 (86.0), 179 (24.4), 178 (14.0), and 165 (8.4).

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 (700 mg, 2.3%, mp 127–128°). The infrared spectrum showed carbonyl absorption at 5.73 μ, and the nmr spectrum showed aromatic protons (δ 7.30, 15 H) and two methine protons as an AB pattern (δ_A 4.25, δ_B 4.94, J_{AB} = 3.0 cps). The mass spectrum showed peaks at *m/e* 299 (M^+, 9.8), 181 (33.8), 180 (100), 179 (22.8), 178 (13.1), and 165 (7.8).

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 tentatively identified as 3,4-diphenyl-3,4-dihydrocarbostyril (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, and 14.28; nmr ($CDCl_3$), one-proton singlet at 9.35, an aromatic multiplet centered at 7.10, and an AB proton pattern, δ_A 4.17, δ_B 4.43 (J_{AB} = 6.0 cps). The mass spectrum exhibited an intense molecular ion at *m/e* 299 (100%) and fragment ions at *m/e* 78 (40.0%) and 180 (67.0%).

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.** To a solution of benzalaniline (1.81 g, 0.01 mol) and triethylamine (1.0 g, 0.01 mol) in anhydrous ether (35 ml) was added dropwise a solution of α-phenylacetyl chloride (1.55 g, 0.01 mol) 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 × 20 in. column prepared with 50 g of silica gel. The column was eluted with benzene (250 ml) which upon evaporation afforded an oil. Crystallization from isopropyl alcohol gave *trans*-1,3,4-triphenyl-2-azetidinone, 180 mg, 6%, mp 127–128° (lit.[11] mp 133–134°). The infrared spectrum (KBr) of the product was superimposable on that of the *trans*-β-lactam isolated from the irradiation of *cis*-α-phenylcinnamanilide. A mixture melting point determination showed no depression.

Acknowledgment. This research was supported by a grant (GP 6740) from the National Science Foundation. The authors are indebted to Dr. H. B. Kagan for helpful correspondence.

Nuclear Magnetic Resonance Studies of 1,3-Butadienes.[1] III. Bromoprene, Iodoprene, 1,1,3-Trichlorobutadiene-1,3, and 1,1,3-Tribromobutadiene-1,3

A. A. Bothner-By and D. Jung

Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 15213.

Received October 25, 1967

Abstract: The proton nuclear magnetic resonance spectra of the title compounds at several temperatures have been recorded and analyzed completely. From these data, as well as ultraviolet spectral data, it is deduced that the haloprenes are largely in the *s-trans* conformation, while the trihalobutadienes are largely in a skew conformation.

The form of the potential energy curve for internal rotation about the central single bond in butadienes is as yet unknown, although evidence has been put forward that the *s-trans* form (Figure 1) is predominant in butadiene itself (microwave,[2] calorimetric,[3] infrared and Raman,[4] electron diffraction[5] studies) as well as in isoprene (microwave,[2] ir and Raman[4]), 2,3-dimethylbutadiene (microwave[2]), chloroprene (ir[6]), 2,3-dichlorobutadiene (ir[6]), 1,1,4,4-tetrafluorobutadiene (microwave,[7] nmr[8]), and a number of substituted butadienes with hydrogens in positions 2 and 3 (nmr[1]). On the other hand, evidence has been reported indicating that a non-*s*-transoid conformation predominates in hexachlorobutadiene (uv,[9] Raman,[10] ir[6]), hexafluorobutadiene (ir and Raman[11]), 2-*t*-butylbutadiene (chemical kinetics,[12] nmr[13]), 2,3-di-*t*-butylbutadiene (chemical

---

(1) Paper II of this series: A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, 87, 3451 (1965).

(2) D. R. Lide, Jr., *J. Chem. Phys.*, 37, 2074 (1962); D. R. Lide, Jr., and M. Jen, *ibid.*, 40, 252 (1964).

(3) J. G. Aston, G. Szasz, H. W. Woolley, and F. G. Brickwedde, *ibid.*, **14**, 67 (1946).

(4) D. J. Marais, N. Sheppard, and B. P. Stoicheff, *Tetrahedron*, 17, 163 (1962); K. Bradacs and L. Kahovec, *Z. Physik Chem.*, 48B, 63 (1940); N. V. Tarasova and L. M. Sverdlov, *Opt. Spectry.*, 21, 176 (1966).

(5) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, 61, 1769 (1939); A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, 12, 1221 (1958).

(6) G. Szasz and N. Sheppard, *Trans. Faraday Soc.*, **49**, 358 (1953).

(7) R. A. Beaudet, *J. Am. Chem. Soc.*, 87, 1390 (1965).

(8) K. L. Servis and J. D. Roberts, *ibid.*, 87, 1339 (1965).

(9) A. Roedig and R. Kloss, *Ann.*, 612, 1 (1958); M. I. Batuev and A. D. Matveeva, *Zh. Obshch. Khim.*, 28, 2903 (1958); *Izv. Akad. Nauk, SSSR*, 1393 (1958).

(10) K. W. F. Kohlrausch and H. Wittek, *Ber.*, 75, 227 (1942).

(11) J. C. Albright and J. R. Nielsen, *J. Chem. Phys.*, 26, 370 (1957).

(12) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, 83, 2885 (1961).

(13) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectry.*, 12, 76 (1964).