

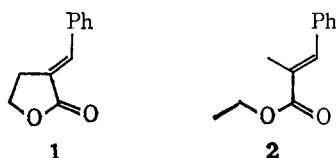
Wavelength-Dependent Photochemistry of α,β -Unsaturated Carboxylate Anions

Edwin F. Ullman, Esther Babad,^{1a} and Ming-ta Sung^{1b}

Contribution No. 9 from Synvar Research Institute, Palo Alto, California 94304. Received March 10, 1969

Abstract: The photochemistry of strongly alkaline solutions of cinnamate and cyclohexene-1-carboxylate anions in alcoholic solvents have been studied at two wavelengths, 2537 and >2800 Å. Unsubstituted and methyl-substituted cinnamates showed wavelength sensitivity and underwent predominant hydrogen abstraction from solvent with >2800 Å and β -lactone formation with 2537-Å light. The phenyl-substituted cinnamates showed no wavelength sensitivity. The α -phenyl derivative gave exclusively β -lactone formation and the β -phenyl derivative gave exclusive hydrogen abstraction. A low yield of product derived by hydrogen abstraction was also obtained from cyclohexene-1-carboxylate. The products of these reactions are described and possible intermediates and excited state precursors are discussed.

In a recent report it was shown that certain α -benzal lactones, such as **1**, display wavelength-sensitive photochemistry in solution.² With long-wavelength light only geometrical isomerization of the double bond was observed. With shorter wavelengths surprisingly long-lived upper excited states were produced that resulted in products derived by hydrogen atom abstraction from the isopropyl alcohol solvent. By contrast the closely related cinnamic ester **2** underwent both reactions with the longest wavelengths that were absorbed. Two structural features were considered that might account for the difference in the behavior of **1** and **2**. First, the *s-cis* conformation of **1** might be a prerequisite for the long-lived upper excited states, and second, rotation about the OC=O single bond in **2** might permit mixing of otherwise discrete excited states.



Unsaturated carboxylic acid anions are a related class of compounds that may be considered to have a *s-cis* conformation and which also have no possibility of rotation about an OC=O bond. These compounds thus also seemed likely to display wavelength-dependent photochemical reactions. However, the literature reveals little information concerning even the qualitative photochemistry of carboxylates. Prior studies have been confined to several isolated observations of decarboxylation,³ and decarbonylation.⁴ In addition there have been several reports of α,β -unsaturated carboxylates which undergo geometrical isomerization,⁵ addition of amines to the double bond,⁶ and solid-state dimerization.⁷ The present study has been directed

primarily toward the elucidation of the qualitative photochemistry of some unsaturated carboxylates as a function of wavelength.

Results

The photochemical reactions in this study were carried out either with 2537-Å light (Rayonett reactor) or Pyrex-filtered light from a 1000-W high-pressure mercury arc (>2800 Å). The solvent generally contained 20% water plus an excess of sodium hydroxide to ensure complete ionization of the carboxylic acid both in its ground and excited state.⁸ Irradiation of sodium cinnamate or α - or β -methylcinnamates **3** in aqueous isopropyl alcohol with >2800 -Å light was found to produce geometrical isomerization together with reductive dimerization to stereoisomeric mixtures of the corresponding 3,4-diphenyladipic acids **4**. In addition, considerable amounts of polymeric products were formed. By contrast, the principle nonpolymeric products using 2537-Å light were the geometrical isomers of the cinnamates and stereoisomeric mixtures of the corresponding β -hydroxy- β -phenylpropionic acids **5**, while the yields of the adipic acids were sharply reduced (*cf.* Table I). When 80% methanol was used as solvent the formation of the reduction dimers **4** was completely suppressed due apparently to the relatively poor hydrogen donor ability of the solvent. Under these conditions it was then possible to observe the formation of **5** even with >2800 -Å light although at a greatly reduced rate.

Similar experiments with the phenyl-substituted cinnamate **6** failed to reveal similar qualitative wavelength dependence. Thus irradiation of **6** with either 2537- or >2800 -Å light in isopropyl alcohol gave up to 80% yields of β,β -diphenylpropionic acid **7** as the exclusive product. On the other hand, in methanol as solvent, **6** could be recovered unchanged even after 25 times longer

(1) (a) Synvar postdoctoral fellow, 1968–1969; (b) Synvar postdoctoral fellow, 1967–1968.

(2) (a) N. Baumann, M. Sung, and E. F. Ullman, *J. Am. Chem. Soc.*, **90**, 4157 (1968); (b) E. F. Ullman and N. Baumann, *ibid.*, **90**, 4158 (1968).

(3) (a) J. D. Margerum, *ibid.*, **87**, 3772 (1965); (b) C. P. Joshua and G. E. Lewis, *Tetrahedron Letters*, 4533 (1966).

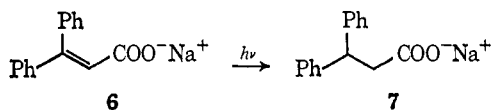
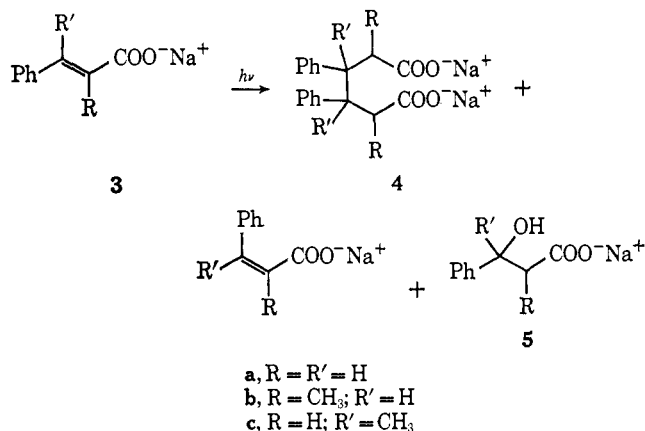
(4) A. W. Bradshaw and O. L. Chapman, *J. Am. Chem. Soc.*, **89**, 2372 (1967).

(5) (a) R. Stoermer, *Ber.*, **44**, 666 (1911); (b) J. M. Gulland and C. J. Virden, *J. Chem. Soc.*, 1478 (1928); (c) D. Vorländer and G. Giesler, *J. Prakt. Chem.*, [2] **121**, 247 (1929).

(6) R. Stoermer and E. Robert, *Ber.*, **55B**, 1030 (1922).

(7) H. Stobbe and K. Bremer, *J. Prakt. Chem.*, [2] **133**, 1 (1929), and references cited.

(8) Although the acidity of the excited singlet states of aromatic carboxylic acids are from six to eight orders of magnitude less than their ground states, cinnamic acids have not been studied. (For leading references, see A. Weller, "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p 199, and H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 156). Even if the cinnamate excited-state acidities should shift by as much as eight orders of magnitude in the opposite direction, the pH ~ 13 employed in the present experiments would prevent protonation of the excited states.



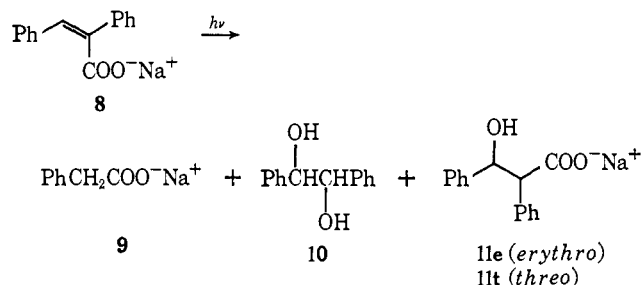
irradiation periods. Similarly, **8** was wavelength insensitive although the relative yields of the reaction products proved to be strongly solvent dependent. Thus in aqueous methanol the principle products were

Table I. Wavelength and Solvent Effects on Product Distribution in Irradiation of Cinnamate Anions^a

Reactant	Reaction conditions		Products, % ^b			
	Solvent	λ, Å	Time, hr	3 ^c	4	5
3a	Isopropyl alcohol	2537	12	26	7 ^d	15
		>2800	48	6	36 ^d	<i>e</i>
	Methyl alcohol	2537 ^f	28	<i>e</i>	<i>e</i>	38
3b	Isopropyl alcohol	>2800	96	99	<i>e</i>	1
		2537	7	<i>e</i>	<i>e</i>	24
	Methyl alcohol	>2800 ^f	19	9	8	<i>e</i>
3c	Isopropyl alcohol	2537 ^g	16	<i>e</i>	<i>e</i>	<i>e</i>
		>2800	144	27	<i>e</i>	29
	Methyl alcohol	2537 ^g	20	<i>e</i>	<i>e</i>	<i>e</i>
	Isopropyl alcohol	>2800	40	32	29	<i>e</i>
		2537	50	5	<i>e</i>	3
	Methyl alcohol	>2800	120	99	<i>e</i>	<i>e</i>

^a 4.7 × 10⁻³ M cinnamate and 0.1 N NaOH in 500 ml of deoxygenated 4:1 (v/v) alcohol-water unless otherwise indicated. ^b Unaccounted for products were largely polymeric. ^c Photostationary mixture of *cis* and *trans* isomers. ^d *dl* and *meso* forms obtained in a ratio of 2:7. ^e Not detected, probably <1%. ^f 9:1 (v/v) alcohol-water. ^g Products may have been destroyed by overirradiation.

phenylacetic acid **9** and 1,2-diphenylethylene glycol (**10**), whereas in aqueous isopropyl alcohol **9** and **10** were only formed in minor amounts and the major products were the *threo*- and *erythro*-α,β-diphenyl-β-hydroxypropionic acids **11** (*cf.* Table II).



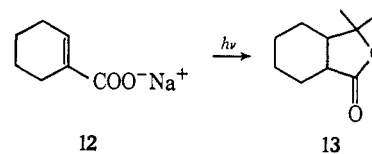
In addition to the cinnamates, one nonaromatic unsaturated carboxylate was studied, namely, sodium cy-

Table II. Wavelength and Solvent Effects on Product Distribution in Irradiation of Phenylcinnamate Anions^a

Reactant	Reaction conditions		Product yields, % ^b					
	Solvent	λ, Å	Time, hr	7	9	10	11e	11t
6^c	Isopropyl alcohol	2537	41	66				
		>2800	200	83				
8	Isopropyl alcohol	2537	5		6	6	18	14
		>2800	16		3	3	16	45
	Methyl alcohol	2537	6		26	31	<i>d</i>	<i>d</i>
		>2800	15		56	50	<i>d</i>	<i>d</i>

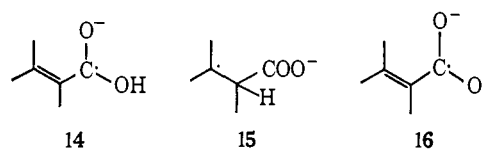
^a 4.5 × 10⁻³ M cinnamate and 0.1 N NaOH in 500 ml of deoxygenated 4:1 (v/v) alcohol-water unless otherwise indicated. ^b Unaccounted for products were largely polymeric. ^c 5.4 × 10⁻³ M cinnamate. ^d Not detected, probably <1%.

clohexene-1-carboxylate (**12**). Like the cinnamates, **12** underwent a reductive photoreaction in isopropyl alcohol but not in methanol. Thus on irradiation of **12** with >2800-Å light followed by acidification a 36% conversion (25% yield) to the bicyclic lactone **13** occurred. Similar irradiation conditions using methanol as solvent produced only very slow disappearance of the carboxylate chromophore, and no discrete product could be isolated.

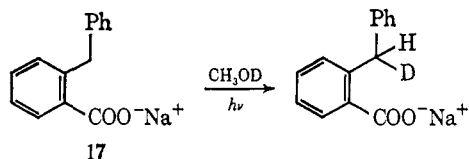


Mechanistic Results and Discussion

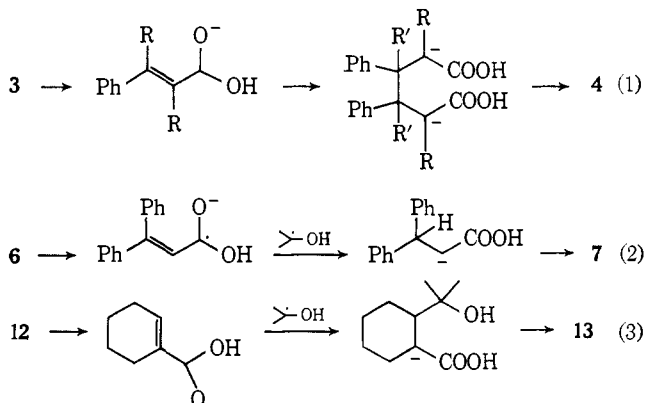
The preceding data demonstrate the tendency of unsaturated carboxylate anions to abstract hydrogen atoms on photoexcitation when a sufficiently good hydrogen donor is available. However, carboxylate anions apparently are significantly less reactive in this respect than ketones, since the latter are known to abstract hydrogen atoms from methanol, whereas methanol was not a suitable hydrogen atom source in the present examples. In principle, hydrogen abstraction by the unsaturated carboxylate anions might occur with initial bonding to oxygen to give hydroxyketyl anions **14** or with bonding to the α-hydrogen to give carbon rad-



icals **15**. Direct evidence on this point is lacking, but our finding that deuterium is incorporated at the methylene group in sodium *o*-benzylbenzoate (**17**) upon irradiation (2537 Å) in deuterium oxide-methanol-*d*₁ suggests that carboxylate oxygens are capable of hydrogen abstraction on photoexcitation. Moreover, **14** should have far greater resonance stabilization than **15**, and decarboxylation products which might be expected to arise from **15** have not been observed. The previously unknown carboxylic acid radical anions **14** are thus favored as the initially formed intermediates. Although proton loss by **14** cannot be rigorously excluded it seems unlikely that the aqueous base would be sufficiently strong to generate appreciable concentrations of the doubly charged radical anion **16**.



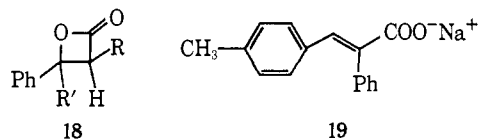
Based on these considerations the most probable routes to the reduction products obtained in this study are given in eq 1-3. Similar types of processes, reductive dimerization, saturation of a double bond, and addition of isopropyl alcohol, are of course well-recognized processes in ketone and ester photochemistry.⁹ The principle factors controlling which of these processes obtains are probably the relative stability of the radical anion intermediates **14** and the steric accessibility of their β -carbon atoms. Thus the cinnamate anion and its methyl derivatives **3** presumably form sufficiently stable radical anions to permit these species to accumulate and subsequently dimerize (eq 1), whereas the more reactive radical anion from the cyclohexene-1-carboxylate probably combines immediately with the simultaneously formed ketyl radical (eq 3). On the other hand, β -phenylcinnamate **6** may give a relatively stable radical anion which is too crowded to dimerize and it thus becomes satisfied by abstraction of a second hydrogen with over-all reduction of the double bond (eq 2).



Several of the cinnamates undergo a second reaction that is competitive with formation of **14**. In the examples **3** this competitive process is obviously more efficient when short wavelengths of light are used (Table I). Although the final products of this reaction are the β -hydroxypropionic acids **5**, it is highly probable that the primary process involves formation of the β -lactones **18**. This follows from the observation that when sodium cinnamate was irradiated in anhydrous methanolic sodium methoxide a 56% yield of the methyl ester of β -hydroxy- β -phenylpropionic acid **5a** was obtained. This ester is not observed under the usual aqueous conditions of the reaction due in part to its rapid thermal hydrolysis under these reaction conditions. Its formation under the anhydrous reaction conditions, and the failure to observe β -methoxy- β -phenylpropionic acid, strongly suggests the intermediate β -lactone. This re-

(9) Illustrative examples include, respectively, (a) M. Pfau and R. Dulou, *Bull. Soc. Chim. France*, 3336 (1967), and W. A. Henderson and E. F. Ullman, *J. Am. Chem. Soc.*, **87**, 5424 (1965); (b) G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962), and H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Baum, *ibid.*, **84**, 4149 (1962); (c) M. Pfau, R. Dulou, M. Vilkas, *Compt. Rend.*, **251**, 2188 (1960); **254**, 1817 (1962), and ref 2a.

action has good analogy in the photochemical formation of β -lactones from some un-ionized cinnamic acids, although in contrast to the present results with sodium cinnamate, α -unsubstituted cinnamic acids reportedly failed to give this reaction.¹⁰



Although one of the products of photolysis of sodium α -phenylcinnamate **8** also was the corresponding β -hydroxy acid, other products, **9** and **10**, became predominant on changing the solvent from isopropyl alcohol to methanol. One possible origin of the additional products is secondary base-catalyzed or photochemical cleavage of initially formed β -hydroxy acid **11** to give phenylacetic acid **9** and benzaldehyde. This might then be followed by a photopinacol reduction of the benzaldehyde to give the observed 1,2-diphenylethylene glycol (**10**). However the β -hydroxy acids **11** proved to be stable toward long irradiation under the alkaline reaction conditions in either solvent. In order to eliminate the possibility that the 1,2-diphenylethylene glycol (**10**) might arise instead by some unspecified mode of decarbonylation and hydration of the α -phenylcinnamate **8**, the methyl-substituted cinnamate **19** was prepared. However, irradiation of this compound in alkaline aqueous methanol gave only phenylacetic acid **9** (98%) and 1,2-bis(*p*-tolyl)ethylene glycol (67%), and there was no evidence for any of the unsymmetrical 1-phenyl-2-(*p*-tolyl)ethylene glycol expected from the hypothetical decarbonylation mechanism.

These results are in good accord with the initially proposed cleavage of the β -hydroxy acid **11** despite the observation that **11** was found to be thermally and photochemically stable. A related proposal that accounts for all the facts is that the benzaldehyde is formed by cleavage of an initially formed ester of the β -hydroxy acid **11**. The origin of the marked solvent dependence is then evident. In aqueous methanol the methyl ester of **11**, formed through methanolysis of the intermediate β -lactone **18** (R = Ph; R' = H), cleaves thermally to benzaldehyde and phenylacetic acid. On the other hand in isopropyl alcohol hydrolysis of the β -lactone competes successfully with alcoholysis by the more hindered alcohol, and the stable hydroxy acid **11** is thus formed. In order to confirm this mechanism the β -lactone **18** (R = Ph; R' = H) was prepared and subjected to the alkaline reaction conditions in which aqueous methanol was used as solvent. As expected, good yields of benzaldehyde (80% as the 2,4-DNP derivative) and phenylacetic acid (95%) were obtained on permitting the reaction mixture to stand in the dark. Moreover on irradiation of sodium α -phenylcinnamate **8** in *anhydrous* isopropyl alcohol containing isopropoxide followed by alkaline hydrolysis of the products, none of the β -hydroxy acid **11** that predominates in the aqueous medium was obtained, and the sole monomeric products isolated were the phenylacetic acid **9** and the glycol **10**.

Little evidence concerning the excited-state precursors of the carboxylic acid radical anions and the β -lac-

(10) O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, **89**, 4243 (1967); **90**, 2333 (1968).

tones is available. It is probable that the carboxylates, like ketones and esters, abstract hydrogen from solvent through their n, π^* excited state. β -Lactone formation from the carboxylates, on the other hand, is a photochemically allowed electrocyclic process provided reaction is from a π, π^* excited state. The ultraviolet spectra of both sodium cinnamate **3a** and sodium cyclohexene-1-carboxylate (**12**) display weak long-wavelength shoulders with very poorly resolved vibrational structure characteristic of $n \rightarrow \pi^*$ transitions (Figure 1). Hence the observations that hydrogen abstraction by **3** is favored with long-wavelength light and β -lactone formation is favored with short wavelengths is at least consistent with the spectral characteristics of these compounds. However, the significance of these spectra is questionable since they do not necessarily reflect the energy relationships in the triplet manifold from which at least part of the photochemistry probably takes place. Nevertheless the wavelength sensitivity of the cinnamate salts clearly demonstrates that two major primary processes occur through different excited-state precursors which may be populated with different wavelengths of light. It is worthy of note, moreover, that the hydrogen abstraction reaction by the cinnamates occurs preferentially with long-wavelength light in contrast to the wavelength-sensitive unsaturated lactones **2** where the excited states responsible for this process are accessible only with short wavelengths. The n, π^* and π, π^* excited states in these groups of compounds may thus possess barriers to interconversion which are independent of the relative energies of these states.

Experimental Section

Irradiations with $>2800\text{-}\text{\AA}$ light were carried out in Pyrex flasks with a G.E. 1000-W B-H6 high-pressure mercury arc. For $2537\text{-}\text{\AA}$ irradiations quartz vessels were used with a Rayonett photochemical reactor. The geometry of each apparatus was approximately the same from run to run. Since the unsaturated carboxylates have much higher extinction coefficients than the products, secondary photolysis of the products was minimized except in those experiments in which the starting carboxylate was completely used up. Prolonged irradiation after complete destruction of the starting material was avoided in most cases (*cf.* Table I) by monitoring the ultraviolet absorption of the reaction mixtures.

Hence the reaction times give a rough indication of the relative efficiencies of reactions carried out with the same wavelength. Reaction solutions were deoxygenated by bubbling with nitrogen for at least 30 min, and a positive pressure of nitrogen was then maintained during the irradiations. Conditions used for irradiation of the cinnamates and yields of products are summarized in Tables I and II. Added detail concerning product isolation and identification as well as untabulated experiments are given below.

Irradiation of Sodium Cinnamate. After evaporation of the irradiated mixtures *in vacuo*, the residues were redissolved in water, acidified with dilute hydrochloric acid, and extracted with ether. The residues obtained on evaporation of the ether extracts were triturated with chloroform and the resulting white solid was recrystallized from chloroform-methanol to give *meso*-3,4-diphenyladipic acid, mp $275\text{--}276^\circ$ (lit.¹¹ mp $274.5\text{--}276.5^\circ$), m/e 298 (M), 280 (M - H₂O), 252 (M - HCOOH), 149 (M/2); nmr (D₂O-NaOD) 7.37 (10 ArH), 3.2 (2 CH, m), and 2.3 ppm (2 CH₂, d, $J = 7$ cps). The remaining chloroform solutions were evaporated and the residues separated by preparative tlc (silica) using 10% acetic acid in benzene as eluent. In this way there were obtained mixtures of *cis*- and *trans*-cinnamic acids (separable by vpc), additional amounts of *meso*- β, β' -diphenyladipic acid, plus *dl*- β, β' -diphenyladipic acid, β -hydroxy- β -phenylpropionic acid, and polymeric material which remained at the origin. The *dl*- β, β' -diphenyladipic acid, after recrystallization from benzene-hexane, melted at $180\text{--}182^\circ$ (lit.¹¹ mp $184\text{--}186^\circ$); mass spectrum similar to the *meso* isomer; nmr (D₂O-

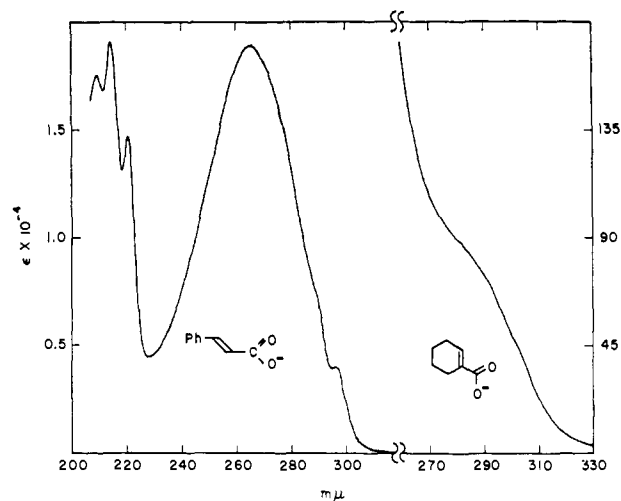


Figure 1. Spectra of carboxylate anions in 4:1 (v/v) isopropyl alcohol-water.

NaOD) 7.06 (10 ArH), 3.30 (2 CH, m), and 2.46 ppm (2 CH₂, AB part of ABX pattern, $J_{AB} = 14$ cps, $J_{AX} = 4.0$ cps, $J_{BX} = 10.5$ cps). Recrystallization of the β -hydroxy- β -phenylpropionic acid from benzene-hexane followed by sublimation gave a white crystalline solid: mp $92\text{--}95^\circ$ (lit.¹² mp 96°); m/e 166 (M), 107 (M - CH₂COOH); nmr (CDCl₃) 7.50 (2 OH), 7.34 (5 ArH), 5.13 (CH, t, $J = 7$ cps), and 2.78 ppm (CH₂, d, $J = 7$ cps).

Anal. Calcd for C₉H₁₀O₃: C, 65.05; H, 6.07. Found: 65.38; H, 6.21.

Irradiation of sodium cinnamate in dry methanol with $2537\text{-}\text{\AA}$ light was carried out over 26 hr using 350 mg of the acid in 500 ml of solvent containing 0.7 g of dissolved sodium. The solution was neutralized with acetic acid and evaporated *in vacuo*, and the residue extracted with ether. Preparative tlc (silica, ethyl acetate-chloroform) of the residue obtained from the ether extracts yielded 220 mg of the oily methyl β -hydroxy- β -phenylpropionate: ν_{\max} 3440 (OH) and 1700 cm^{-1} (COOCH₃); m/e 180 (M), 120 (M - HCOOCH₃), 107 (M - CH₂COOCH₃); nmr (CDCl₃) 7.34 (5 ArH), 5.13 (CH, t, $J = 6.5$ cps), 3.68 (OCH₃), 3.30 (OH), and 2.74 ppm (CH₂, d, $J = 6.5$ cps).

Irradiation of Sodium α -Methylcinnamate. Irradiated mixtures were worked up exactly as in the sodium cinnamate irradiations. A somewhat impure diastereomeric mixture of α, α' -dimethyl- β, β' -diphenyladipic acids obtained by chloroform trituration of the ether extracts (formed only with $>2800\text{-}\text{\AA}$ light in isopropyl alcohol) melted at $295\text{--}300^\circ$; m/e 326 (M), 308 (M - H₂O), 380 (M - HCOOH), and 163 (M/2); nmr (D₂O) 7.20 (10 ArH), 3.00 (4 CH, m), and 1.39 ppm (2 CH₃, d, $J = 7$ cps).

Anal. Calcd for C₂₀H₂₂O₄: C, 73.60; H, 6.79. Found: C, 73.14; H, 7.28.

β -Hydroxy- α -methyl- β -phenylpropionic acid was isolated by preparative tlc in a manner similar to the isolation of its lower homolog. After molecular distillation (100° , 0.05 mm) a viscous liquid was obtained which could not be further purified: m/e 180 (M), 162 (M - H₂O), 107 (M - CH₂CHCOOH); nmr (CDCl₃) 7.28 (5 ArH), 6.50 (2 OH), 5.15 (OCH, d, $J_{AX} = 4$ cps), 2.78 (CH, q of d, $J_{AX} = 4$ cps, $J_{AB} = 7$ cps), 1.09 ppm (CH₃, d, $J_{AB} = 7$ cps). Esterification of this oil with diazomethane followed by distillation and purification of the ester by vpc ($1/8$ in. SE 30 column at 150°) gave analytically pure ester: $\nu_{\max}^{\text{CHCl}_3}$ 3600, 1725 cm^{-1} ; m/e 194 (M). The nmr (CDCl₃) suggests that this product was a mixture of stereoisomers: 7.32 (5 ArH, s), 5.00-5.24 (OCH, m), 3.72 and 3.65 (2 singlets, OCH₃), 2.58-3.00 (OH + CH, m), 1.10 and 0.97 ppm (2 overlapping doublets, CH₃).

Anal. Calcd for C₁₁H₁₄O₃: C, 68.02; H, 7.27. Found: C, 68.19; H, 7.04.

Irradiation of Sodium β -Methylcinnamate. Irradiated mixtures were evaporated *in vacuo* and the residues diluted with water. After acidification, the aqueous solutions were extracted with ether. The residues obtained on evaporation of the extracts were triturated

(11) G. M. Badger, *J. Chem. Soc.*, 999 (1948).

(12) "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.

with chloroform and the insoluble portion was recrystallized from methanol-chloroform to give β, β' -dimethyl- β, β' -diphenyladipic acid of unknown stereochemistry: mp 250–252°; m/e (no molecular ion) 163 (M/2), 105 (PhCHCH₃); nmr (D₂O) 7.18 (10 ArH), 3.05 and 2.93 ppm (2 CH₂, AB pattern, $J_{AB} = 15$ cps).

Anal. Calcd for C₂₀H₂₂O₄: C, 73.60; H, 6.79. Found: C, 72.93; H, 6.92.

Treatment of this product with ethereal diazomethane gave dimethyl β, β' -dimethyl- β, β' -diphenyladipate which, after recrystallization from benzene-hexane, melted at 128–130°; ν_{\max}^{KBr} 1740 cm⁻¹ (COOCH₃); m/e 177 (M/2), 135 (M/2 - CH₂CO), 117 (M/2 - HCOOCH₃); nmr (CDCl₃) 7.10 (10 ArH), 3.38 (2 OCH₃), 3.18 and 2.37 (2 CH₂, AB pattern, $J_{AB} = 16$ cps), and 1.55 ppm (2CH₃).

Separation of the chloroform-soluble fraction by tlc yielded recovered starting material plus (with 2537-Å light in methanol) an oil which had properties consistent with β -hydroxy- β -phenylbutyric acid: ν_{\max}^{KBr} 1710 cm⁻¹ (COOH); m/e 180 (M), 121 (M - CH₂-COOH), 105 (PhCO); nmr (CDCl₃) 7.35 (5 ArH), 7.15 (2 OH), 3.01 and 2.78 (CH₂, AB pattern, $J = 16$ cps), and 1.53 ppm (CH₃).

Anal. Calcd for C₁₀H₁₂O₃: C, 66.65; H, 6.71. Found: C, 66.53; H, 6.90.

Irradiation of Sodium β -Phenylcinnamate. The irradiated solutions were evaporated *in vacuo* and the residues dissolved in water. Acidification of these solutions with hydrochloric acid followed by extraction with ether and evaporation of the extracts yielded a white solid. Recrystallization from benzene-hexane gave β, β -diphenylpropionic acid: mp 153–155° (lit.¹² mp 155°); ν_{\max}^{KBr} 1700 cm⁻¹ (COOH); m/e 226 (M), 180 (M - HCO₂H), 167 (M - CH₂COOH); nmr (CDCl₃) 10.57 (COOH), 7.21 (10 ArH), 4.51 (CH, t, $J = 8$ cps), 3.20 ppm (CH₂, d, $J = 8$ cps).

Irradiation of Sodium α -Phenylcinnamate. Irradiated solutions were evaporated *in vacuo* and the residues redissolved in water and extracted with ether. Evaporation of the extracts and recrystallization from benzene-hexane gave *meso*-1,2-diphenylethyleneglycol: mp 135–136.5° (lit.¹² mp 137–138°); m/e 214 (M), 197 (M - OH), 108 (M - PhCHO); nmr (CDCl₃) 7.22 (10 ArH), 4.78 (2 CH), and 2.40 (2 OH). Acidification of the aqueous layer with hydrochloric acid followed by extraction with ether and evaporation of the extracts yielded an oil. The fraction obtained in this manner from irradiation in methanol was crystallized from benzene-hexane to give phenylacetic acid which was identical with an authentic sample. When aqueous isopropyl alcohol was used as the irradiation solvent, this fraction crystallized from chloroform-methanol to give *threo*- α, β -diphenyl- β -hydroxypropionic acid: mp 178–180° (lit.¹³ mp 177–178°); ν_{\max}^{KBr} 1700 cm⁻¹; m/e 242 (M), 224 (M - H₂O), 136 (M - PhCHO), 107 (M - PhCHCOOH); nmr (DM-SO) 7.11 (10 ArH), 5.10 (OCH, d, $J = 10$ cps), 4.3 (2 OH), 3.76 ppm (CH, d, $J = 10$ cps).

Mother liquors obtained from recrystallization of these acids were further purified by preparative tlc (silica, 10% acetic acid in benzene) which yielded additional quantities of the above acids plus *erythro*- α, β -diphenyl- β -hydroxypropionic acid: mp 144–145° (lit.¹³ mp 142–143°); ν_{\max}^{KBr} 1690 cm⁻¹ (COOH); nmr (CDCl₃) 7.28 (10 ArH), 6.25 (2 OH), 5.25 (OCH, d, $J = 8$ cps), and 3.85 ppm (CH, d, $J = 8$ cps).

Anal. Calcd for C₁₅H₁₄O₃: C, 74.36; H, 5.83. Found: C, 74.03; H, 6.07.

Irradiation of sodium α -phenylcinnamate in anhydrous isopropyl alcohol with >2800-Å light was carried out using 1.5 g of the acid in 1.3 l. of solvent containing 2.8 g of sodium. A 550-W Hanovia medium-pressure mercury immersion lamp was used with a Pyrex immersion well. The irradiation was continued for 70 min. The

solvent was then evaporated and the residue taken up in water and extracted with ether. The extracts were dried over MgSO₄ and evaporated to give 680 mg of oil which yielded 300 mg (42%) of 1,2-diphenylethylene glycol on crystallization from methylene chloride-hexane. Acidification of the aqueous solution and extraction with ether yielded 680 mg (75%) of phenylacetic acid.

Alcoholysis of α, β -Diphenyl- β -propiolactone. A solution of 500 mg of α, β -diphenyl- β -propiolactone (prepared according to the procedure of Chapman and Adams¹⁰) in 500 ml of 1 N NaOH in 4:1 (v/v) methanol-water was stirred under nitrogen at 25° for 30 min. The methanol was then distilled off under reduced pressure and the distillate treated with an acidic solution of 2,4-dinitrophenylhydrazine to give 516 mg (80%) of the 2,4-DNP derivative of benzaldehyde, mp 233–235°. The aqueous solution remaining after the distillation was washed with ether, acidified with hydrochloric acid, and then extracted with ether. Evaporation of the extracts led to the isolation of 290 mg (95%) of phenylacetic acid.

Irradiation of Sodium *p*-Methyl- α -phenylcinnamate. The corresponding acid¹⁰ (500 mg) was dissolved in 500 ml of 1 N NaOH in 4:1 (v/v) methanol-water and irradiated for 30 min as in the previous examples except that a 550-W Hanovia medium-pressure mercury arc was used with a Pyrex immersion well. The methanol was removed *in vacuo* and the remaining solution extracted with ether. The extracts yielded 170 mg (67%) of 1,2-bis-*p*-tolylethylene glycol which was recrystallized from methylene chloride-hexane, mp 127–140°. The nmr (CDCl₃) spectrum suggests that this is a mixture of stereoisomers; 7.13 and 7.03 (2 singlets, 8 ArH), 4.70 and 4.59 (2 singlets, 2 CH), 2.60–2.41 (2 OH), and 2.33 and 2.29 ppm (2 singlets, 2 CH₃); m/e 242 (M), 122 (M - CH₃C₆H₄CHO), 121 (M/2).

Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.27; H, 7.48.

Preparative tlc of this mixture yielded a pure sample of the predominant higher melting isomer: mp 158.5–160° (lit.¹⁴ mp 161°); nmr (CDCl₃) 7.03 (s, 8 ArH), 4.59 (s, 2 CH), and 2.29 ppm (s, 2 CH₃ + 2 OH).

Acidification of the remaining aqueous solution and extraction with ether yielded, after evaporation of the extracts, 280 mg (98%) of phenylacetic acid.

Irradiation of Sodium Cyclohexene-1-carboxylate. The corresponding acid¹⁵ (350 mg) dissolved in 500 ml of 1 N NaOH in 80% aqueous isopropyl alcohol was irradiated for 63 hr with >2800-Å light. The resulting mixture was evaporated *in vacuo* and the residue redissolved in water. Acidification and ether extraction yielded 245 mg of a liquid which was purified by vpc to give 100 mg of the starting acid (29%) and 50 mg (11%) of the lactone **13** of unknown stereochemistry. The product could be crystallized from petroleum ether (bp 30–60°); mp 72–75°; ν_{\max}^{KBr} 1755 cm⁻¹; m/e 168 (M), 124 (M - CO₂); nmr (CDCl₃) 3.0 (O=CCH, m), 1.4 (9 H, aliphatic, broad multiplet), 1.35 ppm (2 CH₂).

Anal. Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.30; H, 9.76.

Deuterium Exchange in Sodium *o*-Benzylbenzoate. A solution of 22 mg of *o*-benzylbenzoic acid in 4 ml of a 1:1 mixture of deuterium oxide and deuteriomethanol containing 0.03 M sodium hydroxide was deoxygenated and then irradiated with 2537-Å light for 15 hr. The starting material was recovered nearly quantitatively at the end of this period. Comparison of mass spectra of samples taken before and after irradiation demonstrated the presence of 44% monodeuterated and 5% dideuterated material.

(14) F. K. Beilstein, "Handbuch der organischen Chemie," 1st Suppl., Vol. 6, 1931, p 494.

(15) W. Treibs and H. Orttmann, *Ber.*, **93**, 545 (1960).

(13) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, **79** 1920 (1957).