# Photochemical Decarboxylation of Sodium Glycidates[1]

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The photolysis of sodium phenylglycidates yielded decarboxylated products analogous to those generated in the presence of acids, although photoprotonation was probably not involved. Aliphatic sodium glycidates did not photolyze, even in the presence of sensitizers.

The photochemistry of epoxy ketones (1) has been intensively investigated, showing the formation of β diketones to be the major process.[3] The photochemistry of glycidic acids (2), on the other hand, was hitherto unknown. Because of the close formal relationship between the two series, we had hoped that

1, R = alkyl or aryl
2, R = OH
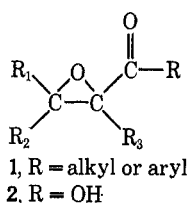
they would behave similarly and that the photolysis of glycidic acids would convert them into β-keto acids and finally into acetophenones after decarboxylation, in contrast with the acid-catalyzed decarboxylation which places the carbonyl at the α position.[4] We now report that the photochemical behavior of sodium glycidates in aqueous solution closely parallels that in presence of mineral acids.

Discussion

Saponification of the glycidic esters prepared by the Darzens synthesis provides a convenient preparation of sodium glycidates.[5] Acid treatment is usually accompanied by epoxide ring opening and does not yield the corresponding glycidic acids, except with simple aliphatic salts.[6] After several disappointing attempts to isolate the aromatic acids required in this study, we decided to investigate the behavior of the sodium salts in aqueous solution.

Aromatic sodium glycidates show a typical absorption maximum near 260 nm. When sodium β-phenylglycidate (3) was irradiated at 253.7 nm under nitrogen, carbon dioxide was immediately evolved and a polymeric precipitate coated the walls of the reaction vessel preventing extensive photolysis. No acetophenone was detected by nmr or glc in the neutral products of the reaction, which consisted almost exclusively of phenylacetaldehyde (4), with some bibenzyl and traces of benzaldehyde.

Phenylacetaldehyde (4) could have been generated from primary products resulting either from decarboxylation or from isomerization, namely from epoxy-

styrene (5) or phenylpyruvate (6), respectively. Neither 5 nor 6, however, produced 4 upon irradiation in the above conditions.[7] When the photolysis of 3 was performed in deuterium oxide, the nmr of 4 showed that one deuterium had been incorporated at the methylene position and that no exchange had taken place at the aldehyde. This result further confirmed that a pyruvate had not been an intermediate since a deuterium would have been introduced at the carbon bearing the aldehyde in the product.

The formation of bibenzyl in the irradiation of 3 is most probably the result of further photolysis of 4, which was found to decarbonylate and to yield bibenzyl upon irradiation in the above conditions.[9a] The detection of traces of benzaldehyde in the photolysis of 3 is in line with the results obtained by Griffin and coworkers in their studies on the photochemical cleavage of oxiranes.[9] Another route to benzaldehyde is through photohydration of 3 to sodium 2,3-dihydroxy-3-phenylpropionate followed by a retroaldol reaction. This is considered much less likely since it requires generating an unstabilized negative charge adjacent to the carboxylate, and since the photohydration of epoxides to glycols is still without precedent. Group migrations accompanying the opening of oxiranes are well known, both in photochemical[3] and in acid-catalyzed reactions.[10] It was desirable, therefore, to check for phenyl migration in the decarboxylation–epoxide opening of 3. Had it taken place, it would have led to the observed products, both in normal and in deuterated water. The starting material was chemically labeled with a methyl at the β position, but, when 7a was irradiated, it yielded 2-phenylpropionaldehyde (8a) rather than a ketone, thereby proving that no substituent had migrated.[11] Similarly, the ketones 8b and 8c were the major products in the photolysis of 7b and 7c. The latter example again indicated the absence of group migration in the reaction. It is also noteworthy that carbonyl products analogous to benzaldehyde were not detected with sodium β-phenylglycidates more substituted than 3.

Aliphatic sodium glycidates, such as 7d and 7e, have an absorption maximum below 210 nm and have no measurable absorption above 230 nm; as expected, they did not photolyze upon irradiation. We also

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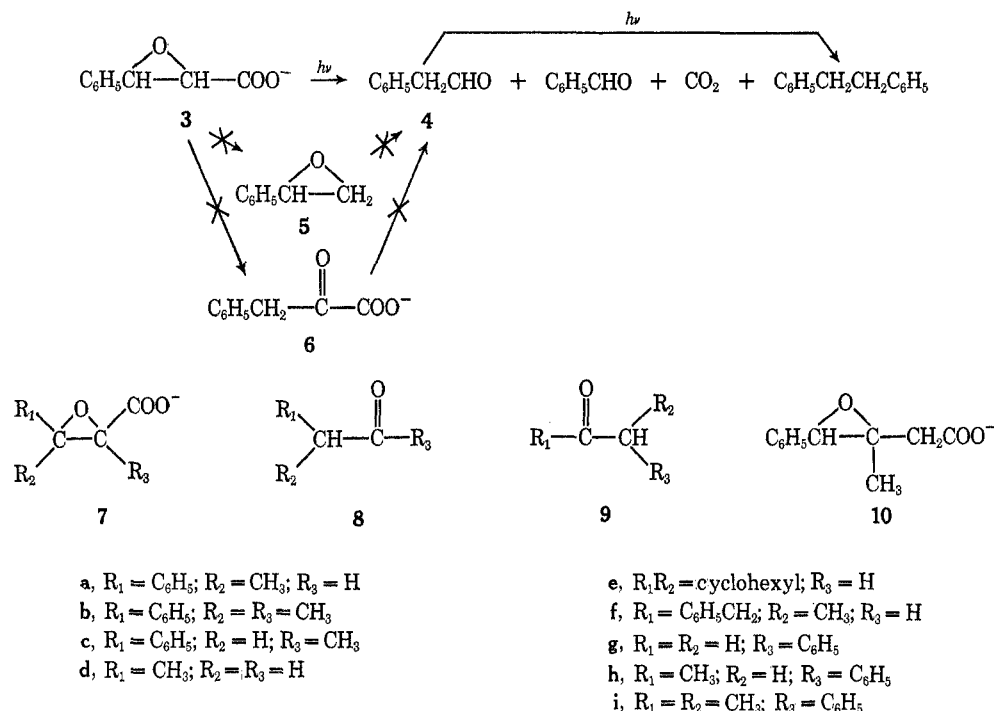
(2) Author to whom inquiries should be addressed.

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(7) Styrene oxide does isomerize to phenylacetaldehyde, however, when irradiated in benzene.[8]

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(11) This is in agreement with the lack of phenyl migration reported in the rearrangement of styrene oxide to phenylacetaldehyde.[9a]

a, $R_1 = C_6H_5$; $R_2 = CH_3$; $R_3 = H$
b, $R_1 = C_6H_5$; $R_2 = R_3 = CH_3$
c, $R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$
d, $R_1 = CH_3$; $R_2 = R_3 = H$

e, $R_1R_2 = $cyclohexyl; $R_3 = H$
f, $R_1 = C_6H_5CH_2$; $R_2 = CH_3$; $R_3 = H$
g, $R_1 = R_2 = H$; $R_3 = C_6H_5$
h, $R_1 = CH_3$; $R_2 = H$; $R_3 = C_6H_5$
i, $R_1 = R_2 = CH_3$; $R_3 = C_6H_5$

failed in our attempts to induce their decarboxylation by triplet energy transfer from sensitizers such as benzoic acid, benzene, and rose bengal. We also tried unsuccessfully to transfer the energy from an aromatic sodium glycidate, by photolyzing 7c in presence of 7e. Finally, even an internal sensitizer proved ineffective, as in 7f where one methylene separates the phenyl from the epoxide and which was unaffected by uv light.

The observed photochemistry of aromatic sodium glycidates must be a consequence of initial excitation of the aromatic moiety. After finding that 7f did not photolyze, we tried to determine the requirements for decarboxylation in the aromatic series. Since there was no reaction upon irradiation of 10, it was clear that the direct attachment of both the phenyl and the carboxylate to the epoxide ring was a prerequisite for decarboxylation. We therefore investigated representatives, 7g, 7h, and 7i, of the sodium α-phenylglycidate series which are not accessible through the usual Darzens synthesis[12] and were prepared from the corresponding unsaturated esters by epoxidation followed by saponification. Photolysis proceeded smoothly, accompanied by decarboxylation. The products, 9g, 9h, and 9i, respectively, indicated that fission of the benzylic carbon–oxygen bond had taken place, placing the new carbonyl at the original β position of the glycidate, unlike the β-phenylglycidate series in which the carbonyl is formed at the α position.

These observations led us to investigate the acid-catalyzed decomposition of sodium α-phenylglycidates, and we have already reported that they yielded "abnormal" products, identical with those obtained photochemically.[1,13] We explained the results in terms of a benzylic carbonium ion intermediate which was formed after protonation of the epoxide, in conflict with the accepted concerted mechanism for the decarboxylation of glycidic acids.[14]

The photodecarboxylation of carboxylic acids and their anions is currently receiving much attention, but the multiplicity of the reactive excited states during decarboxylation has not been established.[15] We failed in all our attempts to sensitize the decarboxylation of aliphatic sodium glycidates, but we achieved limited success in similar experiments in the aromatic series using acetophenone as sensitizer. This suggests to us that although decarboxylation can take place from a triplet state in this latter case, it normally proceeds from a singlet state. The failure which we experienced with the sensitized experiments in the aliphatic series may also be due to a requirement for a singlet excited state or to a prohibitively high triplet energy.

If the epoxide ring cleavage were an homolytic process, products of radical trapping would be expected in solvents which are better hydrogen radical donor than water.[16] Decarboxylation of 7a in methanol, however, did not yield any hydroxymethylated product. This finding also appears to rule out the possibility of initial decarboxylation of the carboxylate anion accompanied by the expulsion of one electron, yielding an oxirane radical, as it was suggested in the decarboxylation of 1-naphthaleneacetic acid.[15c,17] The absence of radical intermediates was further indicated by observing that oxygen had no effect on the course of photolysis of 3.

Heterolytic cleavage of the benzylic carbon to oxygen epoxide bond is an attractive possibility to account for the identity of products obtained in the acid-catalyzed and in the photolytic decarboxylation of aromatic so-

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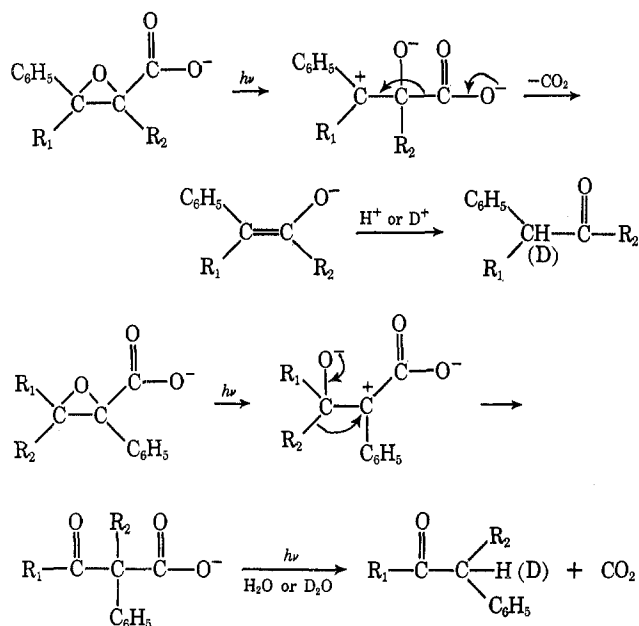
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SCHEME I

dium glycidates (Scheme I). However, when **7c** was irradiated in aqueous solutions containing an excess of sodium hydroxide, the photolysis proceeded smoothly indicating that photoprotonation does not precede decarboxylation.[18] Furthermore, the decarboxylation of **7h** which took place with the loss of the β proton in acid[13] occurred photochemically with migration of that hydrogen from the β to the α position, and finally the formation of glyceric acids which was prominent in the acid-catalyzed treatment of sodium α-phenylglycidates did not occur during photolysis of these salts. These results indicate that the mechanisms of the acid-catalyzed and photochemical decarboxylation reactions are fundamentally different.

Speculations concerning the detailed mechanism(s) of the photochemical decarboxylation of sodium glycidates will be more fruitful when additional experiments, especially those carried out at low temperature, will have been performed.

Experimental Section

All irradiations were performed at 253.7 nm in a quartz vessel using a Rayonet reactor equipped with 16 8-W low pressure Hg lamps. The solutions were deoxygenated by bubbling nitrogen through, for 30 min prior to each run and during the course of each irradiation. The exit stream was bubbled through a Ba(OH)$_2$ solution when the detection of CO$_2$ was required. The nmr spectra were recorded on a Varian A-60A or T-60 spectrometer, and are expressed on the δ scale. The mass spectra were recorded at 70 and at 12 eV with a Perkin-Elmer 270 gas chromatograph-mass spectrometer, equipped with a column of 20% SE-30 on Chromosorb. A F & M 402 gas chromatograph equipped with SE-52 and DEGS columns was also used for comparing the retention times of reaction products with standards.

The ethyl glycidates corresponding to **3**,[5] **7a**,[5,20] **7b**,[21] **7e**,[5] and **7f**[22] were the products of Darzens condensations using potassium *tert*-butoxide as the base. Ethyl glycidates corresponding to

7c[23] and **7d**[24] were obtained according to the literature methods, whereas the ethyl esters of **7g**, **7h**, **7c**, and **10** were prepared in 90, 78, 77, and 85% yields, respectively, by epoxidation of ethyl atropate,[25] ethyl-α-phenylcrotonate,[26] ethyl dimethylatropate,[27] and ethyl 3-methyl-4-phenylbutenoate[28] with 85% *m*-chloroperoxybenzoic acid in refluxing CHCl$_3$ for 15 hr. Each reaction mixture was cooled, extracted with 5% aqueous bicarbonate, dried, concentrated, and chromatographed over silica gel. The nmr and mass spectra of these glycidates were satisfactory. The saponification of the ethyl glycidates was performed according to Claisen[29] with 1 equiv each of sodium ethoxide and water. After standing overnight, the solid was filtered, washed thoroughly with ether, and dried. The salts, obtained in 60–90% yield, had satisfactory nmr spectra in D$_2$O and also in DMSO-d_6 which indicated the absence of hydroxylated impurities. The usual work-up of the irradiated solutions consisted in thoroughly extracting with chloroform or ether, drying the organic phase over MgSO$_4$, and concentrating it under reduced pressure. The per cent composition of the major decarboxylation product(s) was determined by the integration of the nmr spectra of the crude neutral product. The glc analysis and the signals in the non-aromatic part of the nmr spectra accounted for all the reaction products herein reported. However, integration of the aromatic protons was always too high and in calculating the amounts of products, we assumed the presence of polymeric aromatic substances which were not characterized.

Irradiation of 3.—The starting material had nmr (D$_2$O) at 7.35 (s, 5 H), 3.92 (d, $J = 2$ Hz, 1 H), and 3.45 (d, $J = 2$ Hz, 1 H). A solution of 1 g of **3** in 200 ml of water became turbid and evolved CO$_2$ after 30 min of irradiation. The milky white mixture was extracted with ether (four 100-ml portions) after 4 hr of irradiation, yielding 120 mg of a fragrant smelling liquid. It consisted mostly of **4** (59%): nmr (CCl$_4$) 9.60 (t, $J = 2.5$ Hz) and 3.60 (d, $J = 2.5$ Hz) in addition to phenyl protons; gc–mass spectrum major peaks at m/e 120, 92, and 91. The minor products (less than 5%) were identified as benzaldehyde (major peaks at m/e 106, 105, and 77) and bibenzyl (major peaks at m/e 182 and 91.) The aqueous layer was concentrated under vacuum and yielded 0.7 g of residue identical with the starting material by nmr. Bubbling oxygen instead of nitrogen during the irradiation did not affect the course of the photolysis, which yielded **4** as the major product.

Irradiation of 3 in D$_2$O.—A solution of 540 mg of **3** in 10 ml of D$_2$O was irradiated for 4 hr. Work-up yielded **4** which had nmr (CCl$_4$) signals at 9.60 (d, $J = 2.5$ Hz, –CDHCHO) and a broad signal at 3.60 (–CDHCHO) in addition to the phenyl protons.

Irradiation of 4.—A suspension of 1 g of **4** in 250 ml of water was irradiated for 4 hr. Work-up yielded a mixture of **4** (57%) and bibenzyl (15%) by nmr and gc–mass spectrum analysis.

Irradiation of 5.—The starting material was obtained according to literature method.[30] A suspension of 200 mg of **5** in 250 ml of water was irradiated for 3 hr. Neither **4** nor bibenzyl was detected by nmr and gc in a CHCl$_3$ extract.

Irradiation of 6.—A solution of 1 g of the salt in 250 ml of water was irradiated for 3 hr. Extraction with ether and usual work-up did not yield any neutral residue.

Irradiation of 7a.—The starting material was a mixture of cis and trans isomers showing nmr signals (D$_2$O) at 7.25 (s, 5 H), 3.57, and 3.37 (each a s, 1 H) and at 1.57 (s, 3 H). A solution of 1 g of **7a** was irradiated for 4 hr. Work-up yielded 221 mg of a neutral mixture from which the only volatile product was identified as **8a** (59%). It was characterized by its nmr (CCl$_4$) at 9.6 (d, $J = 1$ Hz, aldehydic proton), 3.52 (q, $J = 7$ Hz, showing poorly resolved coupling with the aldehyde), and 1.38 (d, $J = 7$ Hz) in addition to phenyl protons, and by a gc–mass spectrum comparison with an authentic sample (major peaks at m/e 134, 105, and 77.)

Irradiation of 7a in Methanol.—A solution of 500 mg of **7a** in 150 ml of methanol was irradiated for 30 min. After removing

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the solvent under vacuum, the residue was washed thoroughly with CCl₄ and filtered, and the solvent was evaporated to leave a residue (50 mg) which was found to be **8a** by gc–mass spectrum and nmr. The CCl₄ insoluble portion was identical with the starting material.

Irradiation of 7b.—The starting material (mixture of isomers) had nmr signals (D₂O) at 7.30 (s, 5 H), 1.62, 1.53, 1.10 (all s, total of 6 H). A solution of 500 mg of **7b** in 150 ml of water was irradiated for 4 hr. Work-up yielded 80 mg of residue containing **8b** as the only volatile product (66%). It was identified by gc–mass spectrum (m/e at 148, 105, 79, 77, and 43) and nmr at 7.20 (b), 3.60 (q, $J = 7$ Hz), 1.98 (s), and 1.35 (d, $J = 7$ Hz).

Irradiation of 7c.—The starting material had nmr (D₂O) signals at 7.28 (s, 5 H), 3.90 (s, 1 H), 1.60 (s, 3 H). A solution of 1 g of **7c** in 200 ml of water was irradiated for 4 hr. Ether extraction provided 135 mg of residue consisting mostly of **8c** (83%). It was identified by its nmr (CCl₄) signals at 7.20 (s), 3.52 (s), and 2.00 (s), as well as by its gc–mass spectrum analysis using an authentic sample (m/e 134, 92, 91, and 43). The other volatile product (5%) was identified as bibenzyl by direct comparison with a standard sample.

Irradiation of Phenylacetone.—A suspension of 1 g of **8c** in 200 ml of water was irradiated for 3 hr. Ether extraction yielded a mixture of starting material and bibenzyl (14%).

Irradiation of 7c in Basic Solutions.—Irradiation of 0.5 g of **7c** in 200 ml of water containing few drops of NaOH solution (pH 10) for 3 hr and work-up yielded 82 mg of residue consisting of **8c** (40%) and bibenzyl (38%). When the above experiment was repeated in pH 12, 89 mg of residue was obtained which consisted of 50% bibenzyl and 10% **8c**. Repeating the experiment in 200 ml of 1 N NaOH solution yielded 91 mg of neutral residue consisting of bibenzyl (52%) with a trace of **8c**.

Irradiation of 7c in Presence of Acetophenone.—A solution of 1 g of **7c** and 150 mg of acetophenone in 150 ml of water was irradiated using a 450-W medium pressure mercury arc with a Pyrex filter for 6 hr. Usual work-up yielded a mixture of **8c** (6 mg) and acetophenone. Identical irradiation of **7c**, but without acetophenone, did not provide any **8c**.

Irradiation of 7d.—The starting material had nmr (D₂O) signals at 3.00 (m, 2 H) and 1.30 (n, $J = 5$ Hz, 3 H). A solution of 580 mg of **7d** in 5 ml of water was deoxygenated and irradiated in a closed quartz tube for 4 hr. After cooling in ice and extracting with cold ether, glc analysis of the ether layer indicated the absence of propionaldehyde or any other volatile product. Upon concentration of the aqueous phase to dryness, the starting material was recovered quantitatively. Identical results were obtained upon irradiation with a Hanovia 450-W medium pressure lamp.

Irradiation of 7e.—The starting material had nmr (D₂O) at 3.42 (s, 1 H) and 1.61 (s, 10 H). A solution of 800 mg of **7e** in 200 ml of water was irradiated for 3 hr. Usual work-up did not provide any neutral product. Similar results were obtained when the irradiation was carried out in presence of either rose bengal (800 mg) or sodium benzoate (1.5 g) or benzene (saturating the water solution) as sensitizers. When a solution of 500 mg each of **7e** and **7c** in 250 ml of water was irradiated for 3.5 hr, usual work-up yielded 135 mg of neutral product consisting of **8c** (25%) and bibenzyl (48%). The evaporation of the aqueous layer left a mixture of **7e** and **7c** (nmr). Identical results were obtained upon irradiation with a Hanovia 450-W medium pressure lamp.

Irradiation of 7f.—The starting material was a mixture of isomers, with nmr (D₂O) signals at 7.38 (s, 5 H), 3.40 and 3.38 (each a s, 1 H), 2.85 and 2.83 (each a s, 2 H), and 1.22 (s, 3 H). A solution of 750 mg of **7f** in 200 ml of water was irradiated for 4 hr. Usual work-up did not yield any neutral product.

Irradiation of 10.—The starting material was a mixture of cis and trans isomers with nmr (D₂O) signals at 7.20 (s, 5 H), 3.38 and 3.34 (each a s, 1 H), 2.78 and 2.75 (each a s, 2 H), and 1.20 and 1.12 (each a s, 3 H). A solution of 750 mg of **10** in 150 ml of water was irradiated for 4 hr. Usual work-up did not provide any neutral product. The starting material was recovered quantitatively after the evaporation of the aqueous layer.

Irradiation of 7g.—The starting material had nmr (DMSO-d_6) signals at 7.20 (s, 5 H), 3.18 (d, $J = 6$ Hz, 1 H), and 2.75 (d, $J = 6$ Hz, 1 H). A solution of 300 mg of **7g** in 150 ml of water was irradiated for 3 hr. Work-up yielded 48 mg of a mixture consisting mostly of **9g** (57%) and bibenzyl (18%) by nmr and gc–mass spectrum analysis. Evaporation of the aqueous layer left a residue which was found to be identical with **7g** by nmr in DMSO-d_6.

Irradiation of 7h.—The starting material had nmr (D₂O) signals at 7.30 (b, 5 H), 3.40 (q, $J = 6$ Hz, 1 H), and 0.94 (d, $J = 6$ Hz, 3 H). A solution of 590 mg of **7h** in 150 ml of water was irradiated for 2.5 hr. Usual work-up yielded 65 mg of a mixture of phenylacetone (70%) and bibenzyl (13%), characterized by gc–mass spectrum and nmr.

Irradiation of 7h in D₂O.—A solution of 100 mg of **7h** in 30 ml of D₂O was irradiated for 3.5 hr. Usual work-up yielded 8 mg of residue, which showed nmr (CCl₄) signals at 3.52 (b) and 2.00 (s) in addition to phenyl protons; major peaks at m/e 136, 135, 94, 93, 92, and 43. A sample of C₆H₅CD₂COCH₃ was prepared by refluxing 100 mg of **8c** in 10 ml of D₂O and a drop of concentrated HCl for 3 hr. Usual work-up offered a product showing nmr (CCl₄) signals at 7.20 and 2.00; major peaks at m/e 138, 137, 136, 93, and 44.

Irradiation of 7i.—The starting material had nmr (D₂O) signals at 7.40 (b, 5 H), 1.48 (s, 3 H), and 1.10 (s, 3 H). A solution of 400 mg of **7i** in 150 ml of water was irradiated for 3 hr. Ether extraction yielded 40 mg of neutral product which was identified as **9i** by gc–mass spectrum and direct comparison with an authentic sample.