Photolysis of Chlorophenylacetic Acids

Donald G. Crosby and Eriks Leitis

The herbicide fenac is a mixture of chlorinated phenylacetic acids in which the 2,3,6-trichloro isomer predominates. Aqueous solutions of the sodium salt were photolyzed in ultraviolet light to complex mixtures. Similar irradiation of the three isomeric sodium monochlorophenylacetates as models produced phenylacetic acid, benzyl alcohol, benzaldehyde, and benzoic acid in one sequence of reactions, and the corresponding hydroxyphenylacetic acids, hydroxybenzyl alcohols, and humic acid in a simultaneous series. Detection of phenolic compounds and the isolation of dichlorobenzaldehyde, dichlorobenzyl alcohol, and trichlorobenzaldehyde illustrate that the photolysis products of fenac include the many different reduced and hydroxylated compounds suggested by the models.

K nowledge of the photolysis of pesticides has assumed increasing importance in the effective use, environmental safety, and potential for intentional destruction of residues from these chemicals. For example, Crosby and Tutass (1966) reported the rapid photodecomposition of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) to a series of hydroxylated intermediates through stepwise replacement of the ring chlorines with hydroxyl groups and the cleavage of the ether bond, followed by a nonphotochemical oxidation and polymerization to humic acid.

Among the types of herbicides related to 2,4-D are the chlorinated phenylacetic acids of which fenac (principally sodium 2,3,6-trichlorophenylacetate, I) is a commercially important example. Fenac has been tested successfully as an aquatic herbicide (Frank et al., 1963), although its principal use is in sugar cane and in soil sterilization along roadways and on industrial sites (Crafts, 1964). Because of its structural similarity to the phenoxy herbicides and its use in aqueous solution, an investigation of the products resulting from the photolysis of this herbicide in water was undertaken.

MATERIALS AND METHODS

Materials. Fenac was a technical grade analytical standard provided by Amchem Products Co., Inc. (Ambler, Pa.). 3-Chlorophenylacetic acid, 3-hydroxyphenylacetic acid, 4-hydroxyphenylacetic acid, phenylacetic acid, 3-chlorobenzyl alcohol, and 3-hydroxybenzyl alcohol were used as received (Aldrich Chemical Co.), and 2-chloro- and 2-hydroxyphenylacetic acids were obtained from K and K Laboratories, Inc. Other reagents were of the highest available purity, and most solvents were redistilled before use. C.P. grade ether contained an impurity which appeared on programmed gas chromatograms at 270° C. but which was removed by distillation. 4-Chlorophenylacetic acid was prepared by the hydrolysis of 4-chlorophenylacetonitrile (Aldrich), m.p. 103° C.

after recrystallization from water (lit. 105° to 106° C, Heilbron, 1965).

Authentic methyl esters and methyl ethers of the hydroxy acids were prepared by reaction with excess diazomethane in ether followed by gas chromatographic purification. Rechromatography showed each sample to be homogeneous.

Irradiation. Fenac (0.1 gram of the sodium salt) or 0.1 gram of the appropriate acid was dissolved in 1 liter of distilled water containing 1.0 gram of sodium carbonate. The pH of the resulting homogeneous solution was adjusted to 8.0. It was placed in a 21- × 34- × 4-cm. borosilicate glass baking dish and irradiated from above with a 360-watt "Uviarc" high-pressure mercury lamp (G. W. Gates and Co., Franklin Square, N. Y.) at a distance of 10 cm., while being stirred magnetically. The temperature was maintained at 25 ± 2° C. by circulating refrigerated water through glass coils immersed in the solution. The depth of the solution was about 3 cm. Irradiation generally was continued 1 to 3 hours.

Neutral compounds to be irradiated generally were at least partially insoluble in water at the standard level of 100 mg. per liter and so were examined as solution-suspensions.

Irradiations in sunlight were conducted out of doors during July and August in Davis, Calif., in a manner similar to the laboratory irradiations. Volume was maintained by continual addition of distilled water from a separatory funnel.

Isolation and Identification of Photolysis Products. The irradiated solutions (pH 7.8 to 7.9) were extracted with ether or chloroform, and the extract was dried over anhydrous sodium sulfate and concentrated to small volume under reduced pressure to provide the "neutral extract." The remaining aqueous phase was acidified with dilute sulfuric acid to pH 2 and likewise extracted with ether and dried to provide the "acidic extract." Before gas chromatography, aliquots of the acidic extract were esterified by reaction with ethereal diazomethane.

Gas chromatographic (GLC) analyses and separations generally were performed on an F and M Model 720 Temperature-programmed Gas Chromatograph (Hewlett-Packard Corp.) equipped with a thermal conductivity detector and a

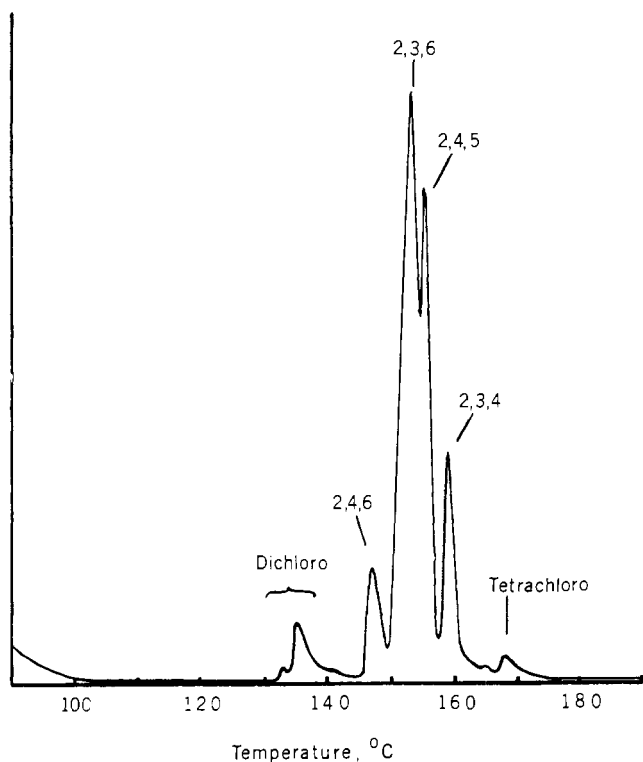Department of Environmental Toxicology, University of California, Davis, Calif. 95616

Figure 1. Gas chromatogram of methylated fenac

2-foot × ⅛-inch o.d. stainless steel column containing 20% Dow 11 silicone oil on 60- to 80-mesh Chromosorb W. Alternatively, a 5-foot × ⅛-inch column of 4% QF-1 on 60/80-mesh Chromosorb P in an Aerograph Model 200 Gas Chromatograph was employed. Fractions were collected from the effluent gas in Pasteur pipets, reinjected, and recollected for identification.

Thin-layer chromatography (TLC) was conducted on 20- × 20-cm. glass plates coated with a 0.5-mm. thickness of silica gel G containing zinc silicate phosphor. Dinitrophenylhydrazones of the substituted benzaldehydes were prepared by applying a band of neutral extract to a thin-layer chromatoplate and spraying with a solution of 2,4-dinitrophenylhydrazine (0.4 gram) and sulfuric acid (2 ml.) in a mixture of 3 ml of water and 10 ml. of 95% ethanol. After 10 minutes at room temperature, the chromatograms were developed in acetone–hexane (1:4 v./v.). The colored bands were scraped off, extracted from the adsorbent with chloroform, and purified by repeated rechromatography with benzene–petroleum ether (3:1 v./v.). For spectral comparisons, the purified dinitrophenylhydrazones were extracted into purified acetonitrile, solvent was removed by evaporation under nitrogen, and the products were dried under vacuum for several hours prior to spectrophotometry.

The diazonium spray reagent was a freshly prepared 1% solution of 4-nitrobenzenediazonium fluoborate in 20% aqueous sodium acetate.

Isolated fractions were identified by comparison of elution temperature (or retention time or R_f value), spectra, melting point, and other physical characteristics with those of authentic specimens. Infrared (IR) spectra were measured in potassium bromide disks with Perkin-Elmer Model 337 and 221 Infrared Spectrophotometers, while mass spectra were measured with a Varian Model M66 instrument by direct insertion into the ion source.

Rate Measurements. Solutions were irradiated in the usual way at the desired pH for an appropriate length of time. They were then extracted, esterified, and subjected to gas chromatography as described, and the area under each chromatogram peak was measured with a planimeter and values determined by reference to a standard curve in each instance. Extraction recoveries were essentially quantitative.

RESULTS

GLC of fenac methyl ester revealed that it consisted of a number of related chlorinated constituents (Figure 1). Among them, 2,3,6-trichlorophenylacetic acid was the major constituent, followed closely in proportion by the 2,4,5-trichloro isomer. The 2,3,4- and 2,4,6-trichloro isomers also were present in significant amounts, while mixed dichloro- and tetrachlorophenylacetic esters were present but were not resolved.

To clarify observations and simplify interpretation, 2-, 3-, and 4-chlorophenylacetic acids were irradiated under ultraviolet light as model compounds.

2-Chlorophenylacetic Acid. The dried neutral ether extract of the irradiation mixture, chromatographed at 80° C on the 20% Dow 11 column, yielded a fraction after 7.0 minutes which was identical to benzyl alcohol in its retention time and IR spectrum. Treatment of the extract with 2,4-dinitrophenylhydrazine reagent followed by TLC provided two colored derivatives identical in R_f values and spectra to the dinitrophenylhydrazones of benzaldehyde and 2-chlorobenzaldehyde.

The acidic extract was methylated and chromatographed on the 4% QF-1 column at 145° C. to provide two fractions. The first (7.5 minutes) represented the methyl ester of unchanged 2-chlorophenylacetic acid, while the second (10.0 minutes) exhibited a retention time and IR spectrum identical to those of methyl 2-methoxyphenylacetate. In addition, two very minor constituents appeared at 3.75 and 6.0 minutes, respectively, and were not investigated further, although the retention time of methyl phenylacetate under these conditions also was 3.75 minutes. The expected 2-hydroxybenzyl alcohol (saligenin) is recognized as being rather unstable and probably was represented by the dark acidic polymer remaining unextracted in the aqueous phase of the irradiation mixture.

3-Chlorophenylacetic acid. The neutral fraction obtained by chloroform extraction of the irradiated solution of sodium 3-chlorophenylacetate contained two major constituents as revealed at retention times of 7.0 and 11.0 minutes by isothermal GLC at 80° C. on the 20% Dow 11 column. The first of these possessed a characteristic almond-like odor, retention time, and infrared spectrum identical with those of an authentic specimen of benzaldehyde. Identity was confirmed by the formation of a 2,4-dinitrophenylhydrazone identical again in its chromatographic properties and spectra with the authentic benzaldehyde derivative.

The retention time and infrared spectrum of the second fraction were identical with those of benzyl alcohol, and its 3,5-dinitrobenzoate exhibited the same melting point (100° C.) and IR spectrum as that of the authentic benzyl 3,5-dinitrobenzoate. Neither 3-chlorotoluene, 3-chlorobenzaldehyde, nor 3-chlorobenzyl alcohol was detected in the neutral extract.

The methylated acidic fraction from the irradiation mixture was subjected to temperature-programmed GLC. Comparison of elution temperatures and IR spectra with those of authentic specimens showed that the substance eluting at 180° C. was the methyl ester of unchanged 3-chlorophenyl-

Table I. Photolysis Rate of Sodium 3-Chlorophenylacetate

Time (Min.)	3CPA,[a] Mg.	3-MPA,[b] Mg.	BzOH,[c] Mg.	Total,[d] Mg.
0	175	0	0	175
15	120	17	20	169
30	74	32	21	139
45	31	62	22	128
75	13	63	36	133
105	4	37	29	87
150	0	15	28	59

[a] 3-Chlorophenylacetic acid.
[b] 3-Methoxyphenylacetic acid.
[c] Benzyl alcohol.
[d] Calculated as 3-chlorophenylacetic acid.

acetic acid; that eluting at 194° C was the methyl ester–methyl ether of 3-hydroxyphenylacetic acid (methyl 3-methoxyphenylacetate); and that eluting at 155° C. was methyl phenylacetate. The small fraction appearing at 128° C possessed the characteristic sweet odor and retention time of methyl benzoate, but attempts at collection were unsuccessful; a small amount of a substance corresponding to 3-hydroxybenzyl alcohol in its chromatographic properties also was observed.

Irradiated solutions of 3-chlorophenylacetic salts always became yellow-brown in color within a few minutes after the start of the experiments. Ether extraction did not remove the color, and on acidification of the aqueous phase a dark brown solid precipitated. This substance was insoluble in acid and in organic solvents, soluble in alkalies, did not melt, and could not be made to migrate on TLC. Its appearance and properties were identical to those of the polymeric humic acids encountered as products of 2,4-D photolysis.

Table I provides an indication of the photolysis rate of sodium 3-chlorophenylacetate. Over a period of 150 minutes, the concentration fell to zero. The level of the principal constituent of the acidic extract 3-hydroxyphenylacetic acid (measured as the methyl derivative) increased rapidly until most of the starting material was depleted, at which point conversion to other products (notably humic acid) became apparent. The principal constituent of the neutral extract, benzyl alcohol, likewise could be seen to be photolyzed in turn. Examination of the total equivalent of 3-chlorophenylacetic acid revealed clearly the steady conversion to end-products. Control recoveries were essentially quantitative.

Upon irradiation of sodium 3-chlorophenylacetate solu-

Table II. Effect of pH on 4-Chlorophenylacetic Acid Irradiation

pH	Irradiation Time, (Min.)	4-CPA,[a] Mg.	4-MPA,[b] Mg.	BzOH,[c] Mg.	Total,[d] Mg.
All	0	120	0	0	120
4.5	30	27	7	17	61
7.1	30	16	4	31	69
10.0	30	8	1	29	55
2.0	60	30	0.1	4	36
4.5	60	10	7	20	49
7.1	60	0.1	5	36	62
10.0	60	0	0	23	37

[a] 4-Chlorophenylacetic acid.
[b] 4-Methoxyphenylacetic acid.
[c] Benzyl alcohol.
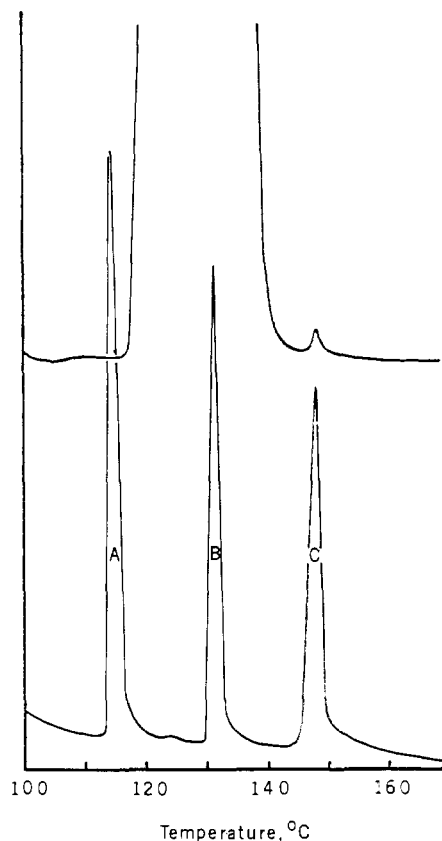[d] Calculated as 4-chlorophenylacetic acid.

Figure 2. Gas chromatograms of esterified acidic extract from sunlight-irradiated 3-chlorophenylacetic acid and standard phenylacetic acid (A), 3-chlorophenylacetic acid (B), and 3-methoxyphenylacetic acid (C)

tions with sunlight, color formation soon was observed and intensified with prolonged exposure. Extraction, methylation, and GLC revealed the presence of a very low level of 3-hydroxyphenylacetic acid after 5 days' exposure (Figure 2), but no phenylacetic acid or neutral products were detected at that time.

4-Chlorophenylacetic Acid. The irradiation of sodium 4-chlorophenylacetate provided results exactly parallel to those observed with the 3-isomer. The neutral fraction contained appreciable amounts only of benzaldehyde and benzyl alcohol, while the acidic fraction contained unreacted starting material, phenylacetic acid, and 4-hydroxyphenylacetic acid (each isolated as its methyl ester). As in the experiments with the other chlorophenylacetates, a dark substance always was formed rapidly which was insoluble in organic solvents and aqueous acid, soluble in dilute aqueous alkali, and which did not produce volatile products upon treatment with diazomethane.

The effect of pH and irradiation time on the ratio and recovery of major constituents of the photolysis mixture is shown in Table II. The rate of 4-chlorophenylacetic acid photolysis increased markedly with increasing pH.

Photolysis Products. To determine the sequence of photolysis reactions leading to the observed products, each of the identified photolysis products was irradiated in turn. 3-Hydroxyphenylacetic acid produced only a nonvolatile, dark polymeric product identical to those isolated after the photolysis of the chloro acids. Comparison of the IR spectrum of this material with that of the humic acid derived from 2,4-D (Crosby and Tutass, 1966) showed that the two substances were very similar in structure.

The acidic extract of irradiated phenylacetic acid contained only unchanged starting material. The neutral fraction, however, contained significant amounts of benzaldehyde and benzyl alcohol as confirmed by retention times and infrared spectra. Irradiation of benzyl alcohol gave rise to benzaldehyde, which was converted exclusively to light-stable benzoic acid. Solutions of benzaldehyde were stable in the absence of irradiation, showing that light was required for oxidation to the acid within the duration of the experiments.

Although never detected as a photolysis product, 3-chlorobenzyl alcohol was considered to be a possible intermediate. Its photolysis yielded the expected 3-hydroxylbenzyl alcohol together with benzaldehyde and benzyl alcohol. Benzyl alcohol provided benzaldehyde upon irradiation, with subsequent conversion to benzoic acid. However, irradiation of 3-hydroxybenzyl alcohol caused almost immediate coloration, and upon acidification of the dark solution there was produced a black precipitate of humic acid identical to that formed from 3-hydroxyphenylacetic acid.

Fenac. Irradiation of fenac (sodium salt) in aqueous solution followed by ether extraction provided the usual neutral and acidic fractions. TLC of the acidic extract (solvent benzene–methanol–acetic acid, 12:2:1) resolved at least 8 constituents which quenched fluorescence of the phosphor and also gave orange to red colors with diazonium reagent. However, methylation followed by GLC revealed a very complex mixture which could not be satisfactorily resolved.

The neutral fraction likewise gave a thin-layer chromatogram (in benzene–petroleum ether, 3:1) which showed the presence of 4 diazonium-reactive constituents and 5 others which only quenched fluorescence. GLC provided at least partial resolution, and the compounds eluting at 143°, 155°, 160°, and 244° C. were collected.

The principal constituent (160° C.) produced an IR spectrum which exhibited absorptions (aliphatic OH 3350, 1060; 1,2,4-trisubstituted phenyl 816, 871; RCH_2 2925 cm.$^{-1}$) characteristic of a substituted benzyl alcohol. The mass spectrum indicated a dichlorobenzyl alcohol (calcd. for C_7H_6-Cl_2O, m/e 175.9; found 176.0, C = 12.00) with the expected fragmentation pattern (Cl_2PhCH_2O 175.0, Cl_2PhCH_2 159.0, $PhCl_2$ 147.0, $PhCl$ 111.0). These data suggest that 2,5-dichlorobenzyl alcohol is the principal photolysis product of fenac.

This major constituent was contaminated with a small proportion of the 155° C. eluate, and the mass spectrum showed the contaminant to possess 3 chlorine atoms and a mass of 208.8 (calcd. for $C_7H_3Cl_3O$ 208.9). Its relative volatility fragmentation pattern and (Cl_3PhCO 207.8, Cl_2PhCO 172.0) together with its IR absorption (C=O 1675 cm.$^{-1}$) indicated this constituent to be a trichlorobenzaldehyde. Likewise, the 143° C. eluate proved to be primarily dichlorobenzaldehyde (m/e 173.8; Cl_2PhCO 172.8, Cl_2Ph 145.0).

The fraction eluting at 244° C. exhibited the IR absorptions characteristic of an aromatic ester (1724, 1274 cm.$^{-1}$), ortho-disubstitution (741, 704 cm.$^{-1}$), and ring chlorine (650 cm.$^{-1}$), but its structure was not investigated further.

DISCUSSION

Chlorinated phenylacetic acids in the form of sodium salts in aqueous solution were photolyzed both in sunlight and under ultraviolet light in the laboratory, but the rate of decomposition was much less than that observed with chlorinated phenoxyacetic acids. The replacement of chlorine by hydroxyl again represented a key reaction in the fate of
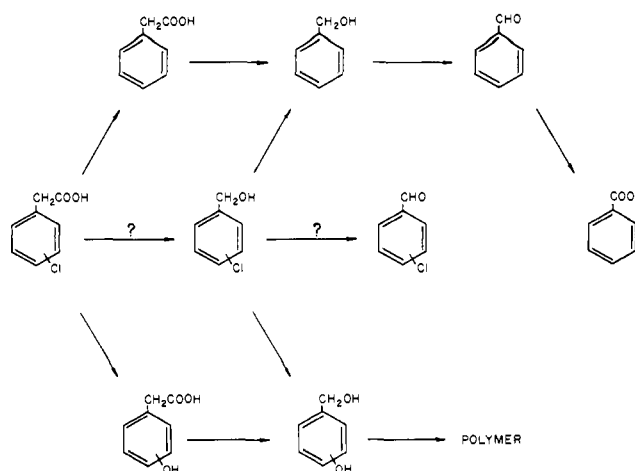

Figure 3. Photodecomposition pathways of chlorophenylacetic acids in aqueous solution

these compounds and likewise resulted in the eventual conversion to a humic acid type of polymer.

Photoreduction was observed to be a major pathway of photolysis under laboratory conditions; the corresponding reduced phenoxyacetic acids had not been specifically sought in our previous investigation. The resulting phenylacetic acid subsequently appeared to undergo what was, in effect, a decarbonylation to benzyl alcohol. While the hydroxylated phenylacetic acids likewise provided the corresponding hydroxybenzyl alcohol, chlorobenzyl alcohols never were detected in quantities sufficient for identification.

Benzyl alcohol produced benzaldehyde upon irradiation (the reverse reaction was not observed), and this compound subsequently was oxidized to benzoic acid which was stable to further photolysis. 3-Hydroxybenzaldehyde was not isolated as a photolysis product of 3-hydroxybenzyl alcohol, the only product being a black, insoluble polymer exhibiting the characteristics of humic acid. Irradiation of 3-chlorobenzyl alcohol resulted only in recovery of starting material, although 2-chlorobenzaldehyde was produced from the corresponding phenylacetic acid.

The reaction pathway proposed in Figure 3 accounts for all of the observed irradiation products and the reactions of tested intermediates. Although it is probable that still other intermediates also occur, as suggested by the repeated observation of a number of very small peaks on gas chromatograms and extremely weak bands on thin-layer chromatograms, the photolysis products already isolated from the model chlorophenylacetic acids provide the required key to an understanding of the reactions of fenac.

The decomposition of fenac solutions in sunlight, and more extensively under ultraviolet irradiation in the laboratory, resulted in what now may be expected to be a very complex system of oxidized and reduced intermediates, based on the original mixture of chlorophenylacetic acid isomers, whose exact composition varied with time. The mixture of photolysis products present in the acidic extract undoubtedly resulted from the replacement of one or more ring chlorines of the fenac isomers by hydroxyl groups and/or hydrogen atoms. Analogous to 2,4-D photolysis, a considerable proportion of the fenac may be converted to o-phenolic acids such as II. Partial replacement of the chlorines by hydrogen could give compounds such as III whose unambiguous synthesis might be very difficult.

Despite our inability to identify the chlorobenzyl alcohols derived from the model compounds, the presence of chloro-
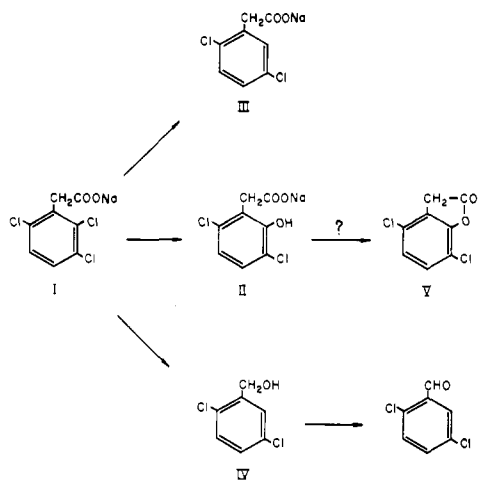
Figure 4. Possible products of photolysis of fenac

Although the photolysis of fenac in sunlight is extremely slow, it may be anticipated that sufficiently long-term irradiation could result primarily in benzoic acid and humic acid polymers as the stable photolysis products. The value of simple model compounds in arriving at an elucidation of the photolytic pathways of complex substances and the pesticide mixtures often encountered in actual field practice also has been clearly demonstrated.

benzaldehydes suggests their intermediate formation; alcohols such as IV and their corresponding aldehydes also appear in the neutral fraction of photolyzed fenac. The ester nature of the other major fraction of this neutral extract might be explained on the basis of cyclization, such as that of II to V, although the irradiation of sodium 2-chlorophenylacetate produced principally 2-hydroxyphenylacetic acid rather than the corresponding lactone (Figure 4).

ACKNOWLEDGMENT

LITERATURE CITED

Crafts, A. S., "The Chemistry and Mode of Action of Herbicides," p. 218, Interscience Publishers, New York. 1964.
Crosby, D. G., Tutass, H. O., J. Agr. Food Chem. 14, 596–9 (1966).
Frank, P. A., Hodgson, R. H., Comes, R. D., Weeds, 11, 124–8 (1963).
Heilbron, I., "Dictionary of Organic Compounds." Vol. 2, p. 674, Oxford, New York, 1965.